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New Polymer Mortar Formulations

- Development, Characterization and Application Forms -

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Resumo

O betão normal de cimento Portland, principalmente quando associado ao aço sob a forma de betão armado, tornou-se num dos materiais de construção mais utilizado nas últimas décadas. As suas propriedades mecânicas associadas, ao seu baixo custo e a um processo de fabrico relativamente simples, massificaram a sua utilização no campo da construção civil, em detrimento de outros materiais de construção mais convencionais, como o aço, a madeira e a pedra. O betão tradicional apresenta contudo uma série de limitações, principalmente em termos de durabilidade, e estas parecem ser o preço a pagar pela sua universalidade. A actual pressão conducente ao desenvolvimento de materiais mais fortes e duráveis trouxe à ribalta um material compósito relativamente novo, o betão polimérico. Este material distingue-se do betão convencional por utilizar como ligante uma resina ou polímero em substituição da tradicional pasta de cimento. Estes novos materiais, os betões de resina, apresentam um leque de vantagens em termos de resistência mecânica e durabilidade que, por si só, justificam a sua crescente divulgação e aplicação. Um comportamento deficiente frente ao fogo e uma alta susceptibilidade à temperatura e aos fenómenos de fluência, derivados do carácter viscoelástico do ligante de resina, constituem as principais limitações associados a estes materiais.

A aplicação e desempenho dos materiais de betão polimérico dependem em grande escala da sua formulação específica, a qual engloba não só o tipo de matérias-primas e a sua proporção relativa, mas também o tratamento de cura, processo de fabrico e a técnica de aplicação utilizada. Diferentes formulações podem conduzir a materiais muito dissimilares com propriedades bastante distintas. O termo betão polimérico nunca deve sugerir assim um único material mas antes uma família de materiais.

Com o presente trabalho pretende-se dar um contributo significativo na área dos betões poliméricos, contribuindo nomeadamente para a clarificação de determinados questões relacionadas com a formulação, procedimentos de teste e avaliação da durabilidade: *Como determinar a melhor combinação de factores materiais de forma a optimizar uma ou mais propriedades do produto final? Quais os métodos de teste que melhor se adequam a estes materiais*? *Que metodologias devem ser aplicadas na avaliação da durabilidade? (Degradação natural versus degradação acelerada e/ou artificial).*

Neste âmbito, desenvolveram-se duas formulações distintas de argamassa polimérica, uma com ligante de resina epóxida e outra de poliéster insaturado, com vista à optimização da sua resistência à flexão. No processo de optimização recorreu-se ao método de Taguchi, para planificar as experiências, e à análise de variância –ANOVA- como ferramenta estatística para análise dos resultados. Os resultados obtidos demonstraram que as metodologias utilizadas podem ser aplicadas com sucesso no desenvolvimento de materiais de betão polimérico. As formulações desenvolvidas foram posteriormente alvo de exaustiva caracterização física e mecânica. No trabalho experimental de caracterização, foi dado especial ênfase aos aspectos relacionados com a durabilidade do material, nomeadamente: à resistência química aos ácidos, alcalis e sais; à resistência aos agentes atmosféricos, ao nevoeiro salino e às radiações ultravioleta; resistência às altas temperaturas e aos ciclos de fadiga térmica; e à reacção ao fogo. Uma vez que nos betões de resina, a resistência à flexão constitui um indicador mais fiável do comportamento mecânico geral do material, recorreu-se sistematicamente a este parâmetro para avaliar o nível de degradação sofrido por ambas as formulações testadas.

Ainda no âmbito deste trabalho, foram idealizados e analisados dois tipos de aplicação distintos para as formulações desenvolvidas: como elemento componente na construção compósita de vigas com perfis pultrudidos de plático reforçado com fibras – *Vigas híbridas de PRF e betão polimérico*-, e como argamassa de base para betão estrutural com agregados leves – *Betão polimérico modificado com agregados naturais leves*-.

O trabalho desenvolvido nesta tese constitui uma base para futuros trabalhos na área da optimização de formulações e condições de processamento de materiais de betão polimérico, e abre potenciais novas vertentes de aplicação destes materiais no campo da construção civil.

Abstract

Ordinary Portland cement concrete is a ready-to-use, widely available building material, but its low durability under some service conditions seems to be the price paid for its universality. The demand for a stronger and durable construction material has focused attention on a relative new type of composite material called polymer concrete. Polymer concrete is a cementless concrete material formed by polymerizing a monomer with an aggregate. The polymer acts as a binder for the aggregate reinforcement replacing, totally, the hydrated cement paste. In comparison with conventional portland cement concrete, this unique composite material offers a number of advantages, such as higher strength, better chemical resistance, and higher impermeability. Deficient behavior under fire, high sensitivity to temperature and creep phenomena, due to the viscoelastic nature of resin binder, seems to be the main shortcomings related with these materials.

Application and performance of polymer concrete materials are highly dependent on the specific formulation which encloses mixing design (polymer type, polymer content, aggregate type and gradation), manufacturing procedures and application techniques. Thus, different mix formulations, mixture and casting procedures lead to distinct materials with a varied range of properties. The term polymer concrete should never, therefore, suggest only a single product but a product family instead.

The present work aims to give a major contribution to resolving certain issues related to polymer concrete materials such as mix design - *How to achieve the better combination of material factors to get an optimal formulation regarding the enhancement of one or more properties?*-, testing procedures - *Which physical and mechanical tests are the most adequate to characterize these materials?*-, and durability assessment -*What* *methodologies should be applied for the assessment of durability? Natural conditions test versus accelerated and/or artificial conditions test-*.

Within this scope, two different polymer mortar formulations, with epoxy and unsaturated polyester matrix binders, were developed and optimized regarding flexural strength property. A Taguchi methodology (for the planning of the experiments) and the analysis of variance ANOVA (for the analysis of results) were applied for that purpose. Obtained results showed that the above techniques can be applied with success for polymer concrete materials' design. The physical and short-term mechanical properties of developed formulations were studied and thoroughly characterized by means of various physical and mechanical tests.

Experimental work was mainly focused on durability issues such as chemical resistance to various aggressive agents, resistance to high temperatures and thermal fatigue cycles, frost resistance, natural and artificial weathering, and fire performance. Since the flexural strength of polymer concrete gives the best indication of its overall behavior, flexural strength parameter was steadily used for the assessment of degradation rate.

Besides the traditional end-use as repair material, two different applications were foreseen and investigated for developed polymer mortar formulations: *i)* as precast component material for composite construction of structural beams with glass fibre reinforced plastic pultrusion profiles -*GFRP-polymer concrete hybrid beams*-; *ii)* and as basis material for lightweight aggregate structural concrete *–PC material modified with natural lightweight aggregates*-. For both applications, models were designed and produced, mechanical performance was analyzed and the viability of their appliances was evaluated.

The work developed provides a scientific base for future studies aimed at optimizing material selection and processing conditions for polymer concrete materials and opens new potential branches for future applications of these materials.

Résumé

Le béton ordinaire à base de ciment Portland est un matériau, prêt à l'utilisation pour la construction, largement répandu. Toutefois, sa faible durabilité, sous différentes conditions de service, semble être le prix à payer pour son universalité. La demande d'un matériau plus résistant et plus durable pour la construction, a conduit au développement d'un matériau composite, relativement récent, appelé le béton polymérique. Ce matériau est un béton, pour lequel, la matrice inorganique de ciment hydraté conventionnelle est remplacée par une matrice polymérique. Le béton polymérique est donc formé par la polymérisation d'un monomère avec un agrégat; le polymère agissant comme liant. En comparaison avec les bétons conventionnels, à base de ciment portland, ce matériau composite unique offre de nombreux avantages, tels qu'une plus grande résistance mécanique, meilleure résistance chimique, ainsi qu'une plus grande imperméabilité. Une réaction au feu déficiente ainsi qu'une sensibilité élevée à la température et aux phénomènes de fluage provenant de la nature viscoélastique de la résine utilisée comme liant, semblent être les principale limitations de ces matériaux.

Les applications et les performances des bétons polymériques dépendent considérablement de leur formulation spécifique, ce qui comprend, non seulement le choix des matières primes (*i.e.* type de polymère et d'agrégat, mais aussi les techniques de fabrication et d'application. Ainsi, différentes formulations peuvent conduire à des matériaux distincts avec une vaste gamme de propriétés. La désignation béton polymérique ne devrait donc jamais suggérer uniquement un matériau mais plutôt une famille de matériaux.

Cette étude prétend donner une contribution significative afin de résoudre certains points liés aux bétons polymériques tel que la conception de la formulation *–Comment atteindre*

la meilleure combinaison de facteurs matérielles afin d'obtenir une formulation optimale considérant l'amélioration d'une ou plusieurs propriétés?-; les procédures de tests –*Quels sont les tests physiques et mécaniques les plus appropriés afin de caractériser ces matériaux?*-; et l'évaluation de la durabilité –*Quelles méthodologies devraient être appliquées afin dévaluer la durabilité?*-.

Dans cet esprit, deux différentes formulations de mortier polymérique, l'une à base d'une matrice époxyde et l'autre de polyester insaturé, ont été développées et optimisées en considérant leur résistance à la flexion. Pour le processus d'optimisation, la méthode Taguchi et l'analyse ANOVA ont été appliqués pour la planification des expériences et pour l'analyse des résultats. Les propriétés physiques et mécaniques à court terme des formulations développées on été étudiées et complètement caractérisées à partir de différents essais.

Le travail expérimental s'est principalement focalisé sur les aspects liés à la durabilité du matériau tel que la résistance chimique à différent agents agressifs; la résistance aux agents atmosphériques, à la radiation ultraviolet et au brouillard salin (vieillissement naturelle et artificielle), la résistance aux hautes températures, à la fatigue thermique et aux cycles de gel-dégel; et la réaction au feu. Étant donné que, dans le cas des bétons polymériques, la résistance à la flexion donne l'indication la plus fiable sur les performances mécaniques générales du matériau, ce paramètre a été systématiquement utilisé afin d'évaluer le taux de dégradation des deux formulations.

Deux types d'application distinctes ont été idéalisées et analysées pour les formulations développées: *i)* comme élément d'assemblage pour la construction composite de poutres avec des éléments de plastique renforcés avec des fibres de verre (PRFV) fabriqués par pultrusion –*Poutres hybrides de PRFV et béton polymérique*-; *ii)* et comme mortier de base pour bétons structurels à agrégats légers –*Béton polymérique modifié avec des agrégats naturels légers*-. Pour les applications, des modèles ont été conçus, les performances mécaniques ont été analysées et la viabilité de leur application évaluée.

Le travail développé dans cette dissertation constitue une base scientifique pour des travaux futurs visant l'optimisation de formulations et de conditions de fabrication des bétons polymériques, et ouvre nouvelles perspectives d'application de ces matériaux dans la construction civile.

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To my parents

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I. INTRODUCTION

Conventional portland cement concrete, specially when associated to steel, became in the last decades the most widely used construction material. Its mechanical properties, in combination with relatively low cost and quite simple manufacturing process, led to its massive application over the more traditional construction materials such as wood, stone or steel.

In spite of their extensive use, cement mortar and concretes present a number of shortcomings such as low tensile and flexural strengths, low failure strain, delayed hardening, susceptibility to frost damage, low bonding strength in repair applications, and poor resistance to aggressive agents.

Some of these drawbacks can be overcome by the incorporation of an organic polymer or resin in concrete mass, instead or in conjunction with portland cement binder. These relatively new materials, the concrete-polymer composites (CPC), offer a number of advantages that justify their growing use and application.

Higher strength, excellent durability, good resistance to corrosion, reduced water permeability and greater resistance to damage from freeze-thaw cycles, are some of the enhanced features presented by CPC materials (Blaga and Beaudoin 1985b). In addition, the improved strength and durability offered by these materials, which are the major requirements for the enhancement of infrastructure materials used in the civil construction industry, reduce the need for maintenance and frequent repairs required by conventional concrete. An other advantage showed by some of these composite materials is their fast curing time, which is an asset in the production of precast elements, as parts can be demolded a few hours only after concrete placement (Fowler 1999).

Although the growing requirement for strong and durable materials to replace cement concrete, specially regarding chemical resistance properties, this need has not yet been translated into widespread usage of concrete-polymer composites. The most likely reasons behind this are the lack of information on the properties of these materials, the technology employed in their production and their higher cost (Gorninski et al. 2004). The polymeric resin used in their production constitutes the major cost component.

Thus, as the incorporation of polymers in concrete leads to a considerable increase of total cost of final product, the use of concrete-polymer composites only becomes advantageous when their higher cost could be justified by the advantages brought by the polymers to concrete. It is therefore necessary that civil and designer engineers have a reasonable awareness of the capacities and limitations of these 'new materials', in order to select the most appropriate product according to its intended application or end-use (Blaga and Beaudoin 1985a).

1.1 Concrete-Polymer Composite Materials

The general concept of concrete-polymer materials, from technical point of view, involves a process by which chemicals (monomers, oligomers, prepolymers polymers) introduced into a concrete mix are subjected to polymerization and polycondensation by thermo-catalytic or other systems (Czarnecki 2001). Thus, concrete-polymer materials can be considered as hybrid composites of concrete using polymers.

Like a composite material, concrete-polymer materials can be understood as poly-phase systems, whose phases cannot be mutually transformed into each other by any treatment, and which attains properties not attainable by any of the constituting phases by themselves, neither by the sum of them.

Similar to conventional cement concretes, polymer concrete composites comprise three phases: a dispersed phase, constituted by the aggregates and reinforcements (if applied); a continuous phase, formed by the binder matrix (cement and/or polymer), and a certain porosity, imposed either by the size grading of aggregate material or by the process technology itself. The properties of these materials arise not only from those of their components, but also from the synergetic effect created by their conjunction.

An infinite number of different mixtures depending on the chemical nature of components, their contents and manufacturing process can be found observing the above definitions. For this reason, it will be useful to clarify some simple categorization and definitions.

The American Concrete Institute Committee 548, Polymers in concrete (1977), recognizes three classes of concrete-polymer composites (CPC), as function of the nature of their matrix and process technology :

▪ Polymer-impregnated concrete (or mortar)	PIC (or PIM);
▪ Polymer-modified concrete (or mortar)	PMC (or PMM);
▪ Polymer concrete (or mortar)	PC (or PM).

1.1.1 Polymer Impregnated Concrete

Polymer Impregnated Concrete (PIC) has been defined as a ‘hydrated portland cement concrete which has been impregnated with a monomer and subsequently polymerized in situ’ (ACI 1977). It is produced by infusing low viscosity monomers into the cracks and voids of already hardened portland cement concrete. After the impregnation process, the monomers are polymerized inside concrete’s voids by the action of chemical agents (catalysts) or physical agents (heat or radiations). The important feature of this material is that a large proportion of the void volume is filled with polymer, which forms a continuous reinforcing network, binding the cement matrix and the aggregates. The impregnation depth, as well as the percentage of voids filled by this process, varies as function of the porosity of the concrete, the viscosity and volatility of the monomers, the setup time of the polymer, and the technique of impregnation applied: full-impregnation, under plant conditions, or partial impregnation, for field applications (Fowler 1986a).

1.1.2 Polymer Modified Concrete

Polymer Modified Concrete (PMC) is defined as ‘a premixed material in which either a monomer or polymer is added to a fresh concrete mixture in a liquid, powdery, or dispersed phase, and subsequently allowed to cure, and, if needed, polymerized in place.

The term polymer cement concrete (PCC) has also been used to refer this same material definition' (ACI 1977). Thus, PMC is a normal portland cement concrete with a polymer admixture. The polymer acts as a modifier of the cement or as co-matrix, forming a polymeric phase simultaneously with cement hydration. As a result, a hybrid matrix is obtained, formed by an interpenetrating structures' network of polymer and cement hydration products that work together, resulting in an improvement in the material properties. The polymer-binder ratio, as function of the specific formulation, is vary variable (between 0.15% and 50%), but the usual amounts of polymers are in the range of 10% to 20% by weight of the portland cement binder. There are only few polymers suitable for adding to concrete; most polymers would produce poor quality PMC due to incompatibility problems with cement. The process technology used is very similar to that of conventional concrete in mixing, placing and finishing. Therefore, PMC can be cast in field applications, whereas PIC has to be used, most of the times, as a precast structure (Blaga and Beaudoin 1985b; Fowler 1986b; Ohama and Ramachandran 1995).

1.1.3 Polymer Concrete

Finally, under the designation of *Polymer Concrete (PC)*, also referred to as resin concrete, it is assembled all concrete materials whose binder matrix is entirely formed by organic polymers. PC is defined as 'a composite material formed by polymerizing a monomer and aggregate mixture. The polymerized monomer acts as the binder for the aggregate' (ACI 1977). Hence, PC is a cementless material. The polymer matrix binds very well to aggregate particles with no transition zone, unlike conventional cement concrete. Since polymer materials are more expensive than portland cement, and can generate heat and undergo shrinkage under curing, PC is made with evenly graded aggregates to achieve close packing, minimizing the space between the aggregates to be filled with binder (Kardon 1997). Therefore, the amount of polymer binder used is generally small and is usually determined by the size of the aggregates. Normally the polymer content will range from 5% to 15% of the total weight, but if the aggregate is fine, up to 30% may be required. Among the different types of concrete-polymer composites, PC is the simplest and the easiest to produce. Further, its processing cost is extremely low, even when compared with that one of conventional concrete (Blaga and Beaudoin 1985a).

Figure 1.1 summarize the classification system of concrete-polymer composites and, in the Table 1.1, the range of values usually found for the mechanical and durability properties of these materials is given.

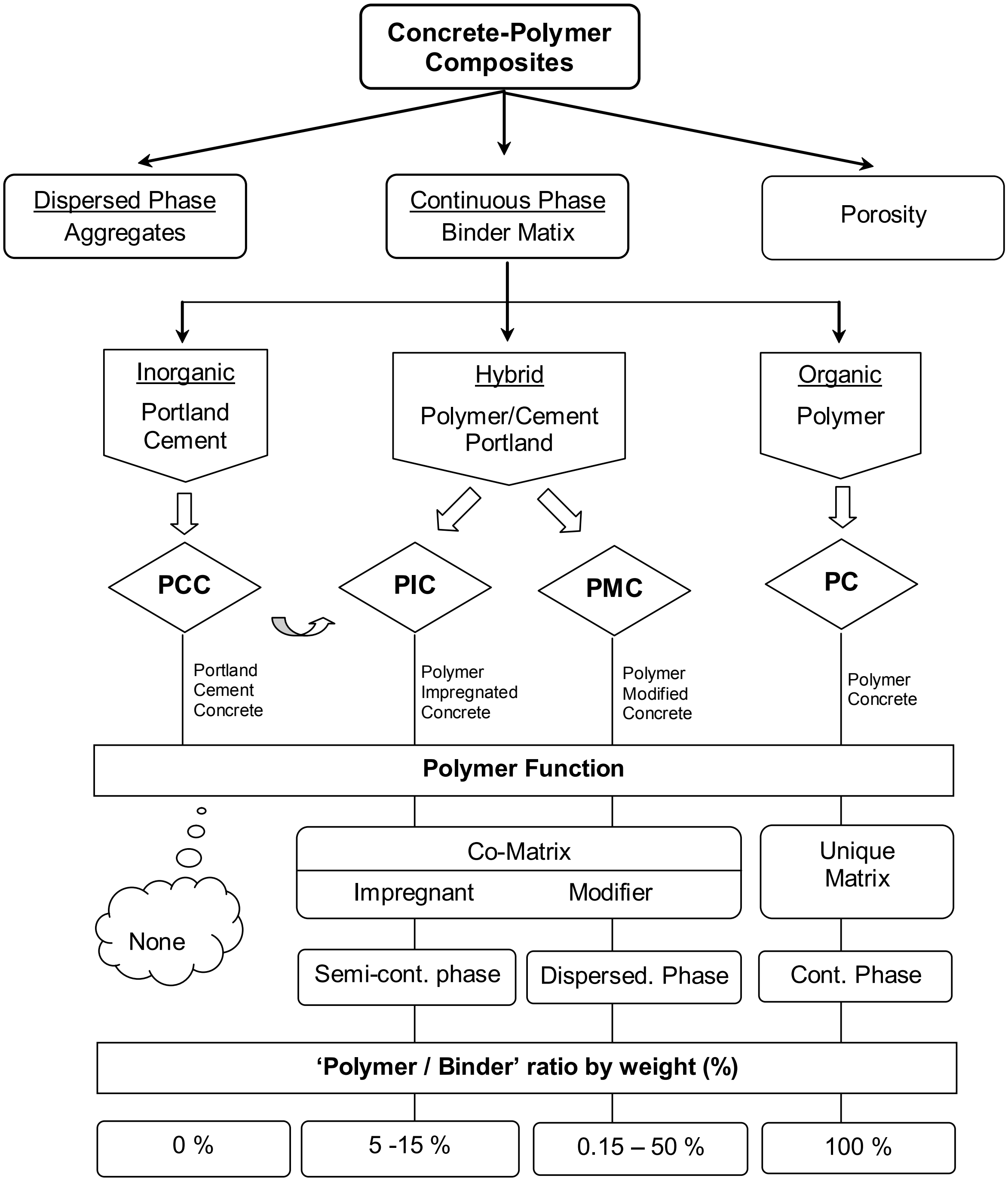

Fig. 1.1. Classification system of concrete-polymer composite materials.

Table 1.1. Mechanical and durability properties of CPC materials (Blaga and Beaudoin 1985a; Blaga and Beaudoin 1985b; Chawalwala 1996; Fowler 1986a; Ribeiro et al. 2004)

Properties	PIC	PMC	PC	PCC*
Comp. Strength (MPa)	100 - 270	30 - 60	50 - 210	20 - 58
Elast. Modulus (GPa)	27 - 50	10 - 17	9 - 40	20 - 31
Flex. Strength (MPa)	10 - 20	-	13 - 45	2 - 8
Tensile Strength (MPa)	7.5 - 15	4.5 – 6.5	8 - 25	1 - 4
Water Absorption (%)	0.05 – 1.50	-	0.05 – 1.00	5.00 – 10.00
Freeze-Thaw Resist. (nº cycles / % wt loss)	2000-5000/ 0-2	-	100 / 0	700 / 25
Sulphuric Acid Resist. 15%(nºdays / % wt loss)	70-120 / 30	-	-	50 / 35
Chloride Acid Resist. 15%(nºdays / % wt loss)	700-800 / 7-9	-	-	100 / 27

* PCC – Portland Cement Concrete

1.2 Scope and Objectives

The major objective of this thesis work is straightforwardly expressed by its title and may be resumed by the following: development, optimization and fully characterization of a PC material with enhanced characteristics according to its foreseen applications.

Specifically, this investigation was undertaken with the following goals in mind:

i) To develop and optimize a polymer mortar formulation with improved characteristics according to its future end-use;

ii) To proceed to a complete characterization in terms of physical and static mechanical properties of optimized formulation(s);

iii) To determine interdependencies or relationships among the mechanical properties;

iv) To evaluate and model the rate of degradation of the material when subjected to different aggressive environments, namely, chemical agents, high temperatures, freeze-thaw cycles and weathering;

v) To investigate the material's behavior under fire and classify its fire reaction, as a construction material, according to the present regulation;

vi) To evaluate the viability of its application either as a component material for composite structural members -*GFRP-polymer concrete hybrid beams*-, or as a mortar for lightweight aggregate structural concretes *–PC material modified with natural lightweight aggregates*-.

1.3 Organization

The investigation study carried out in this thesis work is organized as follows:

Chapter II summarizes the background related to PC materials and their performance as compared to ordinary cement concretes. The review also deals with the concepts and processes technologies associated to concrete-polymer composites, their development and progress over the last decades, and the standardization work that has been made regarding them in the industry.

In Chapter III, all steps of optimization process that led to the most advantageous PM formulations are depicted. Selection of raw materials, process technology and applied design process are here described and the criteria of choice are discussed.

The basic physical and static mechanical properties of optimized formulation(s) such as fresh state properties, setting shrinkage, specific gravity, coefficient of thermal expansion, flexural, compressive and tensile strengths, stress-strain behavior and deformability characteristics are included in Chapter IV. The usual test methods applied to determine these properties are also reviewed and the suitability of their application to PC materials is discussed.

Chapter V investigates the effect of aggressive environments on flexural performance of PM formulation(s). Chemical durability, thermal durability and weatherability are the main issues in analysis. The degradation rate of the material when subjected to different chemical solutions, high temperature levels, positive thermal fatigue cycles, freeze-thaw cycles, salt fog cycles, arc-xenon radiations and natural weathering agents is assessed and modelled (for certain environment conditions).

Behavior under fire is evaluated in Chapter VI. Heat release, ignition time, flame spread, smoke and toxic gases release rates are some of the parameters determined in this part of the study, which allowed the assessment of fire performance of PM formulation(s). The effect of different flame retardant systems on material's fire reaction is also analyzed. Reaction to fire classification, according to French regulation, is performed and expected classification according to the present European Union regulation is discussed.

The concluding remarks of the overall study and the recommendations for future works are summarized in Chapter VII.

Finally, as Appendix, some publish works related with applications forms of developed PM formulations are presented. Two main applications are approached: composites structural beams made with GFRP (Glass Fibre Reinforced Plastics) profiles filled with a PC material, and lightweight structural concretes based on PC materials modified with lightweight natural aggregates, such as cork granules and wood shavings.

1.3 Relevant Publications

Some of the work reported in this thesis has been already published for publication. For an easier reference, these publications are listed below:

i) C.M. Tavares, M.C. Ribeiro, M. Figueiredo, A.J.M. Ferreira, A.A. Fernandes, *"Influence of Material Parameters in the Mechanical Behaviour of Polymer Concrete"*, Mechanical and Materials in Design 3 -MMD3-, Orlando, USA, May 2000, 239

ii) A.J.M. Ferreira, C.M. Tavares, M.C. Ribeiro – *"Flexural properties of polyester resin concretes"* -, Journal of Polymer Engineering, Freund Publishing House, Vol.20, No 6, 2000, 459-468.

iii) C.M. Tavares, M.C. Ribeiro, M. Figueiredo, A.J.M. Ferreira, A.A. Fernandes, *"Caracterização mecânica em flexão de betões de resina poliéster e epóxida"*, Betão Estrutural 2000, Porto, Novembro 2000, 55-64.

iv) M.C.S. Ribeiro, C.M.L. Tavares, A.J.M. Ferreira, A.M.C. Paulo, M.A.G. Silva, *"Mechanical behaviour of degradated polymer concrete"*, International Conference on Composites in Construction –CCC 2001-, Porto, Portugal, October 2001, 83-88.

v) C.M.L. Tavares, M.C.S. Ribeiro, D. Monteiro, P.P. Camanho, A.J.M. Ferreira, *"Experimental investigation into the static and fatigue behaviour of polymer concrete reinforced with GFRP rods"*, International Conference on Composites in Construction –CCC 2001-, Porto, Portugal, October 2001, 329-334.

vi) C.M.L. Tavares, M.C.S. Ribeiro, A.J.M. Ferreira, R.M. Guedes, *"Creep Behaviour of frp-reinforced polymer concrete"*, 11th International Conference on Composite Structures, Melbourne, Australia, November 2001.

vii) M.C.S. Ribeiro, C.M.L. Tavares, A.J.M. Ferreira, A.T. Marques, *"Static flexural performance of GFRP-polymer concrete Hybrid beams"*, International Conference on FRP Composites in Civil Engineering –CICE 2001-, Hong Kong, China, December 2001, 1355-1362.

viii) M.C.S. Ribeiro, C.M.L. Tavares, A.J.M.Ferreira – "*Chemical resistance of epoxy and polyester polymer concrete to acids and salts" -,* Journal of Polymer Engineering, Freund Publishing House, Vol.22, No 1, 2002, 27-44.

ix) A.J.M. Ferreira, A.T. Marques, C.M.L. Tavares, M.C.S. Ribeiro, '*Polymer concrete under severe conditions',* ORGAGEC'02 – Organic materials: A future in the field of civil engineering? Environmental uncertainties? Poitiers, France, 13-15/03/2002, p.42.

x) Cassilda M.L.Tavares, Maria C.S.Ribeiro, António J.M.Ferreira, António T.Marques, *'Flexural analysis of polymer concrete beams reinforced with steel and pultruded rebars'*, 10th European Conference on Composite Materials ECCM10, Bruges, Belgium, 03-07/06/2002.

xi) M.C.S. Ribeiro, A.J.M. Ferreira, A.T. Marques, *'Durability assessment of unsaturated polyester and epoxy polymer mortars'*, ARQUIMACOM'02, S. Paulo, Brasil, November 2002.

xii) M.C.S.Ribeiro, C.M.L. Tavares, A.J.M. Ferreira, A.T. Marques, *"Static flexural performance of GFRP-polymer concrete hybrid beams"*, Key Engineering Materials, Vols. 230-232 (2002), 148-151.

xiii) C.M.L. Tavares, M.C.S. Ribeiro, A.J.M. Ferreira, R.M. Guedes, *"Creep Behaviour of FRP-reinforced polymer concrete"*, Composite Structures 57 (July 2002), 47-51.

xiv) M.C.S. Ribeiro, A.J.M. Ferreira, A.T. Marques, *'Flexural Behaviour of GFRP-Polymer Concrete Hybrid Structural Systems'*, 6th International Symposium on FRP Reinforcement for Concrete Structures (FRPRCS-6), 8-11 July 2003, Singapore, 695-704.

xv) M.C.S. Ribeiro, A.J.M. Ferreira, A.T. Marques, *'Assessment of thermal degradation on polymer mortars'*, Journal of Polymer Engineering, Freund Publishing House, Vol. 23, No 5, special issue, 2003, 299-313.

xvi) M.C.S. Ribeiro, A.J.M. Ferreira, A.T. Marques, *'Analysis and experiments on GFRP-Polymer Concrete Hybrid Beams'*, Journal of Polymer Engineering, Freund Publishing House, Vol. 23, No 5, special issue, 2003, 337-351.

xvii) M.C.S. Ribeiro, C.M.L. Tavares, M. Figueiredo, A.A. Fernandes, A.J.M. Ferreira, *'Bending characteristics of resin concretes'*, Materials Research-Revista Ibero Americana de Materiais, Vol.6, No 2, 2003, 247-254.

xviii) M.C.S. Ribeiro, J.M.L. Reis, A.J.M. Ferreira, A.T. Marques, *'Thermal expansion of epoxy and polyester polymer mortars. Plain polymer mortars and Fibre reinforced polymer mortars'*, Polymer Testing, Vol. 22, Issue 8, 2003, 849-857.

xix) M.C.S. Ribeiro, P.R.O. Nóvoa, A.J.M. Ferreira, A.T. Marques, *'Mechanical behaviour of polymer concrete modified with light organic aggregates'*, 2nd International Conference on Eco-Composites, 1-2 September 2003, Queen Mary, University of London, UK.

xx) M.C.S. Ribeiro, P.R. Nóvoa, A.J.M. Ferreira, A.T. Marques, *'Flexural performance of polyester and epoxy polymer mortars under severe thermal conditions'*, Cement & Concrete Composites, Vol 26, Issue 7, (2004), 803-809.

xxi) A.J. Mendes Ferreira, M.C.S. Ribeiro, A. Torres Marques, *'Analysis of hybrid beams of polymer concrete and composite materials'*, International Journal of Mechanics and Materials in Design, Vol.1 (2004), 143-155.

xxii) P.J.R.O. Nóvoa, M.C.S. Ribeiro, A.J.M. Ferreira and A.T. Marques, '*Mechanical Behavior of Cork-Modified Polymer Concrete',* Key Engineering Materials – Advanced Materials Forum II, Vols. 455-456 (2004), 805-809.

xxiii) P.J.R.O. Nóvoa, M.C.S. Ribeiro, A.J.M. Ferreira and A.T. Marques, '*Mechanical characterization of lightweight polymer mortars modified with cork granules',* Composites Science and Technology, Vol. 64, Issues 13-14 (2004), 2197-2205.

xxiv) M.C.S. Ribeiro, P.J.R.O. Nóvoa, A.T. Marques and A.J.M. Fereira, "*Mechanical characterization of lightweight wood-modified polymer concrete"*, Ciência & Tecnologia dos Materiais, Vol. 16, n.º 2-3, 2004, 81-87.

xxv) C. Novo, P. Nóvoa, C. Ribeiro, C. Ramos, A. Ferreira, A. Marques, *'Health monitoring with FRG sensors applied on polymer concrete structures',* 3rd International Conference on Composites in Construction –CCC 2005-, Lyon, France, July 11-13, 2005, 1053-1059.

xxvi) Paulo J.R.O. Nóvoa, Maria C.S. Ribeiro, António J.M. Ferreira, *'Development of lightweight polymer mortars based on binary aggregate compositions',* 3rd International Conference on Composites in Construction –CCC 2005-, Lyon, France, July 11-13, 2005, 733-740.

xxvii) M.C.S. Ribeiro, A.J.M. Ferreira, A.T. Marques, *'Development of composite hybrid structures based on polymer concrete – GFRP pultrusion profiles assembly system',* 3rd International Conference on Composites in Construction –CCC 2005-, Lyon, France, July 11-13, 2005, 1003-1010.

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II. POLYMERS IN CONCRETE REVIEW

2.1 History of Polymers in Concrete

2.1.1 Ancestor Materials

The use of polymeric compounds in building constructions is an old practice.

In the early history of humankind, there is evidence that people had the experience of combining organic polymers with inorganic materials to produce a high-strength and durable construction material. In the Bible, one of its excerpts mentions the use of bitumen, a natural polymer, to build the masonry foundations of the Babel Tower (Genesis 11:1-4). Other natural polymers such as albumen, glutinous rice paste, asphalt and even blood, were also widely used as binders in the construction of ancient palaces, temples and graves, which remain preserved to the present day (Chandra and Ohama 1994).

As far as we know, polymers have been used in construction as long ago as the fourth millennium B.C., when the clay brick walls of Babylonia were built using natural polymer asphalt in the mortar. The walls of Jericho were also built using a polymer bituminous earth in about 2500-2100 B.C.. Other historic applications of bituminous mortars in construction have been identified in the ancient Indus Valley cities of Monhenjo-Daro and Harappa around 3000 B.C., and near the Tigris River in 1300 B.C. (Kardon 1997). However, the most well known historic application of polymer mortars in construction is perhaps the Great Wall of China (Fig. 2.1). Two thousand years before our age, the glutinous rice paste-lime mortar was used to consolidate the brick walls of this great monument, one of the seven wonders of the world (Wang 1981).

Fig. 2.1. The Great Wall of China – One of the first applications of natural polymer modified mortars.

Apparently, the earliest indication of using natural polymers in cement concrete was in 1909, in the United States, when a patent was granted to L.H. Backland. Thirteen years later, in France, another patent on natural polymer modification for cement mortar was granted to M.E. Varegyas (Chandra and Ohama 1994).

In Britain, polymers in concrete advanced in 1923 with L. Cresson's patent for rubber-modified road surfacing materials (Cresson 1923). The patent refers to paving materials with natural rubber latexes where cement was used as filler.

In 1924, with L. Lefebure's development of natural rubber latex cement (Lefebure 1924), the first patent with the present concept of polymer modification was published, and later, in 1925, another patent concerning the innovation on that product was issued to Kirkpatrik (Ohama 1978).

Throughout the 1920's and the 1930's, the PMCs using natural rubber latexes were extensively developed (Ohama and Ramachandran 1995).

2.1.2 Development of Concrete-Polymer Composites

The first synthetic polymers were developed in the beginning of the twentieth century (Katz 1998) but industrial production of these new materials only saw significant expression from the '40s onward, in response to wartime decline in availability of natural rubber and increasing demand of the war effort. The first syntheses aimed at producing substitutes for two natural polymers: silk and caoutchouc (natural rubber) whose supplying sources in Malaysia were cut by the Japanese during the World War II. However, since then, with increasing advances in polymer technology, hundreds of synthetic polymers have been produced with no equivalent in nature.

Shortly after the end of World War II, began the practice of incorporating synthetic polymers in concrete and mortar materials (Dikeou 1978).

In the '40s, some patents were published on polymer-modified systems with synthetic latexes such as chloroprene and polyacrylic ester rubber latexes (Cooke 1941; Jaenicke et al. 1943). In 1953, Geist et al. reported a detailed study on polyvinyl acetate modified mortar (1953). In the '60s, styrene-butadiene rubber (SBR), polyacrylic ester and poly(vinylidene chloride-vinyl chloride) modified mortars and concretes became increasingly used in practical applications (Anon. 1959; Anon. 1964; Tyler and Drake 1961). Since then, the development of PMCs and PMMs has advanced significantly in various countries, particularly USA, Russia, West Germany, Japan and the UK (Ohama and Ramachandran 1995).

The widespread of knowledge about PIC occurred after researchers at Brookhaven National Laboratory and the Bureau of Reclamation in the United States performed an extensive research on the material during the '60s, although, USSR researchers claimed to have invented it earlier (Fowler 1999). Producing of PIC by full-impregnation technique was one of the most exciting material developments when it was announced. This new material could develop mechanical strengths up to three to four times greater than the concrete from which it was made and in addition, had excellent durability and chemical resistance, due to its extremely low permeability. With such outstanding properties, many applications were foreseen. However, as commented by Fowler, 'like a little girl who was all dressed up with no place to go', PIC by full-impregnation technique remained a material with great potential based on considerable research, but with essentially no cost-effective applications (Fowler 1999). Apparently, at the present, only one company at Ozawa in Japan, is still producing precast PIC components by full-depth impregnation.

PC came into use in the ‘50s, although applications were very limited. It was first used in the building industry in the USA, in 1958, for fabricating innovative precast wall panels and artificial marble (Prusinsky 1978). In Europe, it was used as a prepackage repair material as early as 1961 (Peschke 1978). However, it was only in the late ‘60s and early ‘70s, after PIC was developed that PCs received significant publicity. The increasing interest in the great performances of PICs led researchers to explore the use of monomers and resins as binders for aggregates. PC rapidly proved to be an excellent material for both concrete repair and precasting of construction elements.

Those years, the sixties and the seventies, were characterized by an unlimited belief in new and modern materials and techniques. The use of polymers was considered a sign of progress and a modern attitude in construction (Van Gemert and Knapen 2006). Glass fibre reinforced polyester panels, polyester resin and polyester mortars were known as inexpensive plastics. With the oil crise, the industrialized world realized that mineral oil, as a cheap basis for polymer production, was not longer available. It was also found that oil reserves were limited. As a result, all uses for polymers were questioned. The massive use of polymers as an alternative for classical building materials such as concrete, masonry, timber and metals decreased. However, the research on concrete-polymer composites did not stop and instead, it became part of a search for durable and sustainable construction materials. Polymers began to be used both in a more rational way, in the areas where their specific properties were needed, and in a more synergetic manner in combination with classical construction materials, with which, a more synergetic effect could be exploited (Van Gemert 2003).

This evolution led to new developments of CPCs. A better knowledge of material behavior, specially in the field of admixtures, a better understanding of curing processes, and a higher concern not only for the product’s end properties but also regarding processability, allowed the development of high performing CPC materials (Van Gemert

2003). As a result, CPC-science is now an invaluable element in the development of sustainable construction materials.

2.1.3 Relevant Activities

The progress of CPC-science can be assessed by the relevant amount of international activities, published papers, awarded patents and standardization works that have been developed in the last decades. The relevant activities addressing this subject are reported, in what follows.

Considerable volume of information and studies is presently available on concrete-polymer composites. According to Czarnecki's own estimation, until 2001, over seven thousand papers were published and over five thousand patents were awarded on CPC materials (2001).

The first International Congress on Polymers in Concrete (ICPIC) was held in London in 1975, and since then, ten ICPIC's more have been held, one at every three years. The next congress, the 12th ICPIC will be held at Chucheon, Korea, in 2007. Earlier and throughout this period, regular ACI (American Concrete Institute), RILEM (Union of Testing and Research Laboratories for Materials and Structures) and EASPIC (East Asia Symposium on Polymers in Concrete) symposia have also been held every two or three years, helping to make CPC materials household words in the construction industry. A list of the most important congresses and symposia that have been held up to the present time can be found in Table 2.1.

In the United States, ACI's Committee 548 for '*Polymers in Concrete*', was created in 1971. Its mission was to gather, correlate, and evaluate information on the effects of polymers on the properties of concrete, and to prepare a guide for their use. Since its birth, this committee has sponsored several symposia and convention meetings on a variety of topics relating to the use of polymers in concrete, by publishing the respective volumes of proceedings (ACI SP-40 1973; SP-58 1978; SP-69 1981; SP-89 1985; SP-99 1987; SP-116 1989; SP-137 1993a; SP-214 2003). A state-of-the-art report, entitled '*Polymers in Concrete*', was published in 1977 as ACI 548R-77, and an update edition, with modifications, in 1981. Since then, ACI's Committee 548 has issued several reports and users' guides for PC, PMC and PIC, as described later.

Also in the United States, in 1986, the Society of Plastics Industries (SPI) organized the '*Polymer Concrete'* Committee and prepared 12 test methods for polymer concrete. At few years earlier, the American Society for Testing and Materials (ASTM), under Committees C 09 ('*Concrete and Concrete Aggregates*') and C 03 ('*Chemical-Resistant non Metallic Materials'*), established several subcommittees that issued during recent years several standards on polymer mortars and polymer-modified mortars.

In Europe, RILEM's Technical Committee TC-105-CPC '*Concrete-Polymer Composites*', was organized in 1986. The tasks of this Committee were to make the state-of-the-art report on concrete-polymer composites, to set up classification criteria and to agree on terminology and definitions. Later, another RILEM Committee was created to study suitable test methods for concrete-polymer composites. At that time, although there was worldwide usage of CPC materials, no appropriate test methods were available. The need to prepare standard procedures for testing properties of concrete-polymer composites was urgent. The use of internationally agreed standards for testing would not only allow obtaining comparable and verifiable results, but more important, it would help eliminating products of low or unsatisfactory quality. RILEM endorsed to these points of view and formed the Technical Committee TC-113-CPT '*Test Methods for Concrete-Polymer Composites*'. Thirty-one test methods were prepared for CPC materials, mainly for polymer-modified concretes (and mortars), and polymer concretes (and mortars). An international symposium held at Oostende in 1995 concluded the Committee's work, with the presentation of its results to the international scientific and industrial communities.

In Japan, standardization work on concrete-polymer composites began earlier. In 1987, the Japan Concrete Institute (JCI) issued 17 standard test methods for polymer-modified mortars. Several reports in the area were also published: The '*Plastics Concrete'* Committee of the Architectural Institute of Japan (AIJ), which had a great contribution to the field of CPC materials for many years, published a user's guide and a state-of-the-art report. It was discharged in 1987. The '*Synthetic-Resins-for-Concrete'* Committee of the Society of Materials Science (JSMS) also published a design recommendation for polyester concrete structures in 1985, and a mix design guide in 1992.

Table 2.2 lists the most relevant international and institutional standards, specifications, reports and user's guides addressing CPC materials that have been published up to the present time (or under development).

Table 2.1. Overview of major international events in Polymers in Concrete.

Year	**Venue**	**Congress or Symposium Name**
1967	Paris, France	RILEM Symp., Synthetic Resins in Building Construction
1972	Hollywood, USA	ACI Fall Convention: Polymers in Concrete (1st Session)
1973	Atlantic City, USA	ACI, 1st Symp., Polymers in Concrete (2nd Session)
1975	London, UK	1st ICPIC- Int. Congress on Polymers in Concrete
1976	Mexico City, Mex.	ACI, 2nd Symp., Polymers in Concrete
1978	Austin, USA	2nd ICPIC- Int. Congress on Polymers in Concrete
1980	San Juan, Puerto	ACI, 3th Symp., Applications of Polymer Concrete
1981	Koriyama, Japan	3th ICPIC- Int. Congress on Polymers in Concrete
1983	Kansas City, USA	ACI, 4th Symp., PC: Uses, Materials and Properties
1984	Darmstadt, W.Ger.	4th ICPIC- Int. Congress on Polymers in Concrete
1986	Aix en Prov., France	RILEM Symp., Adhesion Between Polymers and Concrete
1987	Brighton, UK	5th ICPIC- Int. Congress on Polymers in Concrete
1990	Shangai, China	6th ICPIC- Int. Congress on Polymers in Concrete
1992	Moscow, USRR	7th ICPIC- Int. Congress on Polymers in Concrete
1994	Seoul, Korea	1st EASPIC-East Asia Symposium on Polymers in Concrete
1995	Oostende, Belgium	8th ICPIC- Int. Congress on Polymers in Concrete RILEM Symp, Test Methods for Concrete-Polymer Composites
1997	Koriyama, Japan	2nd EASPIC-East Asia Symposium on Polymers in Concrete
1998	Bologna, Italy	9th ICPIC- Int. Congress on Polymers in Concrete
1999	Dresden, Germany	RILEM 2nd Symp. Adhesion Between Polymers and Concrete
2000	Shangai, China Toronto,Canada	3th EASPIC-East Asia Symposium on Polymers in Concrete ACI Symp., Bridging the Centuries with Innovation Value
2001	Honolulu, USA	10th ICPIC- Int. Congress on Polymers in Concrete
2002	Poitiers France	RILEM Symp., Oragec'02 Organic Materials: A future in the field of civil engineering? Environmental uncertainties?
2003	Chuncheon, Korea	3th EASPIC-East Asia Symposium on Polymers in Concrete
2004	Berlin, Germany	11th ICPIC- Int. Congress on Polymers in Concrete
2005	Guimarães, Portugal	ISPIC- Int. Symposium on Polymers in Concrete
2006	Jeju, Korea	4th EASPIC-East Asia Symposium on Polymers in Concrete
2007	Chuncheon, Korea	12th ICPIC- Int. Congress on Polymers in Concrete

Table 2.2. Relevant standards, specifications, reports and users' guides on CPC materials.

Institution	**Designation or Title**
ASTM	ASTM C 267, 307-308, 321, 395, 399, 413, 531, 579-580, 658, 881-882, 884,905
	ASTM D 3262, 3517, 384.
DIN	DIN 51290
BS	BS 6319 Part 1-12
JIS	JIS A 1171-1174, 6203, 6909, 6916 (PMC); JIS A 1181- 1186, 5350. (PC)
JCI	JCI Test Methods for Polymer-Modified Mortar: 1-17.
SPI	SPI Polymer Concrete Test Methods: 1-7, 9-11, 13, 14.
RILEM	RILEM TC113 Test Methods for Concrete-Polymer Composites: PC1-PC13 (PC) PCM1-PCM18 (PMC)
JSMS	Guide for Mix Design of Polyester Resin Concrete;
	Recommendation for Design of Polyester Resin Concrete Structures;
AIJ	Guide for the Use of Concrete-Polymer Composites
ACI	ACI 548R-77(81) Polymers in Concrete;
	ACI 548.1R-97 Guide for the Use of Polymers in Concrete;
	ACI 548.2R-93 Guide for Mixing and Placing Sulfur Concrete in Construction;
	ACI 548.3R-03 Polymer-Modified Concrete;
	ACI 548.4 Standard Specification for Latex-Modified Concrete Overlays.
	ACI 548.5R-94 Guide for Polymer Concrete Overlays;
	ACI 548.6R-96 Polymer Concrete:Structural-Applications State of the Art Report;
	ACI 548.7-04 Test Method for Load Capacity of Polymer Concrete Underground Utility Structures;
	ACI 548.AR Specification for Type ES Polymer Concrete Overlays;
	ACI 548.BR Guide for Structural Analysis of Polymer Concrete Structures;
	ACI 548.C Specifications for Cast in Place Sulfur Concrete;
	ACI 548.XR Report on Precast Sulfur Concrete;
	ACI 548.YR Type EM Polymer Concrete Overlays for Bridge and Parking Decks;
	ACI 548.ZR Specification for Type PM Polymer Concrete Overlays.

The contributions made from all the above relevant activities (conferences and meetings, published reports, users' guides and standardization works), along with the practical experience gained within the growing industry that applies polymers to concrete technology, constitute the basis of CPC applied science, which is at present only limited by the ingenuity of the concrete user.

2.2 Polymer Concretes and Polymer Mortars

2.2.1 Introduction

As stated earlier, polymer concrete (PC), also known as synthetic resin concrete, plastic resin concrete or simply resin concrete, is a composite material in which the aggregate is bound together in a matrix with a polymer binder. The composite does not contain a hydrated cement phase, although portland cement can be used as an aggregate filler (ACI 1997). Polyester-styrene, epoxies and acrylics have been the most widely used monomers/resins, but vinyl ester, furan, urethane and sulfur, have also been applied as binders (Fowler 1999).

PC composites possess a unique combination of properties dependent of the formulation (Fontana and Bartholomew 1981). These include:

- High tensile, flexural and compressive strengths;
- Good chemical and corrosion resistances;
- Low permeability to water and aggressive solutions;
- Good long-term durability with respect to freeze-thaw cycles;
- Rapid curing at ambient temperatures, with quick development of mechanical strengths;
- Good adhesion to most surfaces;
- Excellent damping and electric properties (insulation);
- Low weight;

Application and performance of PC is dependent upon the specific polymer binder and its content, as well as the type of aggregate and its gradation. Fibre reinforcements and chemical additives, or other specific additions, as well as mixture design, mixing procedures and application techniques, also have an important role on final product properties. Therefore, the term PC should never suggest a single product, but a product family instead.

In this section, the main features of PC composites such as the common raw materials used in their production, process technologies, physical and mechanical properties attained, and major application fields, are reported. However, before going on to this review, it is worthwhile introducing a short parenthesis to clarify some basic concepts regarding polymers and polymerization processes.

2.2.1.1 Polymers and polymerization: The basic concepts

The most majority of polymers are organic materials, natural or synthetic, with long chain molecules of high molecular weight, made up of many individual repeated single units – the monomers- connected end to end. The word polymer is derived from the Greek *poly* meaning 'many' and *mero*, meaning 'part'. The term polymer is thus understood as something made up of many parts. Polymers made up of one type of monomer are called homopolymers, and those made up of more than one monomer type are called copolymers. A pre-polymer is a product resulting from the partial polymerization of a group of monomers.

Polymerization is the name of the reaction through which the monomers link to each other to form the long polymeric chains. Polymerization can occur with little energy input or only in the presence of a curing agent, depending on the chemical nature of the monomer. The curing agents can be constituted either by a catalyst system, which usually comprises an initiator and (or) a promoter, or by a hardener, as in the case of epoxy resins.

Initiators, often referred as catalysts, are chemical agents that initiate the growth of polymer chains by decomposing into free radicals that actually start the chain's growth. The rate of reaction, and hence the rate of polymerization, depends on the temperature and initiator concentration. The amount of initiator required is very low, ranging from 0.5 to 4% of monomer weight. The polymerization initiators generally used are either organic peroxides or azo-compounds (ACI 1997).

Promoters, also referred as activators or accelerators, are generally used in polymer composites when it is desired to conduct polymerization at ambient temperatures. A promoter is a chemical compound that greatly increases the decomposition rate of initiators. Promoters are also used in small quantities compared to the monomer. Some of the most commonly used promoters are N,N-dimethyl aniline, cobalt octoate and cobalt naphthenate (ACI 1997).

To prevent premature polymerization, most monomers contain an inhibitor when they are shipped by manufacturers. Inhibitors are free-radical scavengers. More specifically, they serve two functions. First, they can react with and deactivate the free radicals from growing polymeric chains. Secondly, they can act as antioxidants and prevent polymerization by reacting with oxidation products that may be formed in the storage vessel through contamination from oxygen in the air.

2.2.1.2 Thermosetting and thermoplastic polymers

Due to the great capacity of conformation, ‘plastics’ became the common designation for polymers. However, this term can be misleading, as there are many kinds of polymers, with considerable differences between them. In synthetic polymers, the arrangement and morphology of polymer chains can vary significantly. It is the different arrangement of polymer chains, as well as the way as these ones remain linked, that determines the classification of ‘plastic’ materials into two main groups: thermoplastics and thermosets. Each one of these groups is characterized by the type and relative amount of crosslinking of polymer chains.

Thermoplastics have weaker crosslinking of the molecular chains, and these links are lesser effective than in the case of thermosetting plastics. The long polymeric chains are held together by relatively weak liaisons, either by ‘Van der Waals’ forces or by hydrogen bridges, which are reversible links. These materials may be softened by heat and then regain their original properties upon cooling. This cycle of softening by heat and solidifying on cooling can be repeated more or less indefinitely, and is a major advantage in that it is the basis of most processing methods for these materials. It does have its drawbacks, however, because it means that the properties of thermoplastics are more heat sensitive. A useful analogy, which is often used to describe these materials, is that of candle wax: they can be repeatedly softened by heat and will solidify when cooled. Polyethylene, polystyrene, polyvinyl chloride, polyamides, cellulose acetate, polypropylene and polymethyl methacrylate (PMMA) are some examples of thermoplastic polymers (Crawford 1990).

Thermosetting plastics have stronger and more effective crosslinking of the molecular chains. They are produced by a chemical reaction, which has two stages. The first stage results in the formation of long chain-like molecules similar to those present in thermoplastics, but still capable of further reaction. In the second stage, very strong covalent bonds between polymeric chains are formed, assuring a tridimensional network extremely stiff, which is practically irreversible (crosslinking of chains). These materials cannot be remelted by heat. Indeed, heating process can result on a stiffer material due to the forming of superior amounts of crosslinks between polymeric chains. However, if an excess of heat is applied to these materials, they will char and degrade. This type of behavior is analogous to boiling an egg: once the egg has been cooled and hardened, it cannot be softened again by the application of heat. Since the crosslink of molecules involves strong chemical bonds, thermosetting plastics are typically quite rigid materials and their mechanical properties are less heat sensitive (within a certain temperature range) than thermoplastic materials. Epoxy resin systems, unsaturated polyesters, furan, vinyl ester and phenol resins are included in this group of polymers (Crawford 1990).

Both thermoplastics and thermosets can reap the benefit of fibre reinforcement or mineral filler inclusion although they have developed in separate market sectors. This situation has arisen due to fundamental differences in the nature of the two classes of materials, both in terms of properties and processing characteristics.

An important physical characteristic of both classes of materials is their glass transition temperature range (Tg). At temperatures above Tg, the material acts more rubbery, undergoing plastic deformation when loaded. Below Tg, the material behaves more in a glassy manner, deforming elastically and being susceptible to brittle failure (Su 1995). Thermosetting polymers present higher Tg values than thermoplastics materials.

The polymer type, regarding the glass transition temperature range and the effectiveness or density of the crosslinking, influences the physical characteristics of the polymer, which in turn, affects the properties of the hardened polymer composite.

The polymers more frequently used in PC materials are of the thermosetting type; however, in some applications thermoplastic polymers are also applied.

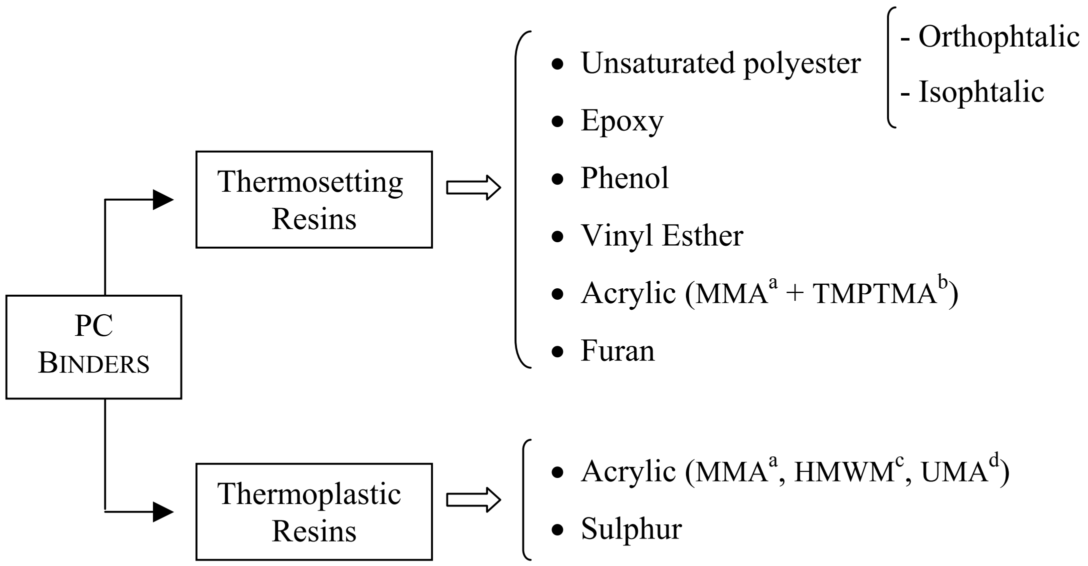
2.2.2 PC Raw Materials

2.2.2.1 Polymer binders

The role of polymer binder in PC technology is threefold: (1) they bond together the aggregates particles; (2) they fill the voids in the aggregate mixture, minimizing moisture absorption; and finally, (3) they provide sufficient fluidity in the mix to give a workable polymer concrete (McBee et al. 1986).

Thermosetting resins that cure at ambient temperature, such as unsaturated polyesters, epoxy systems and acrylic resins are the most often used polymers in PC materials, although thermoplastic materials, such as methacrylate based ones, have also been applied as binders. Sulphur also exists in polymer form, and sulphur concrete has been used for PC applications requiring high acid resistance (Fowler 2001).

In Fig. 2.2, the commercially available resins more widely used in PC composites are listed.



a) MMA -Methyl methacrylate; b) TMPTMA -Ttrimethylol propane trimethacrylate; c) UMA -Urethane methacrylate; d) HMWMA –High molecular weight methacrylate.

Fig. 2.2. Commercially available resins currently used as binders in PC materials.

The specific properties of each type of polymeric binder have a great influence on the final properties of the hardened PC, therefore, the main characteristics of most commonly used polymers in PC materials are here described.

i) Unsaturated polyester resin

The most widely used polymer-binders are based on unsaturated polyester polymers. In most process technologies associated to polymer composites, such as RTM (resin transfer moulding), pultrusion, filament winding, compression moulding and hand lay-up impregnation, the polyester binder became a general purpose choice, due mainly to its excellent performance/cost ratio.

Unsaturated polyester formulations result from the copolymerization of a primary resin (polyester prepolymer) with a vinyl monomer in which the prepolymer is dissolved. These formulations are available in the form of 60% to 80% solutions of the prepolymer in copolymerizable monomers, which act as crosslink agents. During hardening, the polyester prepolymer and the monomer react through their unsaturated groups (double bonds), and the resulting polymer binder is a thermosetting polymer (Blaga 1974b). The addition of a catalytic system (initiator and promoter) is required to initiate the polymerization reaction. Thus, a typical polyester formulation comprises four components: the prepolymer polyester resin, the reactive or crosslink agent, the initiator and the promoter.

The primary polyester resin is in general, a high viscosity material, with a low level of polymerization, produced by the polycondensation (polymerization reaction in which, secondary products are released) of dihidroxy alcohols with dicarboxylic acids. According the nature of the later, one can classify polyester resins into two main groups: isophtalic and orthophtalic polyester. Isophtalic polyester is produced from isophtalic acid while orthophtalic polyester is the result of a reaction with a phtalic acid.

Usually, commercially available polyester resins are already supplied with the reactive monomers. Depending on intended end-use, an additional amount of reactive monomers may be required. This can be done by adding the required amount of monomers to the polyester resin prior to polymerization. Due to low cost, low viscosity and easy handling, styrene and styrene-methyl methacrylate monomers are the most widely used reactive monomers.

The polymerization initiators commonly used in producing polyester PC are organic peroxides, namely dibenzoyl and methyl-ethyl-ketone peroxides (ACI 1997). As accelerators or promoters, cobalt octoates are commonly used. The promoters should first be mixed with the resin system, and only after, the initiators should be added. However, some commercial polyester resin systems are already pre-accelerated by the manufacturer. Hence, in these cases, there is no need of promoter addition to endorse the polymerization process. To prevent premature polymerization, stored unsaturated polyester-styrene resins are usually inhibited by the manufacturer with t-butyl pyrocatechol at levels of 10 to 20 ppm.

Polymerization reaction is exothermic and it occurs by addition, *i.e.* without release of secondary products. Polymerization and heat release rates are relatively high. These features, associated to an elevated setting shrinkage, can lead to undesirable internal stresses, which may inclusively lead to cracks in the component. However, it is possible to adjust environment temperature and catalyst system in order to optimize both, enlarge curing time and slow down the exothermic reaction.

Pot life, for each specific polyester resin, determines the available time for mixture manipulation and can vary as function of environment temperature, type and amount of catalyst system, formwork shape and material, and filler content. Curing process is also highly sensitive to environmental conditions, namely temperature, moisture and contact surface with air.

For temperatures below 18ºC, polymerization rate drops drastically and it may even not occur for temperatures below 10ºC. Parts not properly cured, show poor mechanical properties, not attainable with time. On the other hand, for temperatures above 25ºC, gel times become increasingly shorter, leading to mixture heterogeneities and deficient workability. Generally, moisture has a deleterious effect on curing process of polyester resin systems. For moisture contents higher than 0.1%, catalyst systems that apply cobalt compounds as accelerator are severely affected. Hence, if it is not possible to avoid environment moisture, the use of aromatic amines (promoter) with dibenzoyl peroxides (initiator) as catalyst system is strongly recommended. Oxygen may also inhibit the curing process of certain polyester resins. Components' casting into open formworks are sometimes problematic, as the surfaces in contact with air may not achieve a proper cure, remaining sticky and soft. Small amounts of paraffin or analogous compatible materials, thoroughly mixed in the resin, can solve or minimize this problem, as these compounds tend to migrate to the surface forming a shielding film (San José 1996).

In the absence of thermo post-curing treatment, final properties of polyester resin systems are attained after a minimum period of one week at ambient temperature. These properties vary according to polyester resin type and crosslink process, but in general, they are reasonably good in terms of dimensional stability, mechanical strength and resistance to chemical agents.

PCs made with polyester resin binders have good mechanical strength, relatively good adhesion to other materials, and good chemical and freeze-thaw resistance, especially those made with isophtalic polyester resins. They show, however, large setting and post-setting shrinkage (up to ten times greater than portland cement concrete), which is a serious disadvantage in certain applications (Blaga and Beaudoin 1985).

ii) Epoxy resin systems

The word epoxy is derived from *epi*, the Greek word for 'on the outside of', and *oxygen*, which describes part of the molecular structure of the polymer (Popovics 1993). Epoxy polymer systems, like unsaturated polyesters, are thermosetting polymers.

Epoxy systems constitute a class of plastic materials widely spread in the field of civil engineering, aeronautics and industry in general. They were initially applied as adhesives, but due to their excellent properties, they rapidly gained the status of construction material on their own. Nowadays, epoxy compounds are commonly applied as coating, patching, reinforcing and repair materials, and a large number of new other applications have already be considered for these products as is the case of their use as binder, co-binder or impregnator for CPC materials. The main drawback associated to this kind of polymers is their relatively high cost (San José 1996).

Epoxy compounds are generally formulated in two or more parts. Part A is most often the portion containing the epoxy resin that contains the epoxy groups, and Part B, is the hardener system. The ratio of resin to hardeners varies considerably depending on the formulation of epoxies (ACI 1997).

Most commercial epoxy resins are condensation products of bysphenol A with epychloridrine (dyglicdil ether of bysphenol A), resulting in a primary resin with linear polymeric chains, and with hydroxyl and epoxy groups in each extremity that allow further crosslinking. Reticulation process, leading to a tri-dimensional network, is accomplished by the chemical reaction between the epoxy groups of primary resin and the active hydrogen or free radicals supplied by the curing hardeners.

The epoxy primary resin can be hardened with a variety of curing agents, the most frequently used being polyamines, polyamides and polysulfide polymers (ACS 1979). The use of polyamine hardeners results in PC products with the highest chemical resistance, while epoxy PC products cured with polyamides have greater flexibility, better heat resistance, and reduced tendency to chalk in outdoor exposure. However, the later present lower solvent and chemical resistance than similar products cured with polyamines. The use of polysulfide polymers produces epoxy PC with even greater flexibility (Blaga and Beaudoin 1985).

Polymerization reaction, as in the case of polyester resin systems, is exothermic with rising polymerization rates with increasing temperatures. Heat release may be considerable and it depends of system reactivity, environment temperature and total amount of mixture. Depending upon specific formulation, heat release can lead to significant shrinkage on final product. However, exothermic peak occurs before hardening, which partially prevents the risk of internal residual stresses (San José 1996).

Epoxy formulations present great versatility, which can be demonstrated by the wide range of properties offered by these compounds: a) extremely short curing times, almost instantaneous, or very long working lives, of several hours; b) ability to cure at very low or at high temperature levels; c) chemical resistance concerning specific chemical agents, covering almost the complete spectrum of solvents, alcohols, ketone, alkalis, bases, organic and inorganic acids; d) high flexibility regarding workability (low to high viscosity formulations); etc. (Mendis 1983).

Thus, chemical nature of this group of resins allows a large and varied set of properties, therefore, almost without exception, epoxy systems must be formulated to make them suitable for specific end-uses. An even greater number of flexibilizers, fillers and other chemicals may be combined with these systems to produce several hundred different end-products with various combinations of their unique properties (ACI 1997).

Epoxy PC products exhibit, in general, high adhesion strength to most materials, low-setting and post-setting shrinkage, high chemical resistance, and good fatigue and creep resistances. Because epoxy polymers are relatively expensive, epoxy PC is used for special applications, in situations in which its higher cost can easily be justified, such as mortar for industrial flooring to provide physical and chemical resistances, skid-resistant overlays in highways, epoxy plaster for exterior walls and resurfacing material for deteriorated areas (Blaga and Beaudoin 1985).

iii) Acrylic resins

The most common acrylic polymer used in PC is poly methyl methacrylate (PMMA), obtained by polymerization of methyl methacrylate (MMA) monomers (Blaga 1974a). The low viscosity, high reactivity, excellent wetting ability and relative low cost made MMA monomers very popular in PC industry. PMMA has an excellent weathering resistance, good waterproofing properties, good chemical and impact resistance, and relatively low setting shrinkage. Most of these features are also showed by acrylic-based PC products. In addition, these materials present coefficients of thermal expansion equivalent to that of portland cement concrete, which is an advantage in repair applications.

The main shortcoming associated to these compounds comes from the high flammability and volatility of MMA monomers, which may constitute a safety problem in manufacturing and casting processes of acrylic-based PC materials (ACI 1997).

In structural applications, MMA monomer is usually crosslinked with a reactive agent or poly-functional monomer, most of the times trimethylol propane trimethacrylate (TMPTMA), resulting in a thermosetting plastic material. As a catalyst system (initiator-promoter), dibenzoyl peroxide and dimethyl-p-toluidine are usually applied (San José 1996). The chemical nature of the polymerization reaction is very similar to that of polyester resins. Whereas polyester resins result of copolymerization of a pre-polymer with a monomer, methacrylate resins are copolymers of two different monomers.

Although the MMA monomer is a little more expensive than the prepolymer-monomer used in the more popular polyester PC, its unique properties justify its use in many applications, including the manufacture of stair units, sanitary products, countertops, and façade elements.

A highly successful development of acrylic PC has been its use as a rapid-setting, structural patching material for repairing large holes in bridge decks and highways (Blaga and Beaudoin 1985).

iv) Furan resins

Furan polymers are based on furfuryl alcohol monomer, which is derived from agricultural wastes such as corn cobs, rice hulls or sugar cane bagasse (ACS 1979).

The furan monomer system is usually crosslinked with furfuraldehyde or formaldehyde to yield thermosetting polymers. These resins are highly resistant to most aqueous acidic or basic solutions and strong solvents, such as ketones, aromatic and chlorinated compounds. They also present an excellent heat resistance and good capacity to penetrate into porous materials (Muthukumar and Mohan 2005). In addition, being derived of agricultural residues, they are relatively inexpensive when compared to other synthetic resins. The main inconvenient of furan resins arises from their strong dark colour, which may constitute an aesthetical limitation for certain applications.

Furan polymers are used as binders in mortars and grouts to achieve chemical-resistant brick floors and linings. Precast or cast in-place tanks, repair of existing concrete and the protection of new one from chemical attack are other reported applications. Since these polymers have a very low viscosity, high filler contents are possible with binder content running in the 7% to 13% range (McBee et al. 1986). In addition to exhibiting superior chemical resistance, furan concretes have excellent resistance to elevated temperatures and thermal shocks (Blaga and Beaudoin 1985).

v) Phenolic resins

The first completely synthetic polymer was a phenolic resin and it was introduced by Leo Baekeland under the name of ‘Bakelite’ (1909). It was initially used as a substitute for shellac to make billiard balls, but later, was applied to make valve parts, knobs, knife handles and moulded plastic containers for radios and electronic instruments.

Phenolic resins are thermosetting polymers obtained by condensation of phenol and formaldehyde. Two different polymerization reactions may occur depending upon the phenol/formaldehyde ratio and pH environment.

When polymerization reaction is carried out with an excess of formaldehyde and under alkalis catalysis, a thermoplastic polymer with low molecular weight is produced. This kind of resins may lead to thermosetting polymers at high temperatures (up to 150-170ºC) and under alkalis environments. The crosslinking process may also occur at ambient temperatures if pH environment is decreased to highly acid values (pH<1).

If instead the polymerization reaction is processed with a surfeit of phenol and under acid catalysis, the addition of a hardening agent is required to yield a thermosetting polymer. A typical hardening agent is hexamethylenetetramine, a reaction product of formaldehyde with ammoniac (San José 1996).

The excellent behaviour under fire of phenolic resins is their main advantage over other synthetic polymers. Besides this desirable feature, phenolic resins also present excellent resistance to abrasion, chemical attacks, and high temperatures, good dimensional stability and great adhesion to other resins (Gálan 2001). Their main drawbacks, regarding their use as binder in PC materials, seems to be their availability being limited to dark colours, the high temperatures required for a proper polymerization process and the great sensitivity to pH of the environment (under intermediate pH environments, polymerization reaction may not occur).

vi) Sulphur based polymers

Sulphur polymers are inorganic thermoplastic materials produced by heating sulphur in the temperature range of 120ºC to 150ºC. In this range, sulphur is a liquid with a viscosity slightly higher than that of water. On cooling to ambient temperatures, solid products are formed.

The use of sulphur as a hot-melt bonding agent and sealer for water vessels has been known since prehistoric times (Sheppard 1975). Investigation works in the early ‘60s showed that sulphur concretes with excellent strength properties could be prepared from sulphur and aggregates mixtures (Crow and Bates 1970; Dale and Ludwing 1966; Dale and Ludwing 1968). However, these first sulphur concretes failed when exposed to normal temperature cycling, moisture conditions, or water immersion. Later, these problems were solved by the development of sulphur modifiers that resulted on durable and corrosion-resistant sulphur concretes (McBee and Sullivan 1982; McBee et al. 1981; Sullivan 1982).

By reacting sulphur with unsaturated hydrocarbons, dicyclopentadiene (DCPD) and oligomers of cyclopentadiene (CPD), stable sulphur compounds can be prepared by the formation of long-chain polymeric polysulphides. Other modifiers for treating sulphur include olefinic hydrocarbon polymers, polyol additives, phosphoric acids and organosilanes (McBee et al. 1986).

Since the ‘80s, commercial production and installation of corrosion-resistant sulphur concretes has increased continually, especially in the United States. Sulphur concretes are being precast or installed directly in industrial plants where conventional concrete materials have failed due to acid and salt corrosion. Typical installations are floors, electrolytic cells, drainage ditches, sidewalls and foundations for columns and pumps.

Like phenol based concretes, the main disadvantage of sulphur concretes is the hot-melting process involved in their production.

2.2.2.2 Aggregates

Aggregates for PC composites, as for conventional concretes, are generally obtained from two sources. One is natural sand and gravel deposits produced by natural weathering and abrasion from running water. These aggregates are primarily silica. The second source is quarried rock, which is previously crushed and screened. Stone quarry products include limestone, granite, quartz, marble, sandstone, and in general, all coarse and fined-grained igneous rock. As filler materials (here understood as very fine aggregates), chalk, calcium carbonate, clay, fly ash, silica fume, metallic fillers, and even portland cement, have been successfully used in the production of PC materials.

Generally, any dry, non-absorbent solid material can be used as aggregate. However, in order to achieve the full potential of PC products, aggregates of the highest available quality should be used (*e.g.* silica-based, quartz, granite or good limestone).

When sand is used as single aggregate, the concrete composite material is usually referred as polymer mortar.

All general considerations regarding aggregates in conventional cement concrete are also valid for PCs, with one exception: moisture content. Aggregates for PC production must usually be dry, and always be free of dust, grease, oil, or other organic materials. Moisture reduces the bond strength between most of the monomers and epoxy resins and the aggregate (Fowler et al. 1981). Unless otherwise specified, surface moisture should not be allowed for aggregates used in the production of PC. Moisture contents of less than 1% are acceptable, although some systems can tolerate up to 3% (ACI 1997).

Natural and artificial lightweight aggregates, such as expanded clay, expanded glass, plastic chips, cork and rubber particles, can also be used in order to decrease self-weight or introduce other features into the final product, as thermal and acoustic insulate properties. (Kawakami et al. 2001; Larena et al. 1996; Lee et al. 1998; Nóvoa et al. 2005; Nóvoa et al. 2004; Ribeiro et al. 2003).

Due to the great capacity of conglomeration and hermetic nature of polymer binders, wastes, debris and by-products of other industries, even the hazardous ones for public health, may also be incorporated as aggregates in PC materials. As described later, recycling and wastes' reutilization are some of the possible uses of PC composites that have been exploited in recent years.

2.2.2.3 Fibre reinforcements and other strengthening materials

In certain applications of PC, short chopped fibres are sometimes introduced as reinforcements. These include glass, carbon, polyaramid and metal fibres. Fracture toughness, flexural and splitting flexural strengths are some of the mechanical properties enhanced by the incorporation of fibre reinforcements in PC, and steadily reported in several investigation works (Brockenbrough and Atterson 1982; Griffiths and Ball 2000; Ohama and Nishimura 1982; Ohama and Sugahara 1981; Potapov et al. 2004; Reis 2003; Vipulanandan et al. 1988).

Natural fibres, such as sisal, bamboo, wood, hemp and coconut, which have been used to 'strengthen' conventional cement concrete and mortars, may also be considered for PC materials (Filho et al. 2003; Lundin et al. 2004; Yao and Li 2003).

In structural applications of PC materials, mild steel bars, high-strength steel bars (for pre-stressed concrete), and FRP (fibre reinforced plastics) rods with carbon or glass fibres, have also been used to reinforce PC elements (Ferreira et al. 2002; Rebeiz et al. 1993; San José and Ramírez 1999; San José et al. 1998; Tavares et al. 2002a; Tavares et al. 2002b).

2.2.2.4 Additives, modifiers and other admixtures

Flame retardant systems, plasticizers, stabilisers, pigments and coupling agents are the most common additives used in PCs.

Flame retardants: Most polymers, because they are organic materials, are flammable. Additives that contain chlorine, bromine, phosphorous or metallic salts reduce the likelihood to combustion occurrence or spread.

Plasticizers: Plasticizers are low molecular weight materials that alter the properties and forming characteristics of the binder system. They have a reducing effect on polymer viscosity, improving the workability and mouldability of fresh PC material.

Stabilisers: Stabilisers prevent degradation of the polymer due to environmental factors. Antioxidants, heat and ultraviolet stabilisers are the most widely used.

Pigments: Pigments introduced during mixing process allow a large variety of colours in the final product.

Coupling agents: Coupling agents are adhesion promoters for systems involving organic and inorganic materials. Since they are bifunctional materials, they react with both the organic polymer and the inorganic siliceous aggregate (or fibre reinforcement), improving the adhesion towards the concrete matrix. A variety of silanes and titanates are commercially available for this purpose.

Several other modifiers are also used either in resin binder systems or directly in PC formulations, in order to change both the properties of the mixture and the resulting mechanical properties for the cured material. These include resins modifiers (reactive modifiers), and other additives or admixtures used to modify viscosity, flow, adhesion, wetting, curing time, and naturally, the entire range of mechanical properties such as tensile strength, compressive strength, modulus of elasticity, flexibility, temperature resistance, etc.

2.2.3 Mix Design and Manufacturing Processes

As with portland cement concrete, the best mixture design and manufacturing process for PC must account for the properties desired for specific uses.

2.2.3.1 Mix design

In developing mixture designs for PCs, aggregates and polymer binders with physical, chemical and mechanical characteristics consistent with their future use must be selected. By making the proper material choice, one can obtain concrete resistant to acid, alkali, ultraviolet radiation, solvents, or combination of these.

i) Polymer binder type

The wide variety of resins and polymer binders used in PC materials may result in a bewildering impression. Which resin is the best? Which polymer should be used for a given purpose? There is no simple answer to these questions but a rational approach will lead to satisfactory solutions.

First, no single polymer binder is the best one under all circumstances. Even if cost is ignored, none of the available commercial resins can be regarded as the all-round winner. So, if no single resin is the best all round, one should look at the second question: which polymer binder should be used for a given purpose? Most properties of PC, on both fresh and hardened stages, depend, to a greater or lesser extent, on the properties of the polymer binder used. It is on this basis that the choice of binder matrix could be made. However, in many cases, no one polymer binder is the best one and more than one polymer type met the predefined requirements. The choice will depend on availability, on cost (a very important feature in engineering decision-making), and on the particular circumstances of available equipment and skilled labour force.

ii) Aggregate type and gradation

All the above considerations, regarding the best choice of polymer binder for a specific PC product, are also generally applied for the selection of aggregate component. Intend end-use should be always taken into account. For instance, quartz aggregates are suitable in acid environment, whereas either quartz or limestone aggregates may be used where salt corrosion is the problem (McBee et al. 1986). In general, aggregates for corrosion-resistant PCs must be clean, hard, tough, strong, durable and free from any swelling constituents.

Aggregate gradation design should aim to produce aggregates mixtures with the maximum bulk density and the minimum voids' content. The distribution should be such as to allow for a minimum void volume for dry-packed aggregate. With this design, less polymer binder will be required to assure the proper bonding between all aggregate particles, resulting in a more economical PC. Generally, this leads to higher strength materials, due to improved aggregate agglomeration, and to less shrinkage, as polymer binder content is lower. Usually, suitable aggregate gradation designs for PCs are achieved based on Fuller maximum density curves (McBee et al. 1986).

iii) Polymer binder content

As the most expensive component of PC, in order to decrease the total cost of final product, just the required amount of polymer binder should be used. Therefore, polymer binder content is generally small and is usually determined by the size, gradation and total specific surface of aggregate mixture. Monomer viscosity also has some influence on binder content: the higher the viscosity of the resin system, the higher the amount that will be necessary to achieve the required workability of PC mixture.

Criteria used to determine the best mix design are based on adjusting the binder level to provide the best balance between maximum mechanical strength, maximum specific gravity, minimum absorption water, and workability. Normally, the polymer content will range from 5% to 15% of the total weight, but if average size of aggregate's particles are very small, as in the case of some polymer mortars and grouts, up to 30% may be required (Blaga and Beaudoin 1985).

In chapter III, optimization processes for PC formulations are thoroughly discussed.

2.2.3.2 Manufacturing process

The manufacturing process of PC largely depends of its end-use.

The ACI report 'Guide for the use of polymers in concrete' (1997) considers three main classes of PC products according their specific end uses: polymer concrete patching materials, for repair purposes; polymer concrete overlays, for floorings, bridges and decks; and precast polymer concrete products.

For each class, respective process technology is described.

i) PC patching materials

In order to achieve a successful repair, before attempting any patch up on a concrete surface with a PC patching material, two surface conditions must be met: a) the concrete surface must be strong and sound, without signs of delamination, and b) the concrete surface must be dry and clean (free of dust, oil grease or paint).

All deteriorated and unsound material should be removed. Patching over delaminated areas is not recommended, unless delaminations are made sound (filled and glued) by epoxy injection or other techniques. Moisture on the concrete surface should be also eliminated, unless it is known that the adhesion of PC material to be use is not affected by moisture. Dry-compressed air and gas-fire torches can be employed for cleaning and drying the concrete surfaces.

Several methods have been applied for placing PC patching materials: dry pack placement, premix placement and pre-packaged systems (ACI 1997).

In the *'dry pack placement'* method, the graded aggregate is placed in the area to be repaired and compacted by tamping, and posterior, saturated with a low viscosity monomer mixture. Care should be taken to assure that the aggregate is completely wetted with the monomer; therefore, sometimes several monomer applications are required. This method eliminates the need of using a mechanical mixer, but it is difficult to determine the required amount of monomer.

In the *'premix placement'* method, the mixing and placement of PC is similar to that used for portland cement concrete. Polymer binder is added directly to the mixer (which can be a conventional concrete one, paddle-type or rotating-drum mixer), then fine aggregates are added, and finally the coarse aggregates. Once all particles are completely wetted, the composite mixture is placed over the repair area. Over-mixing should be avoided as it will only serve to shorten the working period and may incorporate air in the mix unnecessarily. Generally, the surfaces to be coated should first be primed with the polymer binder. This method can be used either for high or low viscosity polymer binders, and their quantity is predetermined.

Finally, in the case of '*prepackaged systems'*, all the components are packaged in units so that no field measurements are required. The mixing of the components can be made by hand or through mechanical mixers. The entire composite is then placed and can be consolidated using adequate methods. In all cases, the recommendations of the manufacturer should be strictly followed.

Once the PC has been placed by any of the methods described, it can be finished by using manual or power trowels, or vibrating screeds. Power trowels are not recommended with MMA systems due to their high flammability.

Cleaning tools after placement of PC material is always required. For this purpose, organic solvents such as 1,1,1-trichloroethane, methylene chloride, xylene or methyl ethyl ketone (MEK) may be used. However, other more environmentally friendly cleaners, which act as emulsifiers instead of solvents, are becoming increasingly available and their use is advised. Clean up of mechanical mixers can be accomplished by immediately rinsing the drum with one of these chemicals, followed by operating the mixer with a load of coarse aggregate.

ii) PC overlays

As in the case of PC patching materials, prior to the application of a PC overlay, the surface to be coated must be evaluated, and according to that evaluation, a proper preparation should be conducted. The above general considerations for patching PC materials, regarding removal of delaminated or deteriorated material, and concrete surface cleaning, are also here applied.

The ACI report (1997) recognizes four main types of PC overlays: thin sand-filled resin, polymer seal coat, premixed polymer concrete and pre-packaged polymer mortar overlays' types.

'*Thin sand-filled resin overlays'* are placed by multiple applications of resin and sand aggregates. A thin layer of initiated and promoted resin is applied over the cleaned concrete surface. Immediately thereafter, a slight excess of sand is spread onto the resin layer before it has gelled or cured. When the resin is completely cured, the excess of aggregate is taken off, and the process is repeated until a total of three or four layers have been applied. This results on a nonpermeable overlay with a highly skid-resistance surface.

For the application of a '*polymer-seal-coat overlay'*, a 6 mm layer of dry sand is placed upon the clean and dry concrete surface. A skid-resistant and hard aggregate is then broadcast over the sand and hand rolled. The monomer mixture requires two applications. The first application uses a low-viscosity system to penetrate into the aggregate mixture. A second application of monomer, whose viscosity has been increased by the addition of a pre-polymer, is then spread over the aggregate surface and allowed to cure. Polyethylene films are often used to reduce the monomer evaporation.

In the '*premixed PC overlay'* type, the grade aggregate and the monomer or resin system are mixed together in a portable concrete mixer, placed on the concrete surface, and then spread and compacted. Continuous pavement-finishing machines may be used for highway overlays. Some overlays require a final broadcasting of aggregate onto the finished surface in order to provide a skid-resistance surface.

The *'pre-packaged polymer mortar overlay'* materials are generally applied in thicknesses of 6 to 13 mm. Guide-rails placed on both sides of the lane to be overlaid have been used with success. The mortar mixture, after being mixed in a mechanical mixer, is placed within the forms. The guide forms are moved along as required.

In all situations, the manufacturer's recommendations should always be followed.

iii) Precast PC products

Most of the procedures used for precast portland cement concrete can be applied to making precast PC products.

Mixer selection is dependent on the monomer system being used. Conventional concrete mixers perform well with low-viscosity monomers, but high-viscosity formulations tend to adhere to the mixer paddles or to the rotating drums. Mixers should be selected so that do not generate sparks.

For production casting, a continuous flow, high-speed mixer is far preferable to batch mixers. Such automatic mixers are self-cleaning, requiring much less labour than batch mixers, which should be thoroughly cleaned after each batch. Refined continuous mixers with various degrees of sophistication are now available, including automatic feeding systems for aggregates and resin binders. Automatic and variable metering of initiators and promoters, resin pre-heaters and vacuum systems are also available. These mixers present relatively high output rates and, with continuous delivery, can provide very high daily production with much lower maintenance requirements than batch mixers. Some examples of continuous automated mixers for precast PC products are shown in Fig. 2.3.

Fig. 2.3. Examples of continuous automated mixers for PC with vacuum support and automatic feeding systems for aggregates, resin binders, initiators and pigments.

Formworks and moulds for precast PC products must be extremely durable, solvent resistant, have a low coefficient of thermal expansion, have smooth and cleanable surfaces, and preferably, should be a good heat conductor (ACI 1997). For very low-viscosity monomers, such as MMA, sealed forms are required. Stainless steel, mild steel, silicone rubber, polyethylene, polypropylene, cast aluminium and wood have been successfully used as forming materials for PC materials.

Generally, resin binders adhere strongly to the most conventional forming materials. Selection of proper release agents is therefore important. Plastic sheeting, such as polyethylene, vegetable oils, paraffin wax, or silicone greases may be used for that purpose.

Formwork design must account for the effects of polymerization shrinkage, exothermic heat, accessibility for removing entrapped air, for cleaning, coating, and reinforcing (if applied). In addition, formworks should be designed in order to minimize or eliminate postcasting process and finishing work. If possible, the forms should be conceived so that the unformed surface is not exposed in the finished product, as smooth and high quality finishes are best achieved against formed surfaces. As with conventional concrete, different forming materials produce varying surface textures. Texture variations from glassy smoothness to lightly sandblasted or wood appearance have been achieved.

For mix consolidation, conventional concrete vibrators may be used. Form vibration, achieved by vibration tables or by attached vibrators to the formworks, provides better results than internal vibration (*e.g*. finger vibrators). Amplitude and frequency are more critical with PC than with traditional concrete. Low-viscosity monomers require low-frequency with high-amplitude to remove entrapped air, while higher viscosity monomers are better consolidated by high-frequency, low-amplitude vibrators. According ACI report (1997), for high-viscosity resins, frequencies in the range 6000 to 9000 cycles/second (Hz), with an amplitude of about 1 mm, provide the best results.

In precast production, the temperature development in the PC formulations is very important. As stated earlier, the polymerization reaction is exothermic, with the amount of heat produced dependent on the types and amounts of materials of the specific formulation. This heat development affects the time at which formwork can be removed from the PC. Moulds may be removed after gel state, at a time when the PC has developed enough strength that allow demoulding process without damaging the part that have been casted.

2.2.3.3 Safety considerations

The use of polymers in concrete construction requires careful considerations to safety. The unique nature of these materials and processes in construction requires cautious attention by workers, engineers, contractors and inspectors.

Some chemicals used in the production of PCs may be flammable, volatile, toxic, or a combination of these. Therefore, all job personnel involved in the production of PC materials should be aware of the potential hazards and the safe handling practices related to these chemicals, which include monomers, epoxy systems, initiators and promoters.

The main safety aspects concerning these products are here briefly discussed.

i) Monomers

Generally, monomers are volatile, combustible, and toxic liquids. The principal factors that influence the stability of monomers and determine the methods to be used for safe handling are: a) level and effectiveness of inhibitors, b) storage temperature, c) flammability and combustibility, and d) toxicity. Secondary safety considerations include sensitivity to light, moisture and oxygen. Odour may be an indirect problem because it causes discomfort, but in itself is not a physical hazard.

The inhibitor level should be maintained above a minimum concentration at all times, which is dependent of resin type. If it drops below the critic level, usually due to a long storage, the amount remaining may not be adequate to prevent a premature polymerization. Other factors, such as heat and air may also be responsible for the depletion of inhibitor. Drums containing monomers should not be stored in the sun. As soon as possible after they are received, they should be placed in a cool, shaded area. Data on the effect of temperature and inhibitor level on the storage stability of monomers is available from the manufacturers.

Special attention should be paid to the flash-points and explosive limits of monomers, also available in respective safety data sheets. For instance, MMA, styrene and butyl acrylate have been classified as flammable liquids because their close-cup flash points are less than 38ºC. Other monomers not classified as flammables, such as polyester-styrene, are nevertheless combustibles and should be treated accordingly.

Like most organic chemicals, most common monomers have varying toxic properties, thus some precautions are necessary. The safety and health labour codes established limits for the concentrations in the air of MMA and styrene to which employees may be exposed. Normally, irritation in the eyes or respiratory system becomes noticeable long before explosive or flammable concentrations are reached.

ii) Epoxy systems

Special precautions should be taken when handling epoxy resins, curing agents and solvents with which they are used. Skin irritation as burns, and skin sensitization reaction, constitute two typical health problems that may be encountered when epoxy materials are carelessly handled. Allergic reactions may occur immediately, but in other cases, they occur only after long periods of continual exposure. Safe handling of epoxy materials can generally be accomplished in a well-ventilated area and using disposable gloves, suits and equipment, wherever possible. Safety eyeglasses are also strongly recommended. Involuntary habits, such as face scratching and adjusting eyeglasses should be avoided. In case of direct contact with skin, the user should wash or shower immediately with soap and water. Solvents other than soap and water soluble cleaners are not suitable for personal cleanup, as most solvents merely dilute the epoxy compounds, aiding them in penetrating the skin. Further details on handling epoxy compounds can be found in ACI report 'Use of epoxy compounds with concrete' (ACI 1993b).

iii) Initiators and promoters

The polymerization initiators should be kept in a cool place, well away from heat or any source of sparks and light. They should be stored separately, away from monomers, flammable and combustible materials, and, in particular, away from promoters or other oxidizing materials. Depending upon initiator's nature, these chemicals may present both fire and explosion hazards, can be toxic and skin irritants, chock and sunlight sensitive, and, usually, they easily react with other chemicals. Stocks should be kept to a minimum, as initiators have a limited shelf life losing efficiency with time.

The procedures for handling promoters are similar to those used for monomers. Promoters should be kept in a cool place, but not in the same area as the peroxide initiators, and should be treated as toxic and combustible materials. Particular care must be taken to avoid mixing promoters directly with peroxide initiators, because the mixture can react explosively. Promoters should first be added to the monomer and dispersed thoroughly. Then, and only then, should the peroxide be added.

Smoking should be absolutely forbidden in and around facilities areas where monomers, initiators, and promoters are stored or used. Fire extinguishers should be strategically placed around the working areas. The extinguishers should use foam, dry powder, or carbon dioxide.

Other general safety rules, concerning the handling of chemicals used in PC production, can be found in the safety and health labour codes, which typically govern: a) limitations of chemicals' storage, b) fire protection and detection, c) employee safety, d) plant ventilation requirements, and e) site use restrictions. The safety data sheet of each particular material, given by the manufacturer, constitutes other important information source. When properly used and applied, by well-informed workers under technically competent supervision, the chemicals used in PC production should present no undue safety hazards.

2.2.4 Generic Properties of PC Materials

The properties of the fresh and hardened polymer concrete and mortars are affected by a number of factors such as mix formulation (which includes polymer type, binder content, aggregate type and gradation), air content, mixing process and curing conditions. In particular, the properties of polymer matrix have a strong influence on final properties of PC materials, and most of them, are markedly improved over conventional cement concrete materials.

The general properties of PC materials, regarding their main advantages and principal limitations comparing with conventional cement concrete and mortars, are here discussed.

2.2.4.1 Main assets of polymer mortar and concretes

i) Higher compressive, tensile and flexural strengths

In general, PCs and PMs present considerable higher mechanical strength than ordinary cement mortar and concretes. Typically, PC systems are stronger by a factor of 3 or more in compression, a factor of 4 to 6 in tension and flexure and a factor of 2 in impact, when compared with ordinary portland cement concrete (Dharmarajan 1987; Fowler and Paul 1981).

The increase in mechanical strength is particularly notorious relatively to tensile and flexural resistances. Flexural to compressive strength ratios in the range of 0.2 to 0.5 are commonly found in PC materials. This is interpreted in terms of the contribution of high tensile strength by the polymers themselves and an overall improvement in matrix-aggregate bond.

Strength properties are influenced by various factors that tend to interact with each other. The main factors are the nature of materials used, the controlling factors for mix proportions, mixing processes, curing methods and, of course, applied testing methods. The same mix formulation processed by different mixing techniques (ordinary mechanical mixer and vacuum assisted mixer) result on PC materials with distinct mechanical strengths. Compressive strength is more sensitive to mixing process as air or void content have, in general, a stronger influence on compressive properties than on flexural or tensile ones.

The typical range, of strength properties of PC materials made with different polymer binders, as well as those presented by ordinary portland cement concrete, are presented in Table 2.3 (Blaga and Beaudoin 1985; CEN-EC2 1992; McBee et al. 1986).

ii) Low permeability to water and other aggressive solutions

In a properly designed PC material, in which an optimum balance is achieved between polymer content and aggregate gradation, the larger pores are totally filed or sealed with polymers. This feature is reflected in reduced water absorption, water permeability and water vapour transmission. As a result, PC presents an improved waterproofness over traditional concrete.

Although some air may be entrapped into the mixture during mixing process, this entrained air occurs as discrete bubbles that are not interconnected; thus, the moisture absorption into the material is negligible. This in contrast to portland cement concrete, in which the air forms interconnected voids that increase susceptibility to absorption, decrease resistance to corrosion and freeze-thaw damage.

The good impermeability of PC materials also provides high resistance to chloride ion (Cl^-) penetration, which is one of the most important factors affecting the corrosion of reinforcing steel bars in reinforced concrete structures.

In Table 2.3, the common range of water absorption values found for different types of PC materials is presented.

Table 2.3. Typical range of properties of common PC materials and ordinary portland cement concretes (average values).

Type of binder	Water absorption* [%]	Comp. Strength [MPa]	Flexural Strength [MPa]	Tensile Strength [MPa]
Polyester	0.30 – 1.00	50 - 150	13 - 40	8 - 25
Epoxy	0.02 – 1.00	50 - 150	15 - 45	8 - 25
PMMA	0.05 - 0.60	70 - 210	30 - 35	9 - 11
Furan polymer	0.20	48 - 64	-	-
Sulphur based	0.05 – 1.00	34 - 63	8 - 12	5 - 8
Portland cement	5.00 – 12.00	20 - 58	2 - 8	1 - 4

* After immersion during 24 hours.

iii) Improved chemical and corrosion resistance

PC materials, in general, have great improved resistance to chemicals, including acid, alkaline, salt and sulphate solutions, which are often present in industrial environments.

As closed cell material, PC provides a strong resistance against the penetration of these chemicals and other corrosive agents, such as oils, gasoline, petroleum and aggressive cleaning products. In addition, due to their particular nature, PC products enable fast draining-off of the different corrosive fluids over a mirror-smooth surface, with low roughness factor and moisture absorption. This feature also helps to prevent penetration and cracks occurrence.

The greater or lesser chemical resistance of PC products to specific corrosive agents strongly depends of polymer binder nature. For instance, polyester PC is in general more acid-resistant than epoxy PC, whereas in alkaline environments, shows worst performance than epoxy based concrete.

As an example, chemical resistances of two commercial PC products to most common corrosive agents, in comparison with ordinary portland cement concrete, are presented in Table 2.4. Further relevant data addressed to this subject can be found in chapter V (subchapter 5.2).

iv) Improved durability with respect to weathering and freeze-thaw cycles

PMs and PCs present improved resistance to freezing and thawing over conventional mortars and concretes. Reduced porosity and high waterproofness are the main factors responsible for the higher resistance to frost attack showed by PC materials. In Table 2.4, freeze-taw resistance of some commercial PC precast products are also reported.

Under long-term outdoor exposure, PC materials also show better performance than conventional concretes. Just for exemplifying, the experimental study reported by the U.S. Bureau of Reclamation concerning the weathering resistance of different CPC materials, clearly illustrates the superior weatherabity of PC over ordinary concretes as shown in Fig. 2.4 (USBR 2006). However, depending upon polymer binder, better performances are generally reported under cold climates than under hot environments.

Additional relevant data regarding the freeze-thaw and weathering resistances of various PC materials, can be found in Chapter V, respectively in subchapters 5.3 and 5.4.

Fig. 2.4. Appearance of poly-methyl methacrylathe PC specimens (left) and portland cement concrete specimens (right) after 20 years of outdoor exposure, according to investigation work reported by the U.S. Bureau of Reclamation (USBR 2006). Both types of beam specimens were installed near seawater and at half-tide elevation.

v) Good impact and abrasion resistances

PC materials have an excellent impact and abrasion resistances in comparison with conventional mortar and concretes. This is because polymers themselves have a high impact and wear resistances. The incorporation of short fibre reinforcements, such as glass, carbon or steel fibres, considerably enhances these features (Neelamegan and Parameswaran 1992; Ohama and Sugahara 1981).

In Table 2.4, abrasion and impact resistances of some commercial PC precast products are reported.

vi) Fast curing with quick development of mechanical strengths

A valuable advantage of PC is its fast curing time, which is an asset in the production of precasts as parts can be demoulded few hours only after the concrete placement. Sometimes, depending upon polymer binder, catalyst system and environment temperature, this period may be even further reduced for less than one hour.

Mixture hardening is also accompanied by a quick development of mechanical strength. Therefore, in applications with coatings and repairs, the original structure can be in use again after one single day. In general, after 24 hours, more than 80% of total mechanical strength of PCs is already reached, and after one week at room temperature, all full strength is usually achieved (in contrast with ordinary concrete, whose full strength is only attained after 28 days) (Demura et al. 1993). The fast curing process of PC materials can be even more accelerated by application of thermal treatment.

In particular, furan-based PCs cure very rapidly which led to being designated, in the ‘70s, as ‘30 minute concrete’. At the time, the Air Force of U.S. developed several furan concrete formulations, which could be used to fill bomb craters in airfield runways after an air attack. This concrete material could fill craters up to 23 meters in diameter, cured quickly under any weather conditions and could bear the weight of a landing jet plane few hours after installation (McBee et al. 1986). Nowadays, furan concretes find extensive use as a highway repair material, in areas where traffic cannot be diverted for an extended period of time.

Table 2.4. Freeze-thaw, chemical, abrasion and impact resistances of some commercial precast PC products.

Durability Property	Manufacturer	Test method	PC	PCC
Chemical resistance:				
- H_2SO_4 (1:5)	ULMA	Int. Method (IM) - Comp. strength (Kg/cm^2) / Retained comp. strength (%), after immersion period	1331 / 102	Damaged
- KOH (200g/l)			1078 / 82	256 / 99
- H Cl (1:5)			1206 / 92	190 / 74
- Gasoline			1272 / 97	206 / 80
- Fuel oil			1228 / 94	177 / 69
- Cleaning products			1234 / 94	202 / 78
- H_2SO_4 (0.1N) - Na Cl (5%) - Hydrochloric Ac 0.2 - Na OH (0.1N)	STRONGWELL	ASTM D-543 - Section 7, Proc. 1	Approved	Not satisfy
Freeze-thaw resistance	ULMA	UNE 127 004	Unchanged	Damaged
	STRONGWELL	IM (2500 cycles)	Unchanged	Damaged
Impact resistance	ULMA	UNE 127 007	95 cm	55 cm
Abrasion resistance	ULMA	UNE 127 005/1	0.53 mm	5.03 mm

vii) Improved fatigue strength

Several studies have been published reporting the improved resistance of PC materials over conventional concretes under dynamic fatigue loads (Hsu 1984; Hsu and Fowler 1985; Kwak and Kim 1995; Mebarkia 1993; Tavares et al. 2001).

As in the case of portland cement concretes, the applied stress (S) is the most important factor influencing the fatigue life of PC materials: as the applied stress increases, the fatigue life decreases. The effect of the range between the maximum and the minimum applied stress (R) is also significant: the wider the stress range, the shorter the fatigue life. As an example, in Fig. 2.5, the comparison between the flexural fatigue strength of MMA PC beams and that of portland cement concrete beams is shown. The Wöhler curves were reported by Hsu and Fowler (1985), in which those correspondent to portland cement concrete were adopted from Murdock and Kesler (1958).

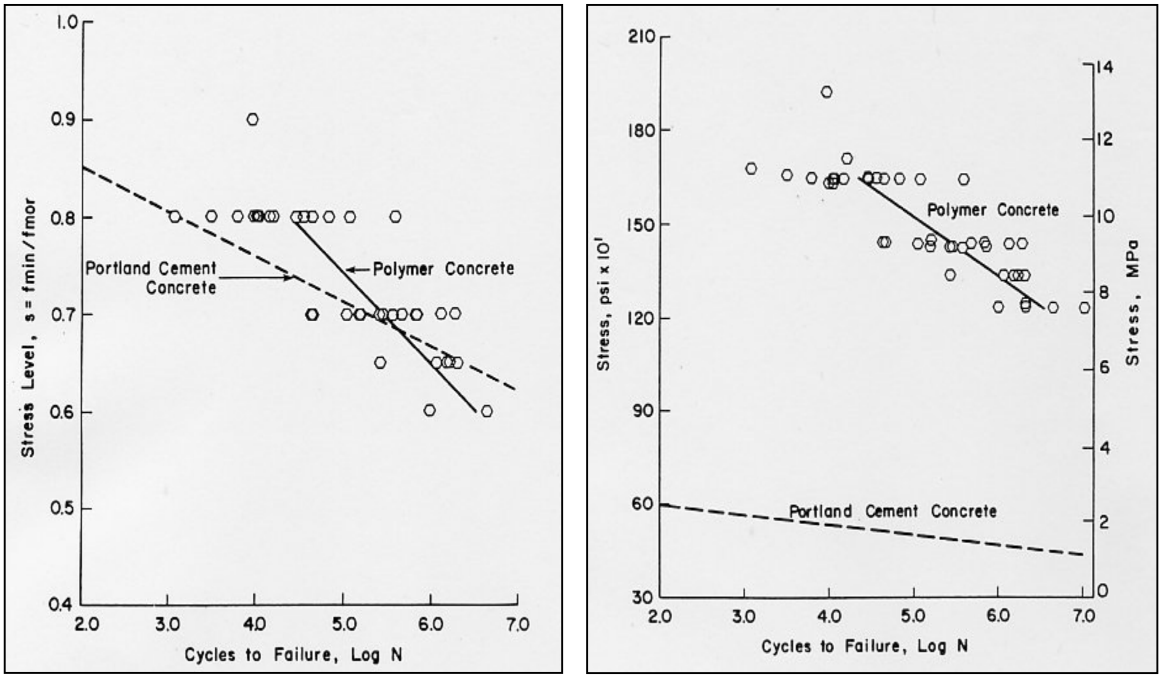


Fig. 2.5. Comparison between flexural fatigue strengths of plain MMA PC and plain portland cement concrete beams: in stress level scale, at left, and in stress scale, at right (Hsu and Fowler 1985). Wöhler curves corresponding to the stress ranges of R=$\sigma_{min}/\sigma_{max}$= 0.05, 0.10, and 0.25 (average values). Beam specimens were cyclically loaded at a constant rate of 5 Hz.

viii) High adhesion and bond strength to various substrates

A very useful aspect of PCs and PMs is their improved adhesion or bond strength to various substrates compared with traditional cement concrete materials. Most of PC composites have an excellent adhesion to brick and ceramic materials, traditional concrete, steel, wood and stone. This feature is attributed to the high bonding capacity of polymers.

For a successfully bonding, the substrates must fill two single requirements: they must be dried and properly cleaned (free of dust, oil or grease). The adhesion is usually affected by the polymer content, polymer type and the properties of the substrates' surface. Smooth surfaces are not suitable for a good adhesion. In order to obtain a strong bond, surface preparation by abrasive blasting or chipping techniques is recommended.

Generally, under normal conditions, it is not possible determining the adhesion of PC materials to prepared cement concrete surfaces, since most PC materials provide more than enough strength and adhesion to rupture the surface of the cement concrete before the bond is broken. This type of test will simply measure the surface strength of concrete substrate in tension. Hence, most PC manufacturers list bond to cement concrete as '*stronger than concrete*' (McBee et al. 1986).

Adhesion to sandblasted steel surfaces is usually on the same order of magnitude as the tensile or shear strength of PC material (San José et al. 2003). Usually, a cohesive failure of PC adjacent to the sandblast profile occurs.

ix) Excellent damping and electric properties

One of the PC advantages is the ability to damp of vibrations. The great capacity of PC to absorb energy makes it very suitable for the manufacturing of machine tool foundations, in a highly competitive basis with cast iron and steel (Ates 1994; Karademir 1997). Damping characteristics of PC materials might be 4 to 7 times higher than cast iron, and in addition, they present other desirable characteristics such as excellent corrosion-resistance, low thermal conductivity and high strength-to-weight ratio (Orak 2000). Nowadays, it is attempted to take advantage of the excellent damping properties of PCs for building structures undergoing dynamic loads.

PC materials also present high electrical resistivity, which is a very useful property for specific applications where non-conductive materials are required (Gunasekarane 1977; Vidaurre et al. 1998). The insulate properties of PC materials eliminate the loss of 'stray current' that occurs when an ordinary cement-based material is used. PC materials present a volume resistivity in the order of 10^{13} ohm-m, whereas conventional cement concretes possess electrical resistivities in the wide range of 40 ohm-m (moist concrete) up to 10^4 ohm-m (air-dried concrete), depending upon water/cement ratio and curing process (McBee et al. 1986; Neville 1995).

x) Lightweight

Since polymers present lower specific weight than hydrated cement pastes, PCs depending upon of applied formulation and manufacturing process are in general lighter than ordinary cement concretes. Specific gravity of PC materials can vary widely, but the common range of values is found between 1.7 and 2.2 kg/dm^3. This feature, lightweight, is further enhanced taking into account that smaller cross-sections are required for the same load carrying capacity. In addition, with lighter concrete, the total mass of materials to be handled is reduced with a consequent increase in productivity. Thus, in precast applications, reduced transportation and labour costs are achieved with the use of PC instead of portland cement concrete.

2.2.4.2 Main limitations of polymer mortar and concretes

i) Cost

One of the primary limitations of PC materials is cost. The cost of polymers usually range from 10 to 100 times that of portland cement, and even considering the higher specific gravity of cement (around 2.5 times higher), the cost per unit volume of polymer composites is still considerable higher than traditional cement concrete (Fowler 1999).

As a more expensive material, the use of PC for high volume applications becomes unpractical, excepting for the specific cases where durability requirements render ordinary concrete unsuitable.

A meaningful comparison of cost, however, cannot be limited to the cost of materials but should be made with basis on the design of the 'structure'. The higher price of PC materials is mitigated by their longer service life, lower labour maintenance and lower life cycle costs. In addition, smaller cross-sections are required to attain a certain load-bearing capacity, when compared to conventional concrete materials, reducing the total cost of final product. Further, it is believed that the development of mass production systems for precast PC materials, and of automated application systems for cast-in-place PMs and PCs, will cause a cost reduction and a good cost-performance balance (Ohama 1997).

ii) High sensitivity to temperature and creep

The mechanical strength of PC materials is highly dependent on temperature due to temperature dependence of the polymers themselves (especially thermoplastic polymers). PCs and PMs show a rapid reduction in strength and deflection with increased temperature. This trend is substantial at temperatures higher than both the glass transition (Tg) and heat distortional (HDT) temperatures of the polymers. Thermal resistance is thus governed by the nature of polymer binders (their Tg and HDT), polymer-aggregate ratio, heating conditions, and at last, by the thermal degradation of polymers. Relevant data concerning this subject can be found in Chapter V (subchapter 5.3)

Due to viscoelastic nature of polymers, PCs are also very sensitive to creep and relaxation. The most characteristic features of viscoelastic materials are that they exhibit a time dependent strain response to a constant stress (creep) and a time dependent stress response to a constant strain (relaxation). In addition, when the applied stress is removed, the materials have the ability to recover slowly over a period of time. These effects can also be observed in metals but the difference is that in plastics they occur at room temperature whereas in metals they only occur at very high temperatures (Crawford 1990). The viscoelasticity of PC materials leads to that quantities such as modulus, strength and ductility are sensitive to straining rate, elapsed time, loading history and temperature.

In the investigation work carried out by Hsu (1984), on flexural behavior of polyester PC formulation, it was found that, for stress levels up to 0.4, the compressive creep in PC was approximately one to two times higher than that found in portland cement concrete. At higher stress levels, creep in PC drastically increased. However, the specific creep, which is the creep strain per unit of applied stress, was found to be within the range of portland cement concrete.

A deep review on creep behavior of PC systems can be found on Dharmarajan thesis work (Dharmarajan 1987) and more recent data on this subject, is available on studies carried out by Hu and Sun(2000), Monteiro (2005), and Tavares et al (2002a).

Irrespective of PC type, main conclusions of all referenced studies are in quite agreement with each other:

- Creep strains increase with polymer content, temperature and stress level applied;
- Stress-to-strength ratios exceeding 0.5 generally lead to catastrophic creep failure;
- PCs creep more than portland cement systems at the same stress levels;
- and Creep failure occurs at lower stress-to-strength ratios in PC materials than in portland cement concrete.

It was also noticed that the sustained creep loads did not affect the ultimate strength of PC materials, and epoxy-based PC systems were, in general, more creep resistant than those formulated with polyester resins.

iii) Deficient behaviour under fire

Reaction to fire is another important shortcoming of PC materials. Most of them are classified as median to highly flammable materials, and therefore they cannot be used as structures for housing buildings (Fowler 1999).

Fire behavior of PC systems may be improved either by the use of fire resistant resins, such as phenol resins, or by the incorporation of flame retardant additives in polymer binder. Fireproofing coatings further applied on the outer surface of the material could also be an efficient solution to minimize this undesirable feature.

This issue will be discussed in Chapter VI.

iv) Relative high coefficient of thermal expansion and shrinkage

In general, depending upon polymer binder type and content, PC materials show higher coefficients of thermal expansion (CTE) than portland cement concrete (2 to 4 times higher). This feature may constitute a problem when PC is used as repair or patching material for concrete structures. Thermal changes can produce high shear and tensile stresses at the interface, which may cause the repair to delaminate or crack (Fowler et al. 2001; McBee et al. 1986). Two different situations may occur:

- At elevated temperatures, the polymeric repair material tries to expand at a rate greater than that of the concrete and steel it is adhered to, and, as a result, it is held in a compressive state. This has not been found to be a problem as far as shear stress developed at the interface remained lower than shear bond strength. Otherwise, delamination will occur.
- When the PC repair material is exposed to lower temperatures after installation, as in summer-to-winter weather cycles, tensile stresses result. Depending on the physical configuration of the material, the stresses produced may result in cracks in the PC material. To prevent this situation, the use of MMA based polymer binders, which present CTE similar to portland cement concrete is advised.

Shrinkage can also be quite large in PC when compared to conventional concrete, especially in the case of polyester based concretes. Generally, polyester PCs and PMs have a setting shrinkage of about ten times that of the cement concrete (Ohama and Komiyama 1979). However, shrinkage occurs quickly and after 24 hours or less, it is negligible due to relaxation.

v) Odour, flammability and toxicity of raw materials

Another limitation, as already mentioned in ‘safety considerations’ issue, is the odour, toxicity and/or flammability of many of the monomers and resins during construction and fabrication. Although these limitations only exist during the relative short period between handling, mixing and curing, the use of these materials can create safety problems and/or user discomfort, which must be taken into account during construction.

vi) Lack of experience with PC by many users

Due to lack of familiarity and experience, polymers are often used to make PCs without considering the demands on the job, resulting on deficient or poor materials. Polymers are also often applied to make repairs without taking into consideration the cause of damage and/or without proper preparation of the repair object. As a result, some failures occurred due to incompatibility of PC and the substrate. Any material used inappropriately can give bad results, but the material itself is not responsible. An additional challenge is the departmentalization of research and knowledge. People knowledgeable about polymers lack background in building materials and, on the other hand, people versed in building materials do not well understand polymer technology (Chandra and Ohama 1994). In fact, both disciplines must be taken into account and a better bridge between both sides is fundamental.

2.2.5 Application Fields of PC Materials Recent and Foreseen Developments

PC materials are not intended as a replacement for portland cement concretes or other conventional construction materials in uses in which those materials have proven being durable and cost efficient. PCs have their own place where durability, strength or other particular requirements render conventional materials unusable.

There are thee main well-known application fields where PC materials revealed to be competitive over conventional materials: overlays for pavements and floorings, precasting, and patching materials for repair and rehabilitation of purposes.

Recently, with the great interest that has been shown in construction materials with ecological and safety characteristics, a new branch market emerged for PC materials: recycling and waste encapsulation. Each one of these successful or under development applications will be discussed.

2.2.5.1 Precast PC products

Precasting is one of the fastest growing applications of polymers in concrete.

Precast represents an excellent use of the material due to its fast curing, high strength-to-weight ratio and ability to form complex shapes. Used at first as concrete replacement, precast PC is nowadays also applied as a substitute for cast iron, steel and other metals, wood and even structural plastics.

The most current and well-known precast PC applications are here described.

i) Artificial marble

PCs were most widely used initially and today for cultured marble for counter tops, lavatories and other sanitary wear, interior wall panels, stairs and worktops for kitchens and laboratories. Marble aggregates, by-products proceeding from marble industry, bind with acrylic or polyester resins, result on highly strong materials that simulate closely (in touch, finishing surface and appearance) natural marble products. Cheaper than those made with natural marble, synthetic marble products made up with PC have the additional advantages of being corrosion and chemical resistant.

ii) Façade panels and tiles

Façade panels, window sills and tiles are another well-known application of PC materials. Their low water absorption, excellent durability, impact and abrasion resistance, make them very suitable for this kind of application. Additionally, due to their great capacity to texture and color, exterior appearances of stone, granite, shale or wood are easily obtained in these products (Kaeding and Prusinsky 2001), allying aesthetic requirements to a strong, light and durable material, with the benefit of saving natural resources.

iii) Drainage and channeling systems

Precast components for drainage systems are another successful and widely spread application of PC materials.

PC drainage systems, which include gutters, sewer pipes, manholes, equipment vaults and drain channels, are commonly found both outdoors and indoors, in transportation infrastructures (driveways, highways and airports), sportive facilities (e.g. football stadiums, motorways, swimming pools and running tracks), industrial and chemical plants, bottling and food processing industries, parking garages, service stations and docks.

High resistance to aggressive solutions and froze attack, excellent axial and compressive strengths, great impermeability, rapid drainage due to an extremely low roughness factor, easy handling and self cleaning process, reduced weight, low installation and maintenance costs, are some of the advantages of PC drain systems over those made with conventional concrete, PVC or steel (Bloomfield 1995).

iv) Tanks and hazardous waste containments

As a closed cell and high corrosion resistant material, PC reveled to be the ideal choice for the manufacturing of acids tanks and hazardous waste containments. PC has also been applied as conditioning and storage tanks in the bottling and food processing industry.

The hermetic nature and easy cleaning of PC surfaces hinders the appearance and growing of fungus and other microorganisms.

v) Components for transportation infrastructure

Products for the transportation industry continue to grow and the applications in this field still have a great potential to explore. The high strength, durability, impact resistance and damping make PC an ideal material for precast tunnel liners, median highway barriers, railroad sleepers, tunnel sidewall panels, bridge pilings and parapet protective panels (Fontana and Bartholomew 1981).

These precast PC products further offer low installation costs, less downtime and traffic disruption and reduced labor costs.

vi) Utility boxes and underground enclosures

Utility boxes such as electrical, telephone and traffic signal bases made up with PC materials are already available in the market (Perry 1981). Precast PC traffic signal bases eliminate forming and pouring, are lightweight for easier handling and lower installed cost. PC bases or pads are also used under electrical transformers and telephone cabinets to add stability, prevent corrosion of metal cabinets, and to protect them from damage caused by mowing equipment. Further, these precast units can be re-used in other locations (excavation and installation of entire unit can be done in one single day).

Precast PC underground enclosures for use as splice boxes, pull boxes, or equipment enclosure for any application requiring easy access to an underground service (*i.e.* electrical, water, gas, fibre optics), are also available in a large variety of sizes and styles. No grounding is required for the box and the skid-resistant covers can fit flush with sidewalk or grass area.

vii) Metal and porcelain replacement applications

Metal replacement is another growing application sector. The high strength-to-weight ratio, low thermal conductivity, high damping and mouldability make PC a strong competitor for many current applications using metals, such as machinery tool bases, where PC has been found to be very competitive with cast iron and steel (see page II-38).

Recently, it has also been found that PMs can successfully be used to make counterweights for shovels and forklifts in the heavy and construction industries, in place of cast iron (Bhutta et al. 2000). The materials and production costs of cast iron counterweights are quite high, and the manufacturing process may cause environmental pollution. PMs using unsaturated polyester resin as binder, calcium carbonate filler and waste iron (cast iron scraps proceeding from cast iron industry) as fine aggregates result on efficient counterweights with densities up to 6.0. Good workability and sufficient strengths are achieved at low binder contents of less than 6% (by mass), and a high waste iron content of 80%. Furthermore, PC counterweights can easily be recycled as aggregates for new counterweights, and materials and manufacturing process costs are found to be inexpensive compared to those of the cast iron counterweights.

Due to their excellent insulating properties and because the processing of the composite is carried out at room temperature, PC materials have been profited for the manufacturing of post insulators in a very competitive basis with traditionally used materials such as porcelains or ceramics. In the US, PC post insulators are now in routine use in outdoor applications at voltages up to and including 138 kV. There is, in fact, interest in developing PC station post insulators for uses at 230 kV, especially in seismic regions, where porcelain insulators have behaved very badly in recent major earthquakes (Gunasekarane and Duguid 1992).

viii) Complex architectural forms

Complex architectural shapes are commonly made with PC materials, taking advantage of their ability to mold, texture and color. Examples include complex façade elements, domes, column covers, statuary, fountains and urban furniture, such as garden seats, ashier, dustbins, and lamp poles.

A larger number of other precast PC products, with innovative end-uses, have been designed and commercialized in the last decades. Many of them are still under development. Some examples include: components for the animal feeding industry, nonconductive support structures for electrical equipment, foundation ventilation systems, truncated dome tactile floor tiles for step-safe projectile impact ballistic panels, infrastructures for wind power turbines, stair treads and large scale pre-insulated wall panels for segmental building construction.

2.2.5.2 PC overlays and protective coatings

PCs have been extensively used for bridge decks, road surfacing and floor overlays where a high corrosion and/or abrasion resistance is required, such as, parking garages, chemical plants, food processing industry and other industries where corrosive and strong wear conditions are encountered.

PC overlays can provide a durable and wear-resistant surface for portland cement concrete. In addition, the overlays may be formulated to provide low permeability to water and chloride ions, and thus also helps to prevent deterioration and spalling of the concrete due to freeze-thaw cycles and corrosion of reinforcing steel. Surface texture of a PC overlay for highway applications can be made to provide a suitable skid-resistant surface and hydroplaning characteristics that are within the required limits. Other advantages of PC overlays include the ability to use thin layers, fast curing, excellent bond strength to concrete and high flexural strength.

Typical applications of PC overlays and coatings are described in Table 2.5.

Table 2.5. Typical applications of PC overlays.

Function/Application	End-uses
Floorings and pavements	Floors for houses, warehouses, schools, hospitals, offices, shops, toilets, passages, gymnasiums, factories, industrial plants, stairs, garages, railway platforms, airport runways, etc.
Waterproofing coatings	Concrete roofdecks, water tanks, septic tanks, swimming pools, silos, etc.
Decorative coatings	Wall coatings, coating materials for textured finishes of buildings, surface preparation materials for coatings, etc.
Anticorrosive coatings	Effluent drains, chemical or machinery plant floors, grouts for acid proof tiles, floors for chemical laboratories and pharmaceutical warehouses, hot spring baths, rustproof coatings for steel roofs decks, etc.
Deck coverings	Bridge decks, internal and external ship decks, footbridge decks, train and subway floors, etc.

2.2.5.3 PC for repair and rehabilitation purposes

Nowadays, concrete polymer composites are mostly used not for build up, but for rebuild or repair, and PC materials have their share on that. Its rapid curing, excellent bond to concrete and steel reinforcement, and excellent strength and durability make it a very attractive repair material (Czarnecki et al. 1999). Surface repair, partial depth repair, full depth or structural repair, and strengthening are typical examples of application. Thus, it is not surprising that among eight existing models applicable to modeling concrete repair (Vaysburd et al. 2000), two of them have been developed by polymer people: Fowler et al. and Czarnecki et al..

i) Concrete pavements and overlays

The fact that PCs cure very rapidly make them of interest in repairs to existing facilities where downtime must be held to a minimum, such as bridge decks, roadways, highways, and airport runways. Since the curing reaction is most of the times exothermic, the heat produced speeds the cure. Additionally, the low-temperature curability of some PC materials, specially those based on acrylic resins, enables that repair works could be made under cold weather conditions (McBee et al. 1986).

For repair of concrete pavements and airport runways, mechanized trains for repair systems have been developed which can prepare the damaged area, batch, place and finish the repair materials in the most economical and fast manner (Marsh et al. 1985).

Bridge decks repairs present, in particular, special problems not associated with other types of repairs. The vibration of bridge decks makes initial concrete applications more heterogeneous and therefore, the constant bending movement frequently creates concrete delaminations. While a variety of fast setting and durable repair products is available on the market, PC patching materials, due to their rapid transition from a liquid to a gel state, are not only rapid setting and high strength, but also the materials most insensitive to traffic vibrations (Dinitz and Ferri 1985).

ii) Concrete structures

Because the rapid deterioration of reinforced concrete structures has become a serious problem in recent years, a strong interest has focused on PCs as repair patching material, and there is a growing demand for them. These CPC materials are currently becoming low-cost, promising materials for preventing chloride-induced corrosion and repairing damaged reinforced concrete structures. After removal of the deteriorated concrete and cleaning of the reinforcing steel, the cement concrete is replaced with a suitable PC or PM. Not only the original load carrying capacity is re-established, but also any further corrosion activity is stopped in the repaired section. Usually, premixed systems are used for this purpose, but recently, some investigation works have been done concerning the use of preplaced graded aggregates with the injection of the monomer or resin system (Murray 2004), eliminating the batching of aggregates and resins.

PMs have also been used as sealer crack in concrete. While plain polymers, such as epoxy and high molecular weight methacrylate (HMWM), are usually applied (injected or sprayed on) to fill the cracks with reduced surface widths, PMs are rather used for sealing larger width cracks (Fowler 1999).

Rehabilitation of deteriorated concrete structures is also possible by means of precast PC products (Barnaby and Dikeou 1984):

- PC bridge parapet panels can encapsulate existing deteriorated concrete structures prolonging the service life of these aged facilities at a fraction of the cost of remove/replace options;
- Thin corrosion-resistant PC pile jackets and panels, installed above the high water and below the low water level, stop the deterioration of conventional concrete structures exposed to sea or river water environments, enabling them to withstand the combined effects of ice flows, corrosive solutions, debris and other environmental hazards;
- PC highway median barriers allow the rehabilitation of deteriorated barriers without costly demolition, thereby eliminating roadway downtime and traffic disruption. The lightweight shell barriers are installed, and then filled with conventional concrete. These barriers, behind the greater resistance to weathering, are quicker and easier to install than cast-in-place concrete barriers;
- PC cladding panels provide a long-lasting and cost-effective solution for bench walls in highway tunnels requiring rehabilitation due to environmental conditions, exposure to de-icing salts and vehicular impacts;
- PC shells for repairing equipment bases are a very cost-effective option. Equipment can be removed, the base cleaned, the precast shell placed over the base, and the void filled with a PC grout, resulting in a fast repair which minimizes the down time of the equipment.

iii) Wood structures

In recent years, it has been shown that PC materials can be used to repair and strengthen deteriorated or broken wooden beams and construction elements (Van Gemert et al. 1998). Repair is accomplished by replacement of deteriorated parts by a PM prosthesis. The decayed part is removed by sawing or cutting. A casing is then installed which reconstitutes the original shape of the wooden element. If the reconstruction has to meet aesthetic requirements, as in the case of heritage or historic buildings, the casing should be made out of the same wood as the original beam, and it will be kept in place to cover the prosthesis of PM. The connection between the original wood and the prosthesis is assured by means of anchoring bars (steel rods or FRP rods).

PM repair of wooden beams is often called polymeric restoration of timber beams. This technique has been further developed for the strengthening of broken beams, were bending as well as shear forces are presented. The technique is often combined with externally bonded steel plates or FRP laminates, glued on the wooden beams (Ignoul et al. 2000).

2.2.5.4 Waste recycling, encapsulation and storage

PC materials are very attractive under an ecological and safety point of view because of their ability for using recycled waste products. This feature of polymer composites has been developed mainly through two different approaches. Firstly, by the use of unsaturated polyester resins from recycled poly(ethyleneterephthalate), usually known by PET, and secondly, by the incorporation of industrial by-products and wastes as fillers or aggregates.

i) Waste recycling for PC binder

As the high cost of the polymers is usually considered the main factor limiting the growth of PCs, unsaturated polyesters based on recycled PET might be a potentially lower source cost of resins for producing useful PC based products (Abdel-Azim and Attia 1995; Rebeiz and Fowler 1996; Soh et al. 1995). PET wastes are typically found in plastic beverage bottles; thus, a large waste stream of PET is available for recycling applications. A main advantage of recycling PET in PC is that the PET waste does not have to be purified, including removal of colors, to the extent that other PET recycling applications might require, which minimizes recycling process cost. The recycling of PET in PC applications also helps in saving energy.

ii) Waste recycling for PC aggregates

The growing awareness of environmental impact of both industrial waste disposal and exhaustion of natural resources, also led that a large number and variety of industrial wastes was attempted to be incorporated into PC materials as aggregates. Most of the successful applications reported, involved either industrial by-products or end-life products.

In the early ‘70s, Steinberg already reported the development of a polymer composite material that (re)used paper waste (1975). Flat paper newsprint soaked in a liquid resin and polymerized in situ under pressure, result on a polymer composite with high compressive strength (50 MPa) and outstanding flexural strength (52 MPa). Inexplicably, no posterior references were found regarding the development and/or application of this new material, called at the time paper polymer composite (PPC) or paper plywood (due to its very good tensile strength along the plane of the paper). The development of this ‘polymer-paper concrete’ as replacement for plywood forms should be reconsidered from the viewpoint of the preservation of forest resources.

Since then, industrial wastes, such as fly ash, slag, wood ships, cork powder and cork granulates, tire rubber, plastic ships from used polyethylene (PE) and polyvinyl chloride (PVC) films, plastic granulates coming from milled waste electrical cables and FRP powders proceeding from waste FRP products, have been successfully used for replacing or partially substituting the filler and aggregate components in PC materials (Bignozzi et al. 2000; Bignozzi et al. 2002; Nóvoa et al. 2005; Nóvoa et al. 2004; Ohama and Yamashita 1984; Rebeiz et al. 2004; Rebeiz et al. 1994; Ribeiro et al. 2003; Ribeiro et al. 2004; Sandrolini et al. 1993; Saurina et al. 1996).

Fine glass fillers, obtained by vitrification of bottom ashes collected from incineration of urban solid wastes or derived from glassy and ceramic waste fractions, have also been used to produce glass fibres for PM reinforcement (Bignozzi et al. 2004).

Development work on these PCs based on recycled waste aggregates or reinforcements, will lead to the conversion of an ecological problem into a positive asset in the form of commercially valuable construction materials. This is of great importance in the recycling and reuse of man’s solid waste.

iii) Hazardous waste encapsulation or storage

Due to hermetic nature of polymer matrix, PC materials have also been used to encapsulate waste hazardous products, such as crushed waste glass, contaminated silica sands proceeding from foundry industry, and geothermal waste with heavy metals (Bignozzi et al. 2004; Fontana 1991; Fowler 1994; Sousa et al. 2004).

Non-returnable glass bottles have been crushed, and the mixed particulate glass has been filled with a monomer system in a manner similar to that for PC. Resultant glass-polymer composites (GPC) present a relative high compressive strength and are highly resistant to attack by corrosion media. One application of this material is for sewer pipes, especially for acid wastes or under aerobic conditions when the hydrogen sulfide gas coming from sewage is oxidized to sulfuric acid.

Moulds made out of silica sands, with a high-grade of silica bind with phenolic resins, are widely used in foundry casting industry. The high melting point of crystalline silica and the high heat resistance of phenol based binder, enable castings to be produced by pouring molten metal into moulds made out of these two components. Disposal of these moulds has been of great concern due to potential risk of environment contamination by phenolic resins. Recently, it has been shown that phenolic foundry sands can be used as aggregates in epoxy PC materials with considerable advantages over those made up with virgin foundry sands.

PC also shows potential for immobilizing radioactive waste from the nuclear power industry for long-term engineered storage. A major problem facing the exponentially growing nuclear power industry is the safe disposal of fission product wastes. A technically and economically reasonable approach is immobilizing fissionable and fission products into long-term durable materials in an engineered storage system. The wastes must be stored for 1000 years before they can be considered biologically safe. PC, with additional durability and strength, appears to be an attractive material for this purpose. In particular, PCs containing polystyrene are especially radiation resistant (Steinberg 1975). However, much more will have to be learned before PC can be confidently recommended as a material that wills last one thousand years ore more.

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III. POLYMER MORTAR FORMULATIONS OPTIMIZATION PROCESS

3.1 Introduction

3.1.1 General

The first objective of this thesis was to develop an optimal polymer concrete formulation, in order to maximize certain desirable properties of resultant composite.

Due to a potential large number of variables or factors involved in an experimental program, the beginning can be troublesome. The complexity of products and processes involved are barriers that not easier the use of a generalized experimentation. Engineering intuition is usually insufficient in the design of polymer concrete and mortars because of complex mechanism of the forming of concrete properties (Piasta and Czarnecki 1988).

Polymer concrete materials cannot be regarded as a simple mixture, which is just a combination of ingredients with properties that are a result only of the simple summation of properties of the components. These materials are instead a ‘composite’, a solid material system consisting of two or more phases with macroscopically distinguishable boundaries among phases, which has properties not attainable by a single component, or by a simple summation of the properties of the components (Czarnecki et al. 1999). In particular, polymer concrete composite materials can be regarded as a triphasic system consisting of a dispersed phase, the aggregates, a continuous phase formed by a monomer system and a certain percentage of porosity imposed either by aggregate size grading or by manufacturing process. The properties of this composite will be given not only by the properties of each of the components, as a function of their weight percentage, but also by interface surface phenomena. Changing the type or the amount of each component, different types of polymer concrete and features, with distinct properties, can be created. The question that remains is how to find the most *cost-effective* way for optimizing suitable polymer concrete formulations.

Optimising overall properties with respect to component properties and proportions is included in the definition of a composite. However, the problem of optimisation is complex because a number of mechanisms in the generation and application of polymer composites can act synergistically, both negatively and positively. Any optimisation process must therefore handle these synergisms quantitatively (Czarnecki et al. 1999).

On the other hand, before going through with any optimization process, it will be necessary to define what properties or attributes should be optimized in the final composite product, which are directly related with specific material requirements imposed by its final application or end-use. The idea is to develop a 'tailor-made' material for each application.

3.1.2 Material Design Methodologies: Significant Applications to Polymer Concrete Materials

Several methods have been proposed in the past to model product design process based either on the description of a sequence of activities or on systematic procedures that attempt to propose a more adequate set of activities. It is not the aim of this chapter thesis to review the different methods used in practice, however the exposition of some of these methods is necessary to understand the choice for the material design methodology used in this work.

Cross (1996) proposed an integrated systematic approach based on rational methods that cover the whole design process, from problem analysis and conceptual design to detailing. The methodology proposed, illustrated in Table 3.1, involve seven steps in the design process, each applying a widely used rational method.

Table 3.1. Stages in the design process - Cross methodology -.

Stage	Relevant Design Method
1. Clarifying Objectives	Objectives Tree Aim: To clarify design objectives and sub-objectives, and the relationships between them.
2. Establishing Functions	Function Analysis Aim: To establish the functions required, and the system boundary, of a new design.
3. Setting Requirements	Performance Specification Aim: To make an accurate specification of the performance required of a design solution.
4. Determining Characteristics	Quality Functional Deployment Aim: To set targets to be achieved for the engineering characteristics of a product, such they satisfy customer requirements.
5. Generating Alternatives	Morphological Chart Aim: To generate the complete range of alternative design solutions for a product. Search for potential new solutions.
6. Evaluating Alternatives	Weighted Objectives Aim: To compare the utility values of alternative design proposals, on the basis of performance against differentially weighted objectives.
7. Improving Details	Value Engineering Aim: To increase or maintain the value of a product to its purchaser whilst reducing its cost to its producer.

The first sets of activities proposed by this method are especially useful to define which properties and attributes of the final product should be enhanced. Although devised primarily for product development an attempt was made to apply this methodology, which integrates Quality Function Deployment (QFD) principles, to the design of a new material.

Fernandes et al (1998) illustrated the application of this methodology for material design, in the case of development of a polymer concrete material. It was concluded that chemical and corrosion resistance, as well as compressive strength should be optimized, as those represent the most significant material properties. These attributes received the importance levels of 4.75 and 4.50, respectively, in a scale of 1 to 5. Other properties, such as tensile and flexural strength, cost effectiveness, water absorption and dimensional stability, also received a good score (between 4.00 and 4.25).

Once defined the specific material requirements that should be met by a polymer concrete, and correspondent desired properties that should be enhanced in the design process, an efficient statistical method for the experimental design and optimisation of final product must be defined. The main advantage of using statistically designed experiments is the minimization of the number of the tests necessary to obtain the desired information on a material. With statistical methods it is possible to significantly decrease the number of tests compared to traditional methods, as well to shorten the experimental period (Cornell 1981). The results are also more amenable to statistical analysis and the error of the estimates obtained from fitting the test results may be decreased over other methods (Piasta 1978).

There are many experimental designs that can be applied on the planning of experiments, such as simplex, factorial and rotatable (Box and Draper 1987).

The rotatable experimental design is based on regression analysis, making possible the formulation of mathematical models and evaluation of their precision. This experimental design enables a mathematical description of an object of unknown characteristics to be determined based on the testing of the values of the input and output parameters.

Szarnecki applied the rotatable experimental design to optimise polymer concrete formulations. Since the latest ‘80s, Szarnecki and co-workers have been involved with research studies concerning material optimisation of polymer concretes by statistical methods (Czarnecki 1984; Czarnecki and Weiss 1988; Van Gemert et al. 1985). The basic idea of these studies is that every application requires specific material properties that can be produced by controlling the material structure. This investigation culminated with a three-year project entitled ‘Polymer Concrete Composite’, carried out collaboratively by the National Institute of Standards and Technology (NIST) and the Institute of Technology and Organization of Building Production (Czarnecki et al. 1999).

The main objective of this project was the development of a statistical method for the material design and optimisation of polymer concrete. Material models for various polymer concrete materials were developed as the basis of the optimisation process, and were formulated in terms of quadratic functions that fit in a regression process to experimental data measured according to a statistical design. An *overall desirability function* was then applied as the metric for the multi-criteria optimisation of polymer concrete. The aim was to produce a PC material that had a certain desired property, which could be obtained without sacrificing other properties of importance. That is why the multi-criteria nature of the optimisation was important, as no variable property was to be optimised without taking into consideration the other variable properties (Czarnecki et al. 1999).

The effect of material heterogeneity on final properties of polymer concretes was determined considering the following experimental variables:

- Type of mineral aggregate;
- Maximum size of aggregate;
- Type of resin;
- and Curing method.

Three categories of properties were assessed:

- Physical property: density;
- Mechanical properties: compressive strength, flexural strength, and elasticity modulus;
- Processing parameters: linear shrinkage on curing.

Optimal results for various polymer concrete formulations were determined, analyzed both analytically and graphically, and compared with experimental results. The following three cases were considered: the use of silica fume in polyester concrete, the production of an expensive highly-filled polyester concrete that did not sacrifice important technical properties, and the production of an epoxy concrete with low flammability but good mechanical properties. The reliability of the proposed method was demonstrated for all polyester and epoxy concrete formulations. The usefulness of the method for product development and identification of the effects of major variables on performance was demonstrated.

Taguchi (1986) used a different experimental design, based on complete factorials, for the planning of experiments . Since the last years of 1940, this research engineer has been involved in the improvement of product quality and industrial processes of his country, the Japan. He developed a new philosophy or methodology, which aims on the improvement of the quality itself. This methodology, known by 'Taguchi Method', depends strongly on statistical concepts and techniques, and is especially related with statistical planning of experiences (Coimbra 1988; Fernandes et al. 1998).

The use of complete factorial in the planning of experiences consists in testing all possible combinations between the different values (levels) adopted by the major variables (factors), in an organized way. '*Traditionally, engineers tend to change only one variable of an experiment at a time. The strength of Taguchi technique is that the engineer can change many variables at the same time and still retain control of the experiment'* (Ashley 1992). This technique allows the assessing of the influence of each factor on the global response (target characteristic), as well as the identification of interactions between them. The effect of each factor is determined by taking into account all different levels adopted by the other major factors.

The following notation is normally used to describe this type of plans:

$$L^F = C \tag{3.1}$$

where L is the number of levels adopted by each factor; F is the number of factors; and C is the number of possible combinations.

The planning of experience is expressed through a complete factorial array, which presents the same number of rows as the number of possible combinations. The number of columns is equal to the number of factors plus the number of all possible interactions between factors.

The main drawback of this type of plans arises from the high number of tests that are necessary to the accomplishment of the method. The number of tests increases, in geometric progression, with the number of variables or factors in study. The experimental program becomes almost unpractical with more than four factors or with more than two levels. For instance, an experimental program considering 4 major factors with 3 variations levels will lead to 3^4 different combinations, *i.e.*, 81 different tests to perform.

An experimental plan with the same advantages than those brought by the complete factorial, but with a significant reduction of number of experiences, was the major contribution of Taguchi method to Quality Engineering (Coimbra 1988). Taguchi found that some columns of the complete factorial orthogonal array, those correspondents to interaction effects with minor value, could be used in a more efficient way to study the principal effects of additional factors.

This technique, explained in detail in several publications (Coimbra 1988; Figueiredo and Fernandes 1996; Taguchi 1986), allows a reduction of the number of test combinations through a library of pre-set orthogonal arrays, which can be applied in many experimental situations without loss of relevant information. A Taguchi orthogonal array is composed by several combinations of levels of factors in such way that any pair of columns obeys to the orthogonal conditions. The usual notation is as follows:

$$L_a\,(b^c) \tag{3.2}$$

where *a* is the number of tests to perform (or combinations of levels); *b* is the number of levels for each factor; and *c* is the number of columns (to attribute to factors or interactions).

The analysis of variance – ANOVA – is used by Taguchi to analyze the data obtained by the orthogonal arrays. ANOVA allows the testing of the significance of the effects relatively to random error (usually called by 'noise', *e.g.*, variability in the environmental conditions, variability in the components or raw materials, variability during the manufacturing process, measuring errors, uncontrollable factors, etc.).

Taguchi method has proven to give good results in practice and many companies in the worldwide, especially in the U.S.A., have successfully applied it for product design and processes in the last years (ASI 2000).

Recently, Ferreira et al. (2000) showed that Taguchi techniques can also be applied in the experimental design of a polymer concrete material. Unfortunately, in their experimental work some parameters were not accurately controlled. Manual mix process of concrete mixtures and the use of deformable molds, conducted to a large variation in the quality of concrete specimens, which made difficult to obtain reliable conclusions. Nevertheless the inconclusive results, it was demonstrated that Taguchi techniques could be applied with success to the design of this particular material.

For this reason and due to its simplicity of application and its comprehensive set of design decision-making tools, this methodology was also chosen in this thesis for the experimental design and optimization process of polymer concrete materials.

3.2 Experimental Program

3.2.1 Material's Design

The aim of this first part of the present thesis was to develop and optimize a polymer concrete material that presented certain improved properties according to its future application. The objective was to determine an optimal PC formulation suitable either for precasting of structural members (GFRP-polymer concrete hybrid beams), or as a matrix of a lightweight structural concrete (Polymer concrete modified by light aggregates).

The first step consisted in defining the property or properties that should be optimized in the final composite, which are related with the specific material requirements imposed by the future application as a construction material.

Once defined the property that should be optimized, the response characteristic, a Taguchi experimental planning can be implemented.

3.2.1.1 Definition of property to be optimized

Some results of previous research carried out by Fernandes et al. (1998) showed that the most desirable properties of a PC construction material, those that should be optimized in design stage, were chemical and corrosion resistance, and compressive strength. Behind those, other properties such as tensile and flexural strengths, low permeability, dimensional stability and cost effectiveness, were also considered as important attributes. However, if it is intended to apply the Taguchi method in the experimental design, one single property to optimize must be chosen.

The above study was conducted considering PC as a new alternative material to cement concrete, for certain applications. The idea was that an improved chemical resistance and compressive strength, relatively to conventional concrete, would turn this new material more competitive in the construction market.

However, the bibliography review conducted in chapter II, shows that PCs present generally, as function of polymer binder, better chemical resistance than Portland cement concretes (Chawalwala 1996; Fowler 1999; Mebarkia and Vipulanandan 1995; Ohama et al. 1886). Therefore, this attribute, brought by resin matrix, is already present. Nevertheless, a special care should be put in the choice of resin binders, if it is intended to improve this property.

On the other hand, although being unquestionable that compressive strength is one of the most important mechanical properties of a concrete material, it's the flexural strength that better define the mechanical characteristics of a PC (San José 1996).

In conventional cement concretes, there is a straightforward correlation between mechanical properties such as compressive, flexural and tensile strengths. Empirical relationships are given on almost of the concrete design codes (CEB/FIP 1990; CEN-EC2 1992) and their use is a common practice in design. As compressive tests are relatively easier to perform and very simple in procedure, compressive strength became the first element of control to normal cement concretes. Its value defines the resistance class of the concrete, and all the other mechanical properties are given as function of this one.

In the case of PCs, it is no possible to establish such relationships. Generally, a PC with a compressive strength higher than other one also possesses higher flexural strength. However, different kinds of PC manufactured with distinct resins may have similar compressive strengths and exhibit very distinct magnitudes of flexural strengths. Therefore, flexural resistance represents a stronger parameter in the assessment of PC quality, allowing a more clear differentiation in terms of mechanical strength. Therefore, this mechanical property will be the material characteristic chosen to be improved in design process.

The other attributes, such as good dimensional stability and cost effectiveness, can be taken into account in the selection process of polymeric resins to use in the experimental program. Low shrinkage and good relationship between cost and mechanical performance will also take part in the selection criteria of resin binder.

3.2.1.2 Planning of experiments

The planning of the various mixtures to test was achieved through a Taguchi methodology. With this technique, a detailed analysis of the effect of several materials factors on a specified property of mix formulations can be obtained. As stated earlier, this method presents the great advantage of reducing the mixture combinations, which represents a considerable saving in time and costs. To perform all possible mixture combinations would not be practical due to the potential high number of parameters involved.

Taguchi experimental planning was accomplished by following the sequential steps:

i. Selection of major factors and interactions to study;
ii. Selection of the levels' values adopted by the material factors;
iii. Selection of the most convenient Taguchi orthogonal array;
iv. Attribution of the major factors and/or interactions to the columns of the orthogonal array.

After these fundamental steps, specimen's manufacture, experimental tests and analysis of obtained data can be performed.

i) Selection of major factors and interactions;

In order to minimize the initial dimension of experimental plan, the use of many factors and few levels is advised. This first experimental planning will allow reducing the number of factors to the most important ones, which could be later investigated with several levels, without producing an excessive dimension of experimental plan.

The following material factors or variables were considered:

▪ Resin type	(A);
▪ Charge content in resin	(B);
▪ Resin content	(C);
▪ Sand type	(D);
▪ and Curing method	(E).

In a Taguchi experimental plan, the reduction of the number of tests is made by re-using some columns related to interactions of the factorial array. This 'confuses' the original plan with new factors, meaning that is not possible to separate the principal effect of a new factor and the effect of the interaction that column represents.

There is some discussion between the classic statistics and Taguchi. The later supports the use of saturated arrays (all columns of the factorial are used to study factors), while the classics advise not to ignore the interaction between two factors, supporting the use of fractioned factorials (only the columns correspondents to interactions between more than two factors are used for the study of new factors) (Coimbra 1988).

In order not to 'mask' in excess the plan and reduce its 'confusion', all interactions between any two factors were considered. Only the interactions between more than two factors were ignored. Thus, the effects of the following ten interactions were investigated:

- "Resin type * Charge content" (A*B);
- "Resin type * Resin content" (A*C);
- "Resin type * Sand type" (A*D);
- "Resin type * Curing method" (A*E);
- "Charge content * Resin content" (B*C);
- "Charge content * Sand type" (B*D);
- "Charge content * Curing method" (B*E);
- "Resin content * Sand type" (C*D);
- "Resin content * Curing method" (C*E);
- and "Sand type * Curing method" (D*E).

i) Selection of the variation levels;

For each material factor, two variation levels were established. The selection criteria used for the variation levels of each factor are explained in what follows.

Resin Type: An epoxy and an unsaturated polyester thermoset resins were chosen for variation levels of the first factor. The choice for these two types of resin was not arbitrary. As mentioned in chapter II, epoxy resins generally lead to better mechanical properties in the final product, whereas polyester resins usually present a good relationship between price and performance. The specific resins of epoxy and polyester were chosen among the available commercial resins in the local industrial market. The main selection parameters were: ability to cure at room temperature and to incorporate charges, low viscosity, reduced shrinkage, and good relationship between price and mechanical properties.

Sand Type: For the aggregates, two types of sand with different size grading were chosen: clean river sand and foundry sand. 'Clean' sand is a well-graded sand but with low content of fines, while foundry sand presents rather a fine uniform grade size. In general, the aggregates grading should provide a material having the lowest possible surface area and void content per unit volume, thus requiring the lowest possible binder content to achieve the desired workability, strength and other concrete properties (Smith and Collis 1999). In general continuously graded aggregates tend to provide relatively straightforward and easy-to-place concretes, whereas gap-graded concretes usually require appreciably more expertise in mix design, production, handling and placing (Schaffler 1979; Shacklock 1959).

Since no coarse aggregates were used in mix formulations, polymer mortar term would be a more proper designation for resultant materials. However, it was decided to maintain the generic term of polymer concrete, as this is the global designation of this class of materials. The option do not include coarse aggregates was determined by the means and equipment available at INEGI lab that did not allow the production and testing of PC specimens with large size aggregates.

Resin Content: The design of concrete mixes is normally based on the premise that the voids in the bulk volume of aggregates, generally between 25% up to 40%, should be filled with binder (Smith and Collis 1999). As mentioned by Beningfield (1980), the inability to fill the voids completely does not necessarily result in failure, but surely increases the probability of trouble arising, as unfilled voids are potential initiators of cracks.

In order to determine the variations levels for resin content, two prismatic moulds were filled with the two types of sand considered in this study. The moulds were placed in a vibrator table in order to reach the maximum of packing. After that, an alcohol was shed into the molds. The volume contents of alcohol, necessary to fill the voids between particles sand, in each mold, gave an orientation for the resin contents to use as variation levels. Volume contents of 27% and 33% were found, respectively, for the clean and foundry sands, which correspond to mass percentages of resin around 17% and 20%. In order to simplify calculation process, the same specific gravity was considered for both resins.

Charge content: The contents of 0% and 25% were chosen as variations levels for charge content in resin. These percentages are related to resin mass. There was no prior experimental study that conducted to these values, but previous studies on PC carried out by Ohama et al. (1981) suggest values around 0 to 60%, according to the size distribution of aggregates. Due to the mean diameter and the maximum aggregate size of both sands, the inclusion of filler with contents higher than 25% led to poor workability even for resin contents of 20%. Therefore, 25% filler content was chosen for superior level of charge content.

Curing Cycle: Two alternative curing methods were considered: seven days at room temperature or three hours at 80ºC after 1 day at room temperature. In general, depending on the type of resin matrix and environment temperature, polymer concrete and mortars reach their maximum strength at seven days after casting process. Thermal treatments are normally used to accelerate the cure process and/or to improve mechanical strengths of composite materials. The temperature at which the thermal treatment must be done and conditioning period are function of resin type and specimen size.

The variation levels for each considered material factor are summarized in Table 3.2.

Table 3.2. Factors and levels considered in mix formulations.

	Factors				
	A- Resin Type	**B**- Charge Content	**C**- Resin Content	**D**- Sand Type	**E**- Curing Cycle
Level **1**	Polyester	0%	17%	Clean	3 hours at 80ºC
Level **2**	Epoxy	25%	20%	Foundry	7 days at 23ºC

iii) Selection of Taguchi orthogonal array;

The selection of Taguchi orthogonal array depends on the number of levels adopted by each factor and the total number of freedom degrees needed to lodge all the factors and interactions considered. The selected orthogonal array should have a number of freedom's degrees larger, or equal, than the total number of degrees of freedom requested by the factors and/or interactions in study. The total number of freedom's degrees of an experimental plan (orthogonal array), is equal to the sum of freedom's degrees of each column, and equivalent to the number of tests less one. If the column represents a factor, its degree of freedom is equal to the number of levels adopted by that factor less one. If the column represents an interaction instead, its degree of freedom is obtained by multiplying the freedom's degrees of the factors involved in that interaction (Coimbra 1988).

In this case, as it is pretend to investigate the effect of five factors with two levels, and ten interactions, an orthogonal array with at least fifteen degrees of freedom is required. A Taguchi orthogonal array L_{16} (2^{15}) fulfills this requisite.

This orthogonal array, illustrated in Fig. 3.3, can lodge up to fifteen factors, each one with two levels. Fifteen columns and sixteen rows compose L_{16} (2^{15}). Each column is coded with 1's and 2's, representing the levels, and each row corresponds to a specific combination of levels determining a test to perform. This array is similar to the complete factorial 2^4.

Table 3.3. Taguchi orthogonal array L_{16} (2^{15}) (Taguchi 1986).

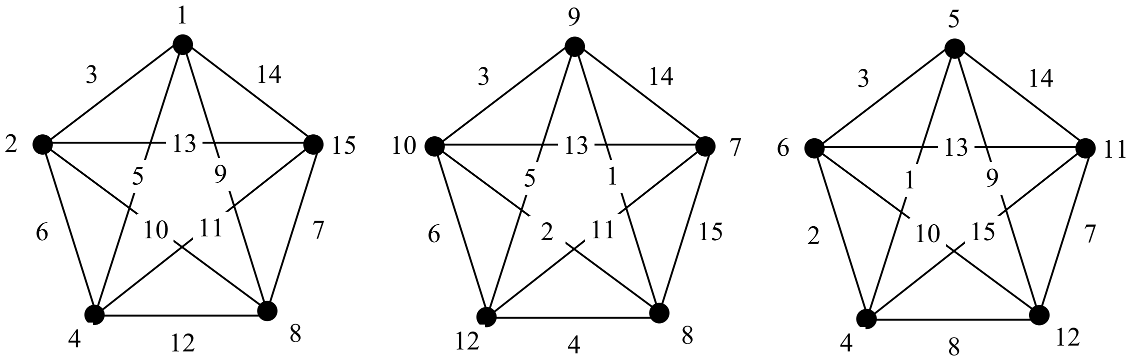
Col. No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
2	1	1	1	1	1	1	1	2	2	2	2	2	2	2	2
3	1	1	1	2	2	2	2	1	1	1	1	2	2	2	2
4	1	1	1	2	2	2	2	2	2	2	2	1	1	1	1
5	1	2	2	1	1	2	2	1	1	2	2	1	1	2	2
6	1	2	2	1	1	2	2	2	2	1	1	2	2	1	1
7	1	2	2	2	2	1	1	1	1	2	2	2	2	1	1
8	1	2	2	2	2	1	1	2	2	1	1	1	1	2	2
9	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2
10	2	1	2	1	2	1	2	2	1	2	1	2	1	2	1
11	2	1	2	2	1	2	1	1	2	1	2	2	1	2	1
12	2	1	2	2	1	2	1	2	1	2	1	1	2	1	2
13	2	2	1	1	2	2	1	1	2	2	1	1	2	2	1
14	2	2	1	1	2	2	1	2	1	1	2	2	1	1	2
15	2	2	1	2	1	1	2	1	2	2	1	2	1	1	2
16	2	2	1	2	1	1	2	2	1	1	2	1	2	2	1

iv) Attribution of factors and interactions to the columns of Taguchi orthogonal array;

If it is intend not to saturate the plan, triangular tables and linear graphics are associated jointly with Taguchi orthogonal arrays in order to select the columns to attribute to the interactions in study. In Table 3.4 and Fig. 3.1, triangular table and linear graphics associated to orthogonal array L_{16} (2^{15}) are presented.

Table 3.4. Triangular table associated to orthogonal array L $_{16}$ (2^{15}) Interactions between two columns.

Col. No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
	(1)	3	2	**5**	4	7	6	9	8	11	10	13	12	15	14
		(2)	1	6	7	4	5	10	11	8	9	14	15	12	13
			(3)	7	6	5	4	11	10	9	8	15	14	13	12
				(4)	1	2	3	12	13	14	15	8	9	10	11
					(5)	3	2	13	12	15	14	9	8	11	10
						(6)	1	14	15	12	13	10	11	8	9
							(7)	15	14	13	12	11	10	9	8
								(8)	1	2	3	4	5	6	7
									(9)	3	2	5	4	7	6
										(10)	1	6	7	4	5
											(11)	7	6	5	4
												(12)	1	2	3
													(13)	3	2
														(14)	1



a) b) c)

Fig. 3.1. Linear graphics, associated to Taguchi orthogonal array L $_{16}$ (2^{15}), for five factors and ten interactions (Taguchi 1986)

How to use triangular tables and linear graphics?

For instance, if factor A was associated to column 1 and factor B to column 4, the interaction between these two factors is represented by column 5 (cross-point on triangular table between row 1 -factor A-, and column 4 -factor B-). To quantify the interaction between these two factors, A and B, it will be necessary to keep column 5 free of any association with another factor.

The information obtained by triangular tables is also available in the linear graphics. These graphics are used so that the attribution of factors and interactions to columns of more complexes plans becomes easier. Each factor is associated to a point in the graphic. The point number indicates the column to attribute to that factor. The interaction between two factors (points) is associated to the straight-line that joints their corresponding points. The straight-line number determines the column to attribute to that interaction.

In this study, to distribute the factors and interactions by the columns of L $_{16}$ (2^{15}), the arrangement displayed in linear graphic a), of Fig. 3.3, was used.

The final disposal of major factors and interactions by columns of orthogonal array is showed in Table 3.5. Resultant sixteen mix formulations to test are summarized in Table 3.6.

Table 3.5. Attribution of factors and interactions to columns of L $_{16}$ (2^{15}) orthogonal array.

Factors:	A	B		C				D							E
Interactions:			A*B		A*C	B*C	D*E		A*D	B*D	C*E	C*D	B*E	A*E	
Col. / No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1	**1**	**1**	1	**1**	1	1	1	**1**	1	1	1	1	1	1	**1**
2	**1**	**1**	1	**1**	1	1	1	**2**	2	2	2	2	2	2	**2**
3	**1**	**1**	1	**2**	2	2	2	**1**	1	1	1	2	2	2	**2**
4	**1**	**1**	1	**2**	2	2	2	**2**	2	2	2	1	1	1	**1**
5	**1**	**2**	2	**1**	1	2	2	**1**	1	2	2	1	1	2	**2**
6	**1**	**2**	2	**1**	1	2	2	**2**	2	1	1	2	2	1	**1**
7	**1**	**2**	2	**2**	2	1	1	**1**	1	2	2	2	2	1	**1**
8	**1**	**2**	2	**2**	2	1	1	**2**	2	1	1	1	1	2	**2**
9	**2**	**1**	2	**1**	2	1	2	**1**	2	1	2	1	2	1	**2**
10	**2**	**1**	2	**1**	2	1	2	**2**	1	2	1	2	1	2	**1**
11	**2**	**1**	2	**2**	1	2	1	**1**	2	1	2	2	1	2	**1**
12	**2**	**1**	2	**2**	1	2	1	**2**	1	2	1	1	2	1	**2**
13	**2**	**2**	1	**1**	2	2	1	**1**	2	2	1	1	2	2	**1**
14	**2**	**2**	1	**1**	2	2	1	**2**	1	1	2	2	1	1	**2**
15	**2**	**2**	1	**2**	1	1	2	**1**	2	2	1	2	1	1	**2**
16	**2**	**2**	1	**2**	1	1	2	**2**	1	1	2	1	2	2	**1**

Once defined the mix formulations to test, the experimental part of this program, which included the specimens manufacturing and testing, is ready to be performed.

Table 3.6. Mix formulations to be tested.

Formulations	A-Resin Type	B- Charge Content (%)	C- Resin Content (%)	D- Sand Type	E- Curing Cycle
1	Polyester	0	17	Clean	7 days / 23ºC
2	Polyester	0	17	Foundry	3 hours / 80ºC
3	Polyester	0	20	Clean	3 hours / 80ºC
4	Polyester	0	20	Foundry	7 days / 23ºC
5	Polyester	25	17	Clean	3 hours / 80ºC
6	Polyester	25	17	Foundry	7 days / 23ºC
7	Polyester	25	20	Clean	7 days / 23ºC
8	Polyester	25	20	Foundry	3 hours / 80ºC
9	Epoxy	0	17	Clean	3 hours / 80ºC
10	Epoxy	0	17	Foundry	7 days / 23ºC
11	Epoxy	0	20	Clean	7 days / 23ºC
12	Epoxy	0	20	Foundry	3 hours / 80ºC
13	Epoxy	25	17	Clean	7 days / 23ºC
14	Epoxy	25	17	Foundry	3 hours / 80ºC
15	Epoxy	25	20	Clean	3 hours / 80ºC
16	Epoxy	25	20	Foundry	7 days / 23ºC

Before describing the procedures adopted in the manufacturing process and testing of PM specimens, a brief characterization of raw materials employed is required.

3.2.2 Characterization of Raw Materials

3.2.2.1 Polymeric binders

An epoxy and unsaturated polyester resins were used as binders of PM formulations.

i) Unsaturated polyester resin

The polyester resin used in this work is commercially known by the designation of S226E (NESTE®). It is a low viscosity mixture of an orthophtalic unsaturated polyester prepolymer and styrene (44%), which acts both as solvent and reactive monomer. The resin system is tixotropic and is pre-accelerated by the manufacturer with a cobalt (II) salt. The catalyst used consisted of a methyl ethyl ketone peroxide solution (2 phr).

The S226E resin is mainly used for RTM (resin transfer moulding) systems. Its low viscosity, low exothermic peak and good resistance to high temperatures make it suitable for products that required a fast demoulding, a good finishing or a reduced shrinkage. This resin allows the incorporation of charge and cures at room temperature.

In Tables 3.7 and 3.8, physical and mechanical properties of S226E polyester resin are presented.

Table 3.7. Properties of S226E polyester resin (not-cured stage).

Properties of S226E (Stage not cured)	Unity	Nominal Value	Standard Method
Viscosity (23ºC)	mPa.s	140	ISO 2255
Density	Kg/dm^3	1.08	ISO 2811
Gel time (23ºC)	min.	25	Int. Method

Table 3.8. Properties of S226E polyester resin after one week at 23ºC.

Properties of S226E (Stage cured)	Unity	Nominal Value	Standard Method
Hardness	Barcol	40-50	ASTM D 2583
Tg (Glass Transition Temp.)*	ºC	87	ISO 6721-5
HDT (Heat Distortion Temp.)*	ºC	50	ISO 75 Mét. A
Flexural Resistance	MPa	119	ISO 178
Tensile Resistance	MPa	58	ISO 527
Flexural Elasticity Modulus	MPa	4100	ISO 178

* -Determined at INEGI lab.

ii) Epoxy resin

The epoxy resin used in this study is commercialised by SILICEM and is designated by EPOSIL-551. This resin system is based on diglycidil ether of bisphenol A and an aliphatic amine hardener and it is processed with a maximum mix ratio to the hardener of 2:1.

EPOSIL -551 presents low viscosity, good impregnation, and it cures at room temperature. As a binder, allows the incorporation of high percentage of agglomerates, exceeding largely the conventional systems.

Physical and mechanical properties of EPOSIL-551 resin system are presented in Tables 3.9 and 3.10.

Table 3.9. Properties of EPOSIL-551 epoxy resin system (not-cured stage).

Properties of EPOSIL-551 (Stage not cured)	Unity	Nominal Value	Standard Method
Viscosity (23ºC)	mPa.s	400-600	ISO 2255
Density	Kg/dm^3	1.18	ISO 2811
Gel time (23ºC)	min.	27	Int. Method

Table 3.10. Properties of EPOSIL-551 epoxy resin system after one week at 25ºC.

Properties of EPOSIL-551 (Stage cured)	Unity	Nominal Value	Standard Method
Hardness	Shore D	85	ISO 868
Tg (Glass Transition Temp.)*	ºC	45	ISO 6721-5
HDT (Heat Distortion Temp.)*	ºC	35	ISO 75 Mét. A
Flexural Resistance	MPa	70 +/- 5	ISO 178
Tensile Resistance	MPa	40 +/- 5	ISO 527
Flexural Elasticity Modulus	MPa	2200 +/- 200	ISO 178

* - Determined at INEGI lab.

3.2.2.2 Sand aggregates

As the larger part of the total volume of concrete mixes is formed by the aggregate, its characteristics have a strong influence on the performance and properties of the fresh or hardened concretes in many ways.

The inherent properties of the sand, such as chemical inertness and durability are important but, in particular, the shape, surface texture and grading of aggregate particles are likely to have a major influence on the properties of the mortar or concrete mixes. Particle shape and surface texture, whilst easily ascertained for coarse aggregates, are more difficult to determine for finer grained particles, as it is the case of clean and foundry sands. Microscopy study can show the particle shape but, unfortunately, the surface texture (*e.g.* glassy, smooth, etc.) is not so easy to describe. For this reason, this last parameter was not defined for both sands in this study.

i) Clean sand

‘Clean sand’ was the designation given to certain river sand supplied by a local extractive industry. It is well- graded sand with a continuously graded particle between 0-1.2 mm. The chemical and physical properties of clean sand, as well as size grading, are presented in Tables 3.11 and 3.12.

Table 3.11. Physical and chemical properties of ‘Clean sand’.

Chemical properties		Physical properties	
SiO_2	98.0 %	Bulk Density	1.52 g/cm^3
Al_2O_3	0.78 %	Particle Density	2.61 g/cm^3
Fe_2O_3	0.10 %	Hardness	7 mohs
K_2O	0.08 %	pH	7
Na_2O	0.02 %	Average Diameter D_{50}	800 μm
CaO	0.01 %	Particle shape	Roundness
MgO	0.01 %		

Table 3.12. Size grading of ‘Clean sand’.

Sieve size (μm)	Restrained mass percentage
1200	5.5
1000	16.5
850	25.0
710	23.5
600	18.5
300	6.1
212	3.2
150	1.2
106	0.3

ii) Foundry sand

Foundry sand is a generic term to denote sand with a high-grade of silica.

Silica is hard, chemically inert and has a high melting point due to strength of inter-atomic bonds. These are prized qualities in various industrial uses, particularly in foundry casting. Crystalline silica has a higher melting point than iron, copper or aluminium. This enables castings to be produced by pouring molten metal into moulds made out of silica sand and a binder. Silica sand deposits are normally exploited by quarrying and the material extracted may undergo considerable processing before sale. The objectives of processing are to reduce impurities, to increase the grade of silica and to produce the optimum size distribution of the product.

The foundry sand used in this work has a rather uniform particle size with an average diameter of 245 μm. This silica sand is extracted/processed by 'Sibelco, Lda', and has been commercialised by 'Fundipor' under the technical name SP55. The physical and chemical properties and size grading of SP55 sand are presented in Tables 3.13 and 3.14.

Table 3.13. Physical and chemical properties of foundry sand SP55.

Chemical properties		Physical properties	
SiO_2	99.0 (min.)	Bulk Density	1.56 g/cm^3
Al_2O_3	0.40 (max.)	Particle Density	2.65 g/cm^3
TiO_2	0.10 "	Hardness	7 mohs
Fe_2O_3	0.07 "	pH	6.5 – 7.5
K_2O	0.07 "	Average Diameter D_{50}	245 μm
Na_2O	0.05 "	Particle shape	Roundness
CaO	0.03 "		
MgO	0.03 "		

Table 3.14. Size grading of foundry sand SP55.

Sieve size (μm)	Restrained mass percentage
850	0.05
600	0.15
300	24.9
212	57.0
150	15.0
106	2.5
75	0.3
53	0.05

3.2.2.3 Charge

Ground calcium carbonate was used as charge or filler material. The calcium carbonate used in this study is commercialized by 'COMITAL' under the designation 'Plastex 25'.

The main characteristics of this product are very fine particle size, low abrasion and excellent whiteness. Technical specifications are shown in Table 3.15.

Table 3.15. Physical and chemical properties of calcium carbonate Plastex 25.

Chemical specifications		Physical properties	
Ca O	56.24 %	Density	0.75 g/cm^3
PF	43.32 %	Abrasion	5 mg (Einiehner)
Al_2O_3	0.46 %	Hardness	2.5 mohs
Fe_2O_3	0.06 %	pH	9.5
TiO_2	0.00 %	Average Diameter D_{50}	4.05 µm
K_2O	0.00 %	Mass finer than 36 µm	99 %
Na_2O	0.00 %	Whiteness	L 95.83 a -0.21 b +4.31
SiO_2	0.00 %	Volatiles	0.18 %
Mg O	0.00 %	Oil Absorption	19 ml / 100 g

3.2.3 Manufacturing and Casting process of PM Specimens

Mix concrete formulations were manufactured following as close as possible the procedures described in RILEM recommendations PC-1 (1995a) and PC-2 (1995b).

3.2.3.1 Mix procedure

The mixing of each concrete formulation was accomplished according to the following steps:

- The aggregates and the charge (if the case) were previously oven dried in order to ensure moisture contents lower than 0.1 %;
- The raw materials were measured, separately, by weight and stored in suitable containers to prevent moisture absorption and evaporation;
- The liquid resin, polyester or epoxy, was poured in a container and mixed with the initiator or the hardener. If the concrete formulation considered the incorporation of charge, this one was added at this stage to the resin system, and the paste was thoroughly mixed until uniform aspect;

- Finally, sand aggregates and binder were put together into an automatic mixer, and mixed until all the aggregate were thoroughly ‘wetted’ (during approximately 2 min.).

In Fig. 3.2, the mechanical batch mixer used to prepare the concrete mixtures is shown.

3.2.3.2 Moulds and casting process

According to RILEM recommendation PC-2 (1995b), polymer mortar specimens for flexural tests shall be prismatic with square cross-section, 40 mm by 40 mm, and 160 mm in length. For this purpose, steel prismatic molds with convenient dimensions were used. The prismatic molds, illustrated in Fig. 3.3, consisted of steel side plates and a steel base plate assembled with metal fastenings.

The inside surfaces of the moulds were previously coated with a suitable release agent before the placing of the polymer concrete paste. A silicone wax (‘Paste Wiz’, supplied by AXEL) and a strippable paint (‘QZ-13’, supplied by CIBA) were used as release agents, respectively, for the polyester and epoxy mortar formulations.

In Fig. 3.4, the steps of casting process are illustrated. The photos are referred to the moulding of PM specimens used for creep tests. Although the different size of specimens and moulds, the procedures followed in the casting process were similar to those used in this investigation.

Polymer concrete mass was placed into the moulds by a spatula in three approximately equal layers, and each layer was consolidated through the application of pressure. Rodding and tamping were also performed to assist in the consolidation of the material. No internal or external vibration was used. After the completion of placing, the excess of polymer concrete on the top surfaces was struck off and a trowel achieved the finishing surface.

Batches with nine specimens were cast for each mortar formulation.

In order to ensure uniformity of procedures and to avoid variability in the manufacturing process, the same two operators accomplished the casting process of all specimens used in this study. In early studies, carried out by San José et al. (2002), it was found that the casting procedure is the most important factor for the understanding of the micro and macroscopic behavior of polymer concretes.

Fig. 3.2. Automatic batch mixer used to mix the polymeric resins with the aggregates.

Fig. 3.3. Standard steel prismatic moulds for flexural testing purposes of polymer mortar specimens.

Fig. 3.4. Casting steps for moulding polymer mortar specimens.

Other influences, such as different resin formulations and aggregate nature, are not so important in order to explain internal differences in the interface aggregates-resin matrix. Porosity, interface aggregates-matrix configuration, strength and deformability, are narrowly linked. Attempting to this, a special care was taken in the casting process of PM specimens in terms of homogenization of procedures. They were previously specified and systematic repeated in all casting processes by the same two operators.

3.2.3.3 Curing treatment

The specimens were allowed to cure in the moulds during 24 hours before removal. A climatic chamber ensured a controlled environment during these first hours.

After removal from moulds, as function of PM formulation and correspondent curing method, PM specimens were submitted to different treatments:

- PM specimens, belonging to formulations nº 1, 4, 6, 7, 10, 11, 13 and 16, were stored at room temperature in a climatic chamber during one, three and six days. Afterwards they were tested in bending. For each conditioning period, three specimens of each mortar formulation were tested in order to access flexural strength development with cure time. Only the flexural test results of the specimens conditioned during seven days after casting process were taken into account in the application of Taguchi methodology.
- The remaining PM specimens were submitted to oven post-curing treatment, at 80ºC during 3 hours. Before being tested in bending, the specimens were allowed to cool at least until all concrete mass had reached the room temperature. All nine specimens of each mix formulation were tested at the same time. For the accomplishment of Taguchi method, only three test results, randomly chosen among the nine tests performed, were taken into account. The limitation of the number of results is imposed by the analysis of variance (ANOVA) used for data treatment. This test is minimally affected by violations of population normality and homogeneity of variance so long as the samples are the equal size.

The oven and the climatic chamber used in this study (to dry the aggregates and for specimens conditioning), are illustrated in Fig. 3.5.

3.2.4 Flexural Tests Procedure

3.2.4.1 Specimens' preparation

All specimens were conditioned in a climatic chamber at room temperature, during at least 3 hours, before being tested in bending.

Fig. 3.5. Oven (at left) and climatic chamber (at right) used to dry the aggregates and for conditioning of PM specimens.

Specimens' loading surfaces were previously sandpapered in order to obtain a desirable and adequate contact between the loading nose and supports of loading apparatus, and the specimen.

For effects of flexural strength calculation, width and height of middle cross section of each specimen were measured with the accuracy of a micrometer.

3.2.4.2 Test set-up

An Instron universal testing machine, displacement control type, with a load cell of 100 kN was used to perform the flexural tests. The loading apparatus followed the RILEM recommendation (1995c) for the three-point loading method of flexural test, with a span length of 100 mm.

In order to ensure a homogeneous cross section throughout the loading plan, test specimens were placed in the loading apparatus support in such way that the casting surface was not a loading surface.

Load was then applied at a crosshead rate of 1.0 mm.min^{-1} until failure occurred. An electronic measuring device connected to the testing machine recorded load-displacement curves and maximum load corresponding to the collapse bending moment.

Testing set-up and specimen geometry, as well as the mechanical testing machine, are illustrated in Fig. 3.6.

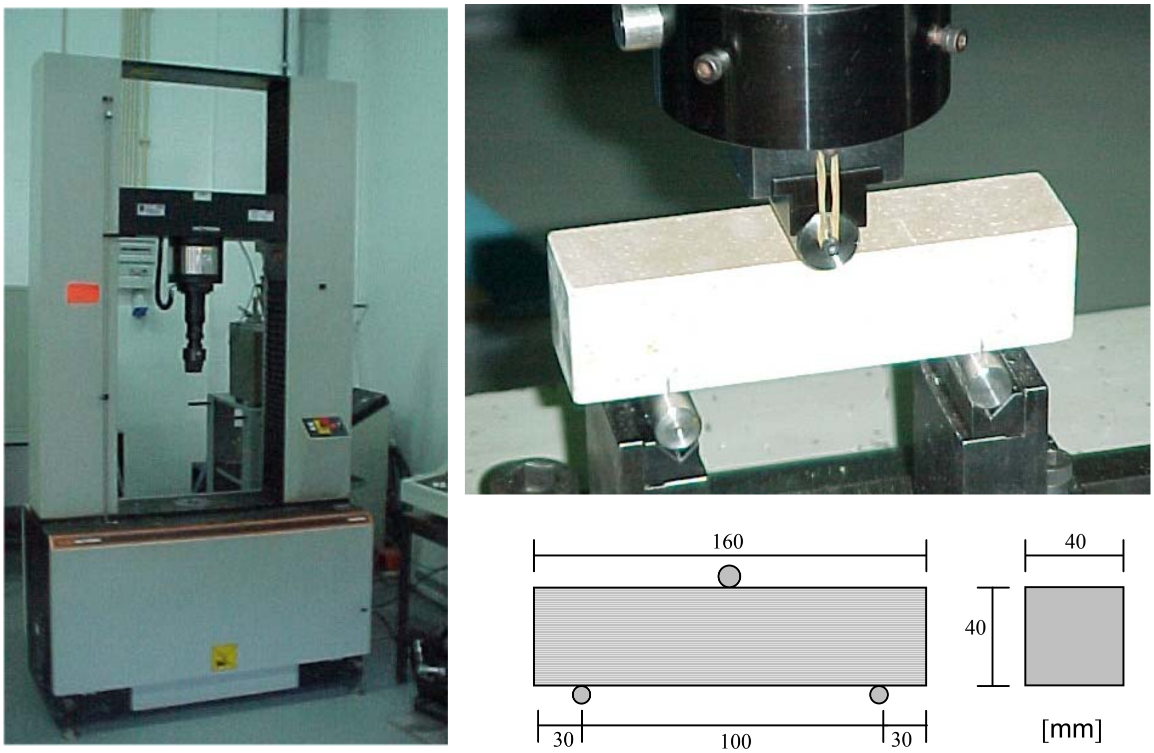


Fig. 3.6. Mechanical testing machine, flexural testing set-up and specimen geometry.

3.3 Experimental Results and Treatment of Data

3.3.1 Flexural Tests Results

3.3.1.1 Flexural strength

Flexural strength was calculated according to the following equation:

$$\sigma f = \frac{3Pl}{2bh^2} \tag{3.1}$$

where σf is the flexural strength (MPa); P is the maximum load recorded (N); l is the span length (mm); b is the width of specimen (mm) and h is the height of specimen (mm). For each test series, arithmetic mean of flexural strength results and correspondent standard deviations were calculated, and shown in Table 3.16.

Table 3.16. Flexural test results: average values and correspondent standard deviations.

Concrete formulation Nº	Failure load (kN)		Failure stress (MPa)	
	Average	St. Deviation	Average	St. Deviation
1	10.04	0.50	23.52	1.17
2	8.82	0.12	20.67	0.28
3	10.15	0.22	23.79	0.52
4	14.02	0.46	32.85	1.07
5	6.90	0.39	16.18	0.91
6	2.15	0.11	5.04	0.26
7	11.26	0.75	26.38	1.75
8	8.34	0.49	19.55	1.16
9	12.71	0.67	29.80	1.58
10	15.31	0.03	35.87	0.08
11	12.74	0.05	29.85	0.11
12	16.52	0.94	38.72	2.20
13	12.82	0.89	30.04	2.08
14	12.55	0.72	29.41	1.68
15	14.71	0.65	34.47	1.53
16	14.91	0.91	34.94	2.14

3.3.1.2 Load- deflection curves

In Figs. 3.7 to 3.9, typical bending load-displacement curves are displayed.

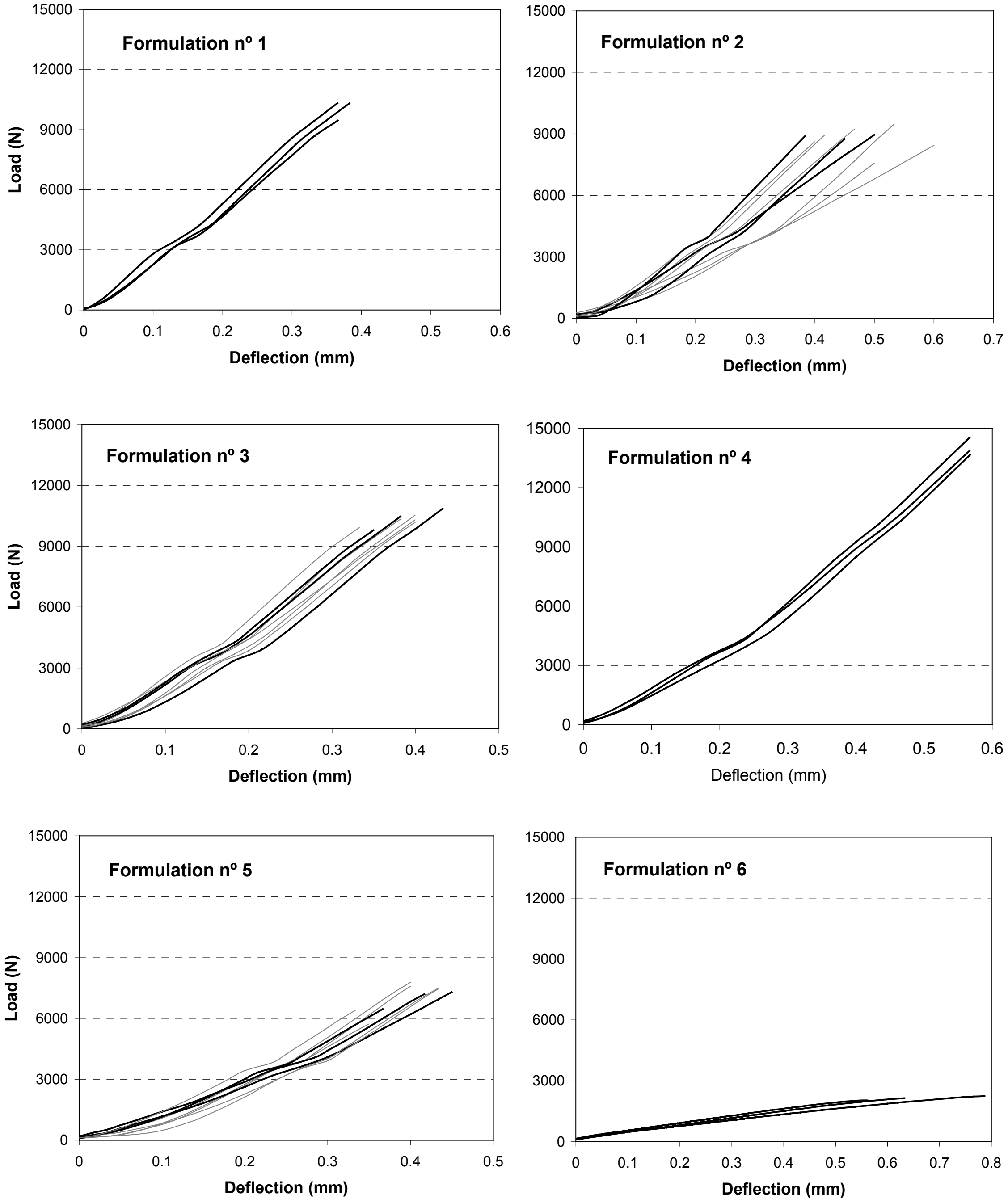


Fig. 3.7. Load-deflection curves obtained from flexural tests performed on PM specimens of formulations nº 1 to 6.

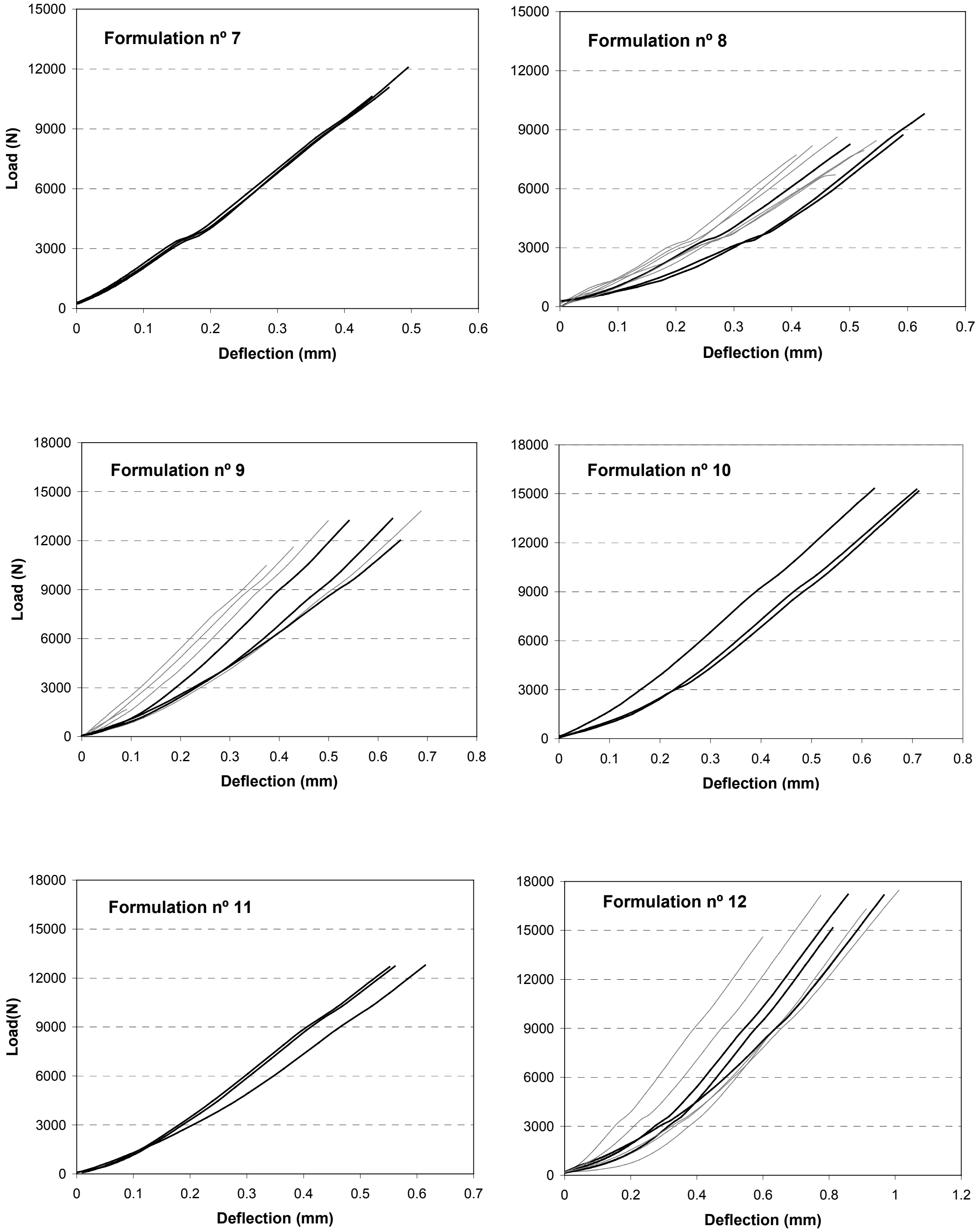


Fig. 3.8. Load-deflection curves obtained from flexural tests performed on PM specimens of formulations nº 7 to 12.

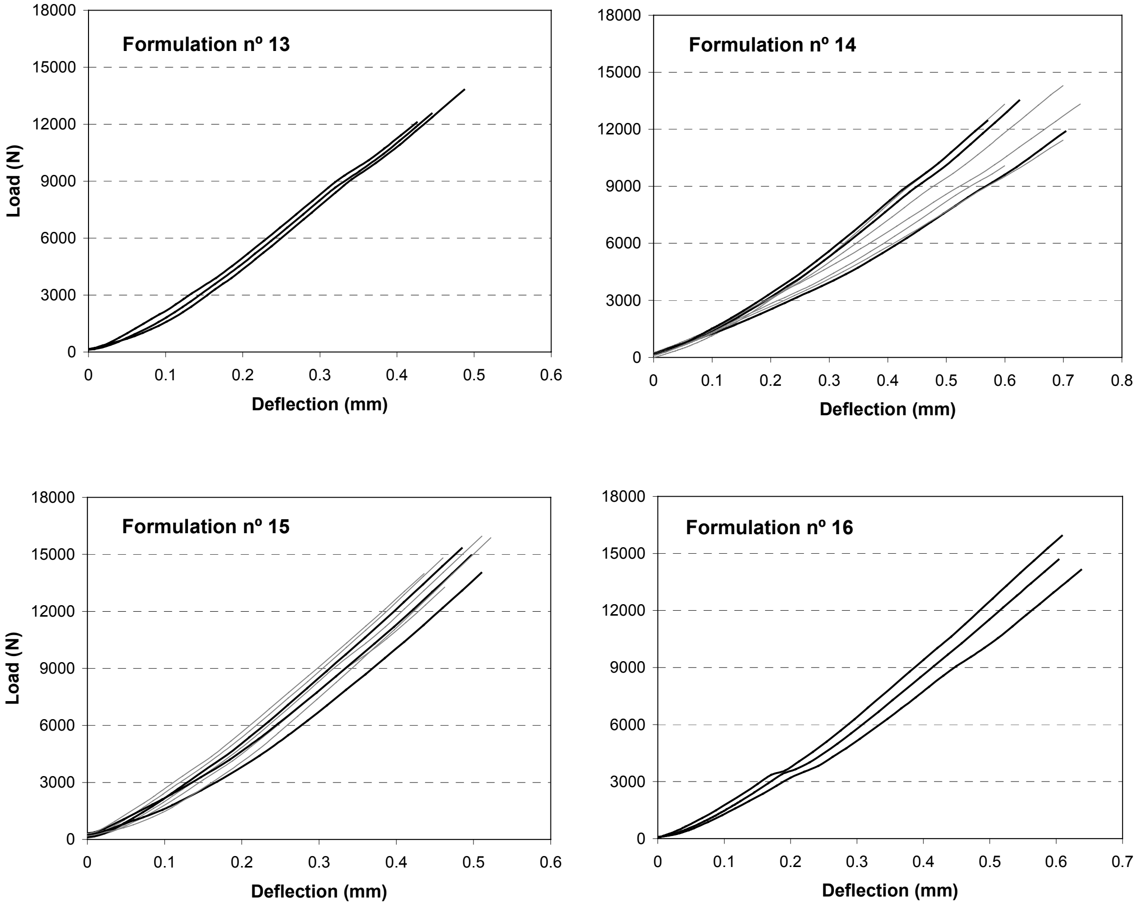


Fig. 3.9. Load-deflection curves obtained from flexural tests performed on PM specimens of formulations nº 13 to 16.

From the experimental graphs displayed in Figs. 3.7 to 3.9, it seems clear that load-displacement curves, for each concrete formulation, are relatively quite similar, and the maximum load values are also very close, which is a good indication of prediction of material behavior.

In these figures, black curves are correspondent to flexural test results considered for data treatment by way of average and variance's analysis. Grey curves correspond to flexural tests performed on PM specimens belonging to batches of formulations that were post-cured at 80ºC during 3 hours, which results were not considered for data treatment.

3.3.2 Principal Effects and Interactions' Effects on Bending Strength

The influence of a factor or an interaction on the global variance can be determined as a function of the numeric values of the effects and they indicate the level of influence in the global response, which is, in this case, the bending resistance in terms of failure load.

The calculus of the effects can be processed, through the analysis of averages, by way of the columns of the orthogonal array.

3.3.2.1 Numeric values of principal and interactions' effects

The numeric value of factor's effect, E_X, or principal effect, is not more than the difference between the average values obtained on the two levels adopted by that factor. To calculate each of these averages, all response values where that factor interacts with the level in question are considered. This effect is designated by 'principal effect', as each average used in the calculation of the effect, involves response values corresponding to several levels of the other factors, as given by expressions 3.2 to 3.3.

$$E_X = \overline{X}_2 - \overline{X}_1 \tag{3.2}$$

$$\overline{X}_i = \frac{1}{n} \sum R\,(X_i) \quad {}_{i = 1, 2} \tag{3.3}$$

where $\overline{X}_i$ represents the average value corresponding to all responses involving factor X with level *i,* and *n* is the number of responses obeying to those conditions.

The determination of the interaction's effect value between two factors, $IE_{(X*Y)}$, is not so straightforward and involves the calculus of four different average values:

$$IE_{(X*Y)} = \frac{1}{2}\left[(\overline{XY}_{22} - \overline{XY}_{21}) - (\overline{XY}_{12} - \overline{XY}_{11})\right] \tag{3.4}$$

or

$$IE_{(X*Y)} = \frac{1}{2}\left[(\overline{XY}_{22} - \overline{XY}_{12}) - (\overline{XY}_{21} - \overline{XY}_{11})\right] \tag{3.5}$$

where $\overline{XY}_{ij}$ represents the average value corresponding to responses involving factor X with level *i*, factor Y with level *j* and the other factors with any levels.

The numeric values of principal and interactions' effects can be calculated, directly, with basis on the coded columns of orthogonal array.

In Table 3.17, the $L_{16}(2^{15})$ orthogonal array is presented, from which the calculation of numeric values of principal and interactions effects can be followed.

Table 3.17. Calculus process of numeric values of principal and interaction effects.

Nº	Factors					Interactions										Response (kN)
	A	B	C	D	E	A*B	A*C	A*D	A*E	B*C	B*D	B*E	C*D	C*E	D*E	
1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	10.04
2	1	1	1	2	2	1	1	2	2	1	2	2	2	2	1	8.82
3	1	1	2	1	2	1	2	1	2	2	1	2	2	1	2	10.15
4	1	1	2	2	1	1	2	2	1	2	2	1	1	2	2	14.02
5	1	2	1	1	2	2	1	1	2	2	2	1	1	2	2	6.90
6	1	2	1	2	1	2	1	2	1	2	1	2	2	1	2	2.15
7	1	2	2	1	1	2	2	1	1	1	2	2	2	2	1	11.26
8	1	2	2	2	2	2	2	2	2	1	1	1	1	1	1	8.34
9	2	1	1	1	2	2	2	2	1	1	1	2	1	2	2	12.71
10	2	1	1	2	1	2	2	1	2	1	2	1	2	1	2	15.31
11	2	1	2	1	1	2	1	2	2	2	1	1	2	2	1	12.74
12	2	1	2	2	2	2	1	1	1	2	2	2	1	1	1	16.52
13	2	2	1	1	1	1	2	2	2	2	2	2	1	1	1	12.82
14	2	2	1	2	2	1	2	1	1	2	1	1	2	2	1	12.55
15	2	2	2	1	2	1	1	2	1	1	2	1	2	1	2	14.71
16	2	2	2	2	1	1	1	1	2	1	1	2	1	2	2	14.91
$\overline{X}_1$	9.0	12.5	10.2	11.4	11.6											
$\overline{X}_2$	14.0	10.5	12.8	11.6	11.4											
$\overline{XY}_{11}+\overline{XY}_{22}$						12.2	10.9	12.2	11.7	12.0	10.4	11.8	12.0	11.3	11.6	
$\overline{XY}_{12}+\overline{XY}_{21}$						10.8	12.1	10.8	11.3	11.0	12.6	11.2	11.0	11.7	11.4	
	5.1	-2.1	2.6	0.2	-0.3	1.5	-1.3	1.4	0.5	1.0	-2.1	0.7	1.1	-0.5	0.2	

In Table 3.17, the last column presents the average responses obtained from flexural tests results, and the last row, the calculated effects on global response for each factor and interaction.

From Table 3.14, the following relevant information can be extracted:

- Which or whose factor(s) influence(s) the most the concrete bending strength;
- The existence (or not) of interactions between factors that may affect bending resistance.

3.3.2.2 Response graphics

Response graphics allow the evaluation of the relative importance of each factor, or interaction, in a much easier way than the numeric values of effects.

For principal effects, the interpretation of response graphics is straightforward. Each point in each graphic represents the average response for a certain level of the factor. The numeric value of the effect is the difference between the two points: the higher the difference, the higher the influence of the factor.

In Fig. 3.10, the response graphics of principal effects, with 95% confidence error bars, are presented.

To analyse response graphics of interactions effects, the principal effects of the factors involved must be ignored and attention should be focused on their interactions. Each point represents the average response for two levels of the factors in question. Therefore, to draw response graphic of an interaction, the previous calculation of partial averages $\overline{XY}_{11}$, $\overline{XY}_{12}$, $\overline{XY}_{21}$ and $\overline{XY}_{22}$ is required.

The four average points define two straight lines: between $\overline{XY}_{11}$ and $\overline{XY}_{12}$ (or $\overline{XY}_{21}$) points, and between $\overline{XY}_{22}$ and $\overline{XY}_{21}$ (or $\overline{XY}_{12}$) points. The interaction is graphically defined by the parallelism between the two lines: the smaller the parallelism, the higher the interaction.

The parallelism between the two lines can be quantified through a numeric value, which is straightforwardly comparable with the numeric values of principal effects.

Response graphics of interaction effects are displayed in Figs. 3.11 and 3.12.

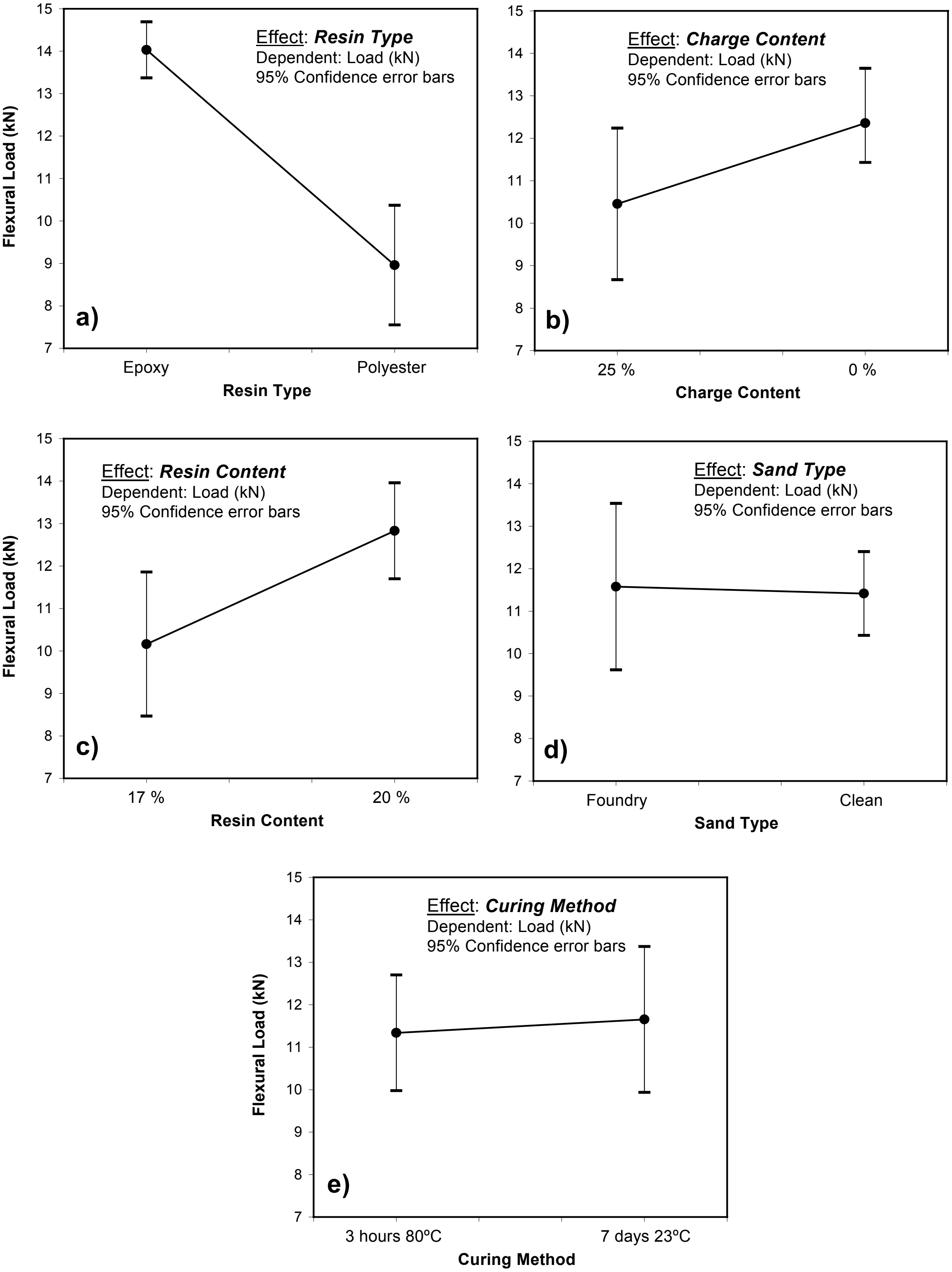


Fig. 3.10. Response graphics of principal effects: a) Resin Type; b) Charge Content; c) Resin Content; d) Sand Type and e) Curing Method.

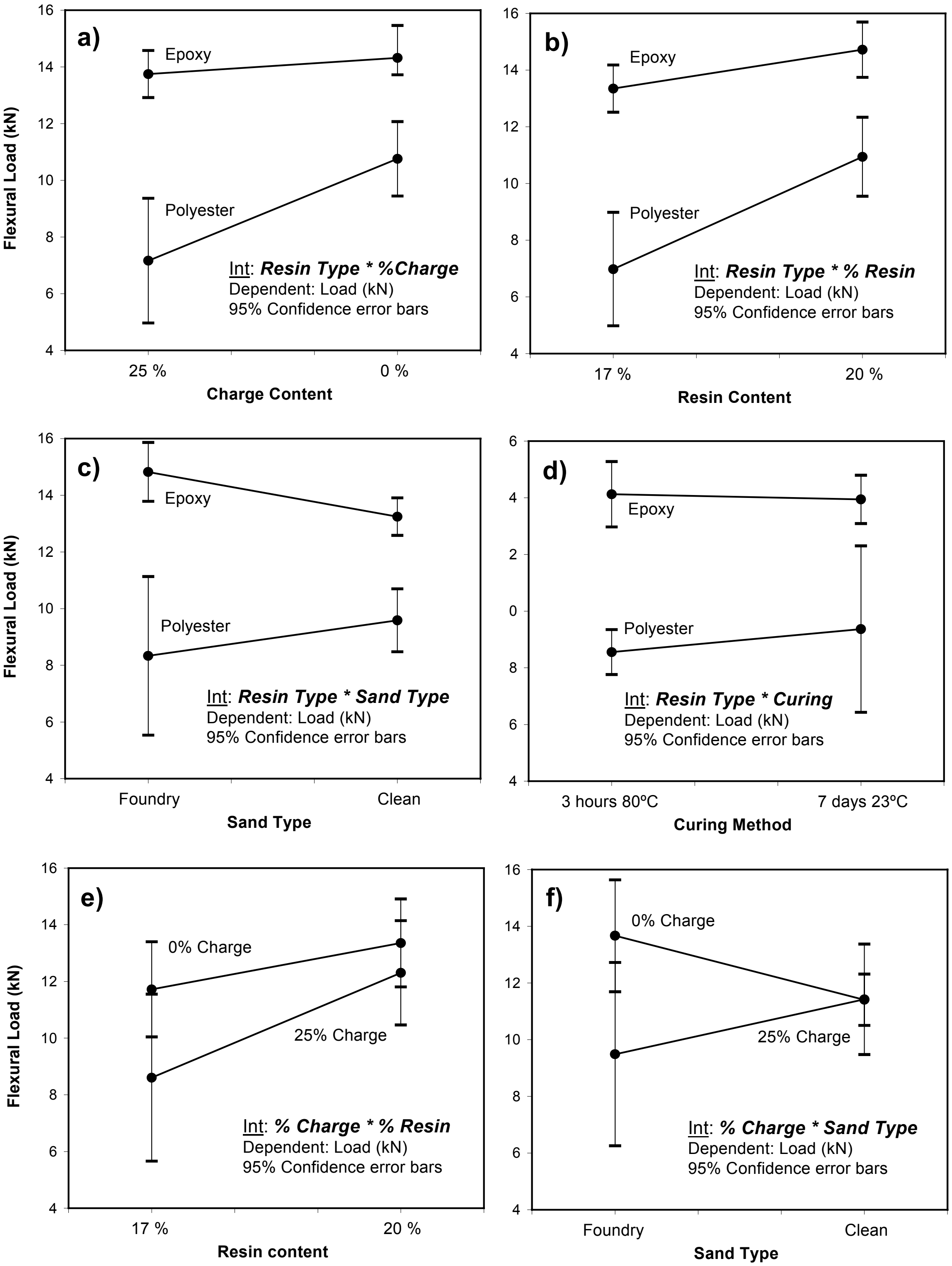


Fig. 3.11. Response graphics of interactions' effects: a) Resin Type*Charge Content; b) Resin Type*Resin Content; c) Resin Type*Sand Type; d) Resin Type*Curing Method; e) Charge Content*Resin Content and f) Charge Content*Sand Type.

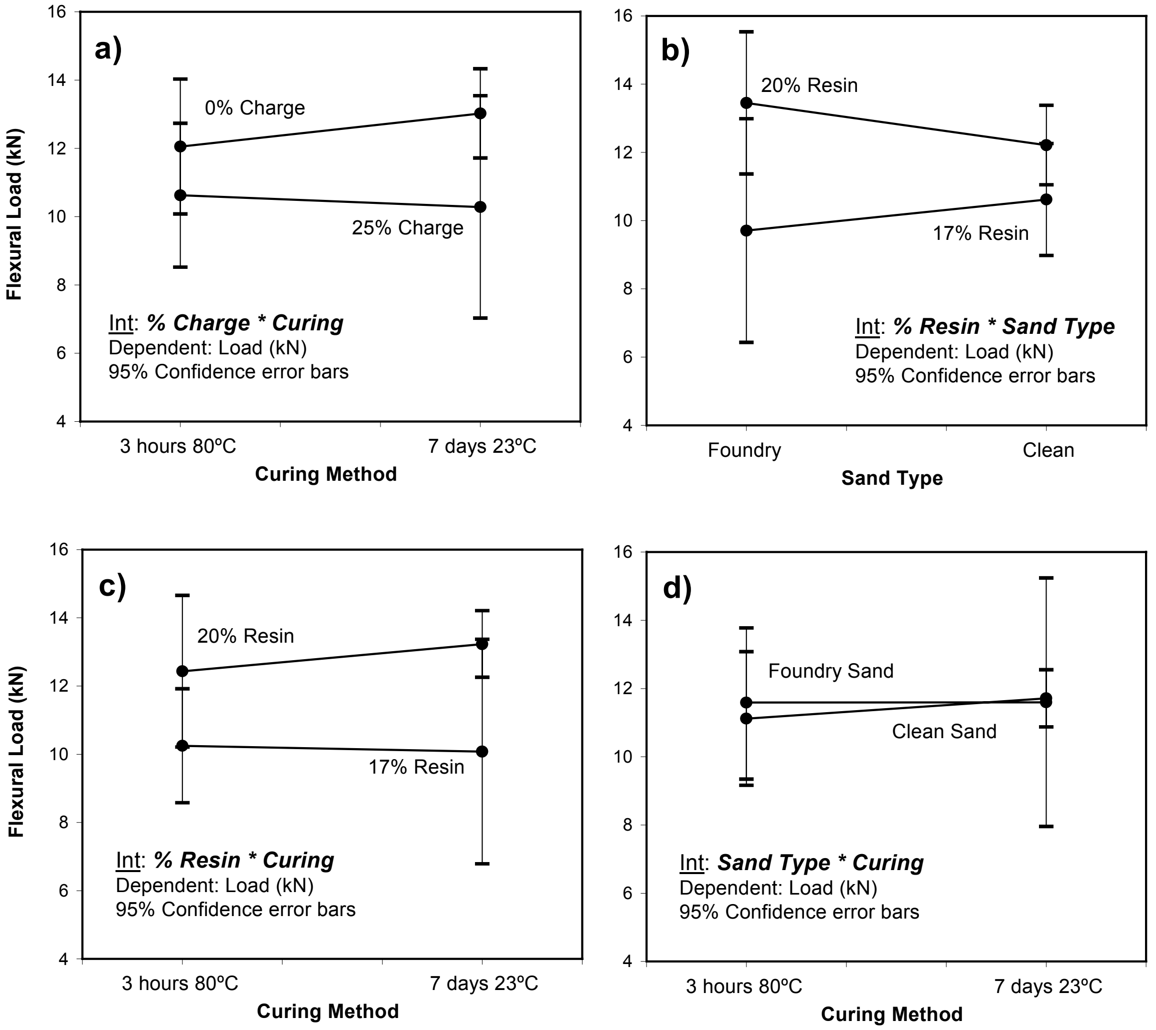


Fig. 3.12. Response graphics of interactions' effects: a) Charge Content*Curing Method; b) Resin Content*Sand Type; c) Resin Content*Curing Method and d) Sand Type*Curing Method.

3.3.3 Analysis of Variance –ANOVA-

The Taguchi method uses the analysis of variance ANOVA to analyse data obtained from the execution of the experimental planning. The analysis of variance ANOVA allows the analysis of the global variation in a set data or sample, identifying its origins and assessing the contribution of each variable or factor to the global dispersion (Guimarães and Cabral 1997). This statistical analysis revealed being a powerful tool, and it has been widely used as an efficient method for data treatment in many investigation fields, inclusively in the assessment of PC compounds (Gorninski et al. 2004).

3.3.3.1 Concept of analysis of variance

The basic concept of 'analysis of variance' is not a difficult one to grasp. Some basic understanding of regression analysis combined with computer statistical skills are important prerequisites to interpret the data for ANOVA, but the concept of the analysis itself is quite simple.

An ANOVA calculation is derived from a statistical calculation for significance based on a T or F-Statistic calculated from the regression formula based on the least squares fit. A relatively higher mean or average compared to the errors indicates a more precise system or group from which the data was derived. In an ANOVA analysis, the relationship between measurements of the mean and the variance or 'random error' of each group provides the information needed to determine if the difference between them is significant. When the statistical significance of the differences of means is assessed, then a more accurate comparison between groups can be made (Rehberg and Trochim 1996).

In order to better illustrate this concept of mean, variance, and analysis of variance, a part of a lecture given by Karl Popper could be useful (Popper 1972). Popper imagined that scientific measurement ran the continuum of measuring systems with precision ranging in randomness from clouds to clocks:

"…some natural phenomena, such as the weather, or the coming and going of clouds, are hard to predict: we speak of the *vagaries of the weather*. On the other hand, we speak of *clockwork precision* if we wish to describe a highly regular and predictable phenomenon. There are many things, natural processes and natural phenomena, which we may place between these two extremes, the clouds on the left and the clocks on the right. The changing seasons are somewhat unreliable clocks and may therefore be put somewhere towards the right, though not too far."

Karl Popper's discussion on clouds and clocks describes the fundamentals of ANOVA. At one end of the continuum are clouds. Clouds are associated with higher random error, with all of the imprecision associated with higher variance. In terms of clouds, they are systems with an average or mean, but far more variance. Clocks, on the other hand, are far more efficient systems, with much smaller measurements of random error. Clouds would have high errors associated with the mean. Clocks would have low errors associated with the mean and the difference between clouds and clocks is highly significant. However, in groups that are more alike than different, the ANOVA analysis provides a logical tool to assess the significance of the difference between those groups. Therefore, the analysis of variance becomes an important tool to understand the statistical differences between the averages of two or more different populations or samples. The differences are not so clear unless an ANOVA analysis is used to compare the averages and the errors for levels of significance.

3.3.3.2 Variance analysis results. Calculation process

The analysis of variance was performed for a significance level of 5%, or for a confidence level of 95%. Variance analysis results are shown in Table 3.18.

Table 3.18. ANOVA variance analysis.

Factors and Interactions	df*	Sum of Squares SS (N^2)	Mean Square MSD (N^2)	F-values	Contribution P (%)
Resin type	1	308848754.32	308848754.32	919.13	49.66
% of Charge	1	52092015.42	52092015.42	155.03	8.33
% of Resin	1	85382646.52	85382646.52	254.10	13.69
Sand type	1	314706.55	314706.55	0.94	0.00
Curing	1	1186241.50	1186241.50	3.53	0.14
Resin type * % of Charge	1	27367979.98	27367979.98	81.45	4.35
Resin type * % of Resin	1	20147315.13	20147315.13	59.96	3.19
Resin type * Sand type	1	24047207.40	24047207.40	71.56	3.82
Resin type * Curing	1	2954330.26	2954330.26	8.79	0.42
% of Charge * % of Resin	1	12723477.52	12723477.52	37.86	1.99
% of Charge * Sand type	1	52713912.21	52713912.21	156.88	8.43
% of Charge * Curing	1	5173855.17	5173855.17	15.40	0.78
% of Resin * Sand type	1	13817761.19	13817761.19	41.12	2.17
% of Resin * Curing	1	2805697.22	2805697.22	8.35	0.40
Sand type * Curing	1	920905.13	920905.13	2.74	0.09
Residual	32	10752703.10	336021.97		
Total	47	621249508.63			

* df – degrees of freedom.

In the calculation process of the parameters needed to the analysis of variance ANOVA the main steps described below were followed. All these calculus can be made by computational means, through available software such as 'Statgraphics' (Statistical Graphics Corporation 1988) or 'Analyse-it General Statistics' (Analyse-it Software Lda 1997)

i) Calculus of sum of squares (SS) of each column of Taguchi orthogonal array

The variations due to factors and/or interactions are characterized by the sum of squares deviations (differences from the mean), or more simply SS (third column of Table 3.18). The SS of a certain column gives the variation due to the factor or interaction represented by that column. The SS of a column correspondent to a factor X, with two levels, is given by the following expression:

$$SS_X = \sum_{i=1}^{2} n(x_i)\,(\overline{X}_i - \overline{T})^2 \qquad (3.6)$$

where $\overline{X}_i$ represents the average value of all responses involving factor X with level *i;* $n(x_i)$ represents the number of observations obeying to that condition; and $\overline{T}$ the average value of all responses or global average.

ii) Calculus of total variation (TSS)

The total variation is the total of sum of squares (last cell of third column of Table 3.18). The TSS can be calculated as follows:

$$TSS = \sum_{n=1}^{N} (y_n - \overline{T})^2 \qquad (3.7)$$

where N is the total number of responses or observations; and y_n is the nth observation.

iii) Calculus of variation due to random error (ESS)

The variation due to random error, sometimes called residual or error sum of squares, ESS, can be calculated indirectly as shown in expression 3.8, as the total variation (TSS) is equal to the sum of partial variations (factors, interactions and error). This value can be visualized in penultimate row of third column of Table 3.18.

$$ESS = TSS - SS_X - SS_Y - \ldots - SS_{XY} - \ldots \tag{3.8}$$

iv) Calculus of mean of squared deviations or variance's estimators (MSD)

The mean of squared deviations is derived from the sum of squared differences averaged over the degree of freedom correspondent to the factor, interaction or error, as shown by expressions 3.9 and 3.10.

$$MSD_X = \frac{SS_X}{df_X} \tag{3.9}$$

$$MSD_E = \frac{SSE}{df_E} \tag{3.10}$$

where df_X, df_E represents the number of freedom's degrees, respectively, of the factor X and the error.

In this particular case, the number of degrees of freedom (df's) of each factor or interaction is one, and the number of df's of the error is equal to the total number of df's (N-1, with N equal to the total number of observations (48)) minus the number of df's correspondent to all factors and interactions in study (15).

v) F-test of significance

The F-test statistic is a measure of variances, allowing the comparison between variances of several groups. For a certain chosen level of significance, the F-test allows verifying if the effects are significantly different from zero. The F-test statistic is calculated as the ratio between the mean of squares of the group (factor or interaction) and the mean of squares of the random error, as shown in expression 3.11. Just like for the T-test, critical F-value, F_{crit}, is found from a table giving the freedom's degrees, of the numerator and denominator, and the level of significance (Zady 1999).

$$F_{calc\ X} = \frac{MSD_X}{MSD_E} \tag{3.11}$$

If F_{calc} is greater than F_{crit}, then the null hypothesis is rejected which indicates that the effect or interaction is significant in statistical terms. If F_{calc} is less than F_{crit}, then the null hypothesis is accepted, which means that the groups are not significantly different, *i.e.*, the effect or interaction is not significant. The calculated F-values are shown in the fifth column of Table 3.18.

The value of 5% is commonly used in practice for the level of significance (α). It represents the probability of accepting an effect or interaction as significant, when the null hypothesis is being false reject (Type I error).

For the significance level of 5%, the tabulated F_{crit} value is 4.15 (Guimarães and Cabral 1997).

v) % Contribution (P)

The percentage of contribution indicates the relative influence of a factor and/or interaction on the global variation observed, and it is derived from the expected value of the variance due exclusively to that factor or interaction. The expected value for the variance of a factor includes a certain value associated to the error, which must be previously subtracted before the determination of the percentage of contribution, as shown by the following:

$$MSD''_X = MSD_X - MSD_E \Leftrightarrow SS''_X = SS_X - (MSD_E) \times df_X \tag{3.12}$$

$$P_X(\%) = \frac{SS''_X}{TSS} \times 100 \tag{3.13}$$

where MSD''_X, SS''_X are the mean of squared deviation and the sum of squares, respectively, of the factor X due exclusively to that factor.

3.4 Discussion of Results

3.4.1 Variance Analysis Results

From Table 3.18, it can be concluded that ‘resin type’ is the most influencing factor, followed by ‘resin content’ and ‘charge content’. The interaction between ‘charge content’ and ‘sand type’ also presents a significant contribution to global response.

▪ Resin type	49.66 %
▪ Resin content	13.69 %
▪ Charge content	8.33 %
▪ Interaction ‘Charge content * Sand type’	8.43 %

The remaining major factors and interactions have very small influence in the total variation. In particular, sand type and curing conditions factors, as well as the interaction involving these two factors, have been rejected for a significance level of 5%, as calculated F-values are less than 4.15, the critical F-value.

3.4.2 Analysis of Response Graphics

3.4.2.1 Principal effects

From the analysis of the response graphics of principal effects, it is clear that the bending strength is strongly increased with the use of epoxy resin instead of polyester resin. Response values of epoxy mortar formulations are not only higher, but also more reliable due to a smaller scatter found in the results (see graph *a)* of Fig. 3.10). Despite the higher mechanical strength of polyester resin, epoxy mortar formulations show better flexural performance than polyester based ones. Improved adhesion between aggregates and epoxy matrix could be the main reason for the observed behavior.

Global response is also increased, at a lower level, in all mortar formulations that present the highest resin content (20%) and/or the lowest charge content (0%), as shown respectively in graphs *c)* and *b)* of Fig. 3.10. The relative high specific surface of clean and foundry sands used in mix formulations, is probably the main factor responsible for this behavior.

Sand type and curing treatment, when considered alone, have no significant influence on bending strength, which can be confirmed by the small slope in corresponding response graphics (graphs *d)* and *e)* of Fig. 3.10).

3.4.2.2 Interactions' effects

Analyzing interaction effects response graphics, in Figs. 3.11 and 3.12, the following conclusions can be drawn by descending order of interaction significance (Ribeiro et al. 2003).

i) Interaction between 'Charge content' and 'Sand type' – 8.43 %

Foundry sand formulations are very sensitive to charge incorporation in resin matrix. The best mechanical results are obtained for 0% charge content. Clean sand based formulations are instead hardly affected by variation of charge content (the two average points are coincident – graph *f)* of Fig. 3.11).

The observed distinct behaviors can be explained by each sand particle's size distribution. Foundry sand, with rather fine grain size, has a larger specific surface, and therefore, it reacts poorly to the incorporation of more fine particles. Clean sand, with a smaller specific surface, requires less binder. Thus, mortar materials made from this kind of sand and 25 % of charge content, balance the lower effective resin content with a better void filling through the incorporation of calcium carbonate.

ii) Interaction between 'Resin type' and 'Charge content' – 4.35 %

Charge incorporation in polyester formulations has a rather negative influence in global response. This effect is not so pronounced when epoxy resin matrix is used. An average reduction of 4 % in bending strength of epoxy PM formulations occurs, when charged, against a 33 % reduction in the case of polyester based ones (graph *a)* of Fig. 3.11).

This phenomenon is probably explained by the lower wetting ability of polyester resin, which turns correspondent formulations more susceptible to the incorporation of filler.

Although the higher viscosity of epoxy resin, it was experimentally observed, that polyester resin presents a lower wetting ability than epoxy resin providing, as a result, a poorer workability of final mixture.

iii) Interaction between 'Resin type' and 'Sand type' – 3.82 %

Epoxy resin formulations present better bending behavior when manufactured with foundry sands. On the other hand, polyester based ones present better performance when incorporating clean sands (graph *c)* of Fig. 3.11).

Higher wetting ability of epoxy resins relatively to polyester resins, enabling the use of finer sands, also justifies these distinct preferences for sand type.

iv) Interaction between 'Resin type' and 'Resin content' – 3.14 %

Polyester formulations are more susceptible to resin content than epoxy formulations. An increase of 17 % to 20 % in resin content increases global response in about 56%, for mix formulations with polyester resin, against an increase in 10 % for those with epoxy resin (graph *b)* of Fig. 3.11).

Once more, the distinct wetting abilities of resins are in the basis of this different susceptibility to resin contents.

v) Interaction between 'Resin content' and 'Sand type' – 2.17 %

By incorporating higher resin content (20 %) better results are obtained when foundry sands are used, while when smaller content is used (17 %), better response is obtained with clean sands (graph *b)* of Fig. 3.12).

Lower resin contents require sands with lower specific surfaces, in order to reach an appropriate wetting of all aggregate material. However, if an excess of binder occurs, the glut resin tends to migrate to the surface reducing concrete mass homogeneity.

vi) Interaction between 'Charge content' and 'Resin content' – 1.99 %

Global response values increase much more with the resin content in samples with 25% charge than in those with 0% charge (graph *e)* of Fig. 3.11).

Charge incorporation, leading to an increase in the totally of particles' specific surface, turns mix formulations more susceptible to binder content than those without any charge.

vii) Other interactions - < 1.0 %

The remaining interactions, all of them involving the factor 'Curing treatment', have no significant influence on the global response. This can be confirmed by the almost perfect parallelism of the two straight lines of corresponding response graphics (graph *d)* of Fig. 3.12 and graphs *a)*, *c)* and *d)* of Fig. 3.12).

It must be pointed out that all considerations discussed here, were made, accepting the hypothesis that the effect of a factor or interaction on global response varies linearly between the two levels adopted by that factor (or those factors), which might not be completely correct. It would be necessary at least three variation levels to verify if the effect of a factor or interaction is linear or not.

3.4.3 Optimal Formulation

The analysis of variance and the analysis of principal effects allowed the definition of the most interesting levels for the three more influential factors on global response: *Resin type*, *Resin content* and *Charge content*.

It was found that flexural performance of polymer mortars is significantly improved with the use of epoxy resin, with a level content of 20%, and without incorporation of charge. This means that mechanical behavior of polymer mortar formulations is improved by using these factors' levels in detriment of the other ones also in study.

The analysis of interactions' effects, not only confirms the last conclusions, but also allows the determination of the preferable levels for the two remain missing factors: *Sand type* and *Curing treatment*.

With basis on response graphics of the interactions *'Charge content * Sand type'*, *'Resin type * Sand type'* and *'Resin content * Sand type'*, foundry sand was chosen for *Sand type* level, as this type of sand, jointly with 20% of epoxy resin content without charge, conducted to better results than clean sand.

Taking into account the analysis made to the response graphics of principal effect and interactions concerning *Curing treatment*, the choice for one of the two possible levels adopted by this factor has no relevant consequences on flexural strength of resultant formulation. It was concluded that seven days cure, at room temperature, has the same effect than three hours cure, at 80ºC.

The optimal formulation, corresponding to the best combination of factors' levels that leads to a PM with improved flexural strength, was finally determined. It is composed by:

- Epoxy *Resin type;*
- 20% (in mass) of *Resin content*;
- 0% of *Charge content*;
- Foundry *Sand type*;
- and submitted to *Curing treatment*: seven days at room temperature or three hours at 80ºC.

This particular mix formulation was actually tested. It corresponds to mortar formulation nº 12, which presented an average bending strength of 38 MPa (Table 3.16 and Fig. 3.8). Thus, there is no need to predict the bending strength of mortar formulation corresponding to the optimal formulation by the Taguchi method, neither to perform the advised confirmation test. However, in order to compare experimental bending strength value with that one that would be predicted by Taguchi method, the following prevision formula can be used:

$$R_{PRED} = \overline{T} + (\overline{A}_2 - \overline{T}) + (\overline{B}_1 - \overline{T}) + (\overline{C}_2 - \overline{T}) + \left[(\overline{BD}_{12} - \overline{T}) - (\overline{B}_1 - \overline{T}) - (\overline{D}_2 - \overline{T})\right] \quad (3.14)$$

$$R_{PRED} = 17.53 \text{ kN}$$

where R_{PRED} is the predicted failure load given by Taguchi method; $\overline{T}$ is the global average of all observations; $\overline{A}_2$, $\overline{B}_1$, $\overline{C}_2$ are the average values corresponding to responses involving the most influencing factors on bending resistance (*Resin type*, *Charge content* and *Resin content*, respectively), with the levels that improved that characteristic; and $\overline{BD}_{12}$ is the average value corresponding to responses involving simultaneously the factors *Charge content* and *Sand type* with the levels that lead the highest value for that significant interaction. This prevision formula is derived from the global average of results plus the contribution of the effects of each significant factor (or interaction) for the optimum level.

The average failure load predicted by Taguchi technique,17.53 kN, overestimates only in 6% the value obtained experimentally (16.52 kN). Thus, a quite good reproducibility was obtained as the effects of significant factors were enabled to be replicated.

Although presenting the best flexural performance, PM formulation nº12 is not the most desirable one in economical terms, taking into account the higher cost of epoxy resin (7.5 €/kg against 1.75 €/kg of polyester resin) and resin content involved. The best price/performance relationship was presented by combination nº4. It is similar to nº12, but with polyester resin instead of epoxy resin. This formulation is almost five times cheaper, and its bending strength is only 17% smaller than the optimal combination.

A compromise solution must be sought according the specifications required by material's specific application.

The ideal would be to go on with the optimization process in order to refine and accurate optimal formulation. To repeat Taguchi experimental program with fewer factors, but considering intermediate levels each one, would be advised. For instance, the second experimental program could be performed eliminating the factors with minor relevance, such as *Curing treatment* and *Sand type*, and considering an intermediate level for the other factors (*e.g.*: another type of resin, 18.5% of resin content and 12.5% of charge content).

However, attending to thesis schedule limitations, it was decided not to go beyond the obtained results, accepting them as quite satisfactory for the intended purpose.

3.5 Conclusions

The first objective of this thesis work was to develop and to optimize a polymer concrete material suitable either for the precast of structural members, either as a matrix of a lightweight structural concrete.

For that purpose, a number of mortar mix formulations, with different combinations of material factors and curing treatments, were manufactured and tested in bending. Load-displacement curves and failure loads were recorded.

In order to reduce the total number of formulations to be tested, an experimental planning was achieved through a Taguchi methodology. The influence of material factors and their interactions on flexural strength of polymer mortar materials was assessed. A variance analysis – ANOVA - was used for data analysis.

Taking into account the material factors and levels considered in this study, the following conclusions can be drawn:

- The most decisive factor for bending strength of PM formulations is the resin type, followed by resin content and charge content;
- Curing cycle has not significant influence on PM final characteristics. Seven days cure, at room temperature, has the same effect than three hours cure, at 80ºC.
- The analysis of principal effects and their interactions allowed establishing the most desirable levels for each factor.

  The optimal combination, corresponding to the most flexural resistant PM was found. It is composed by:

  - 20 % (in mass) epoxy resin;
  - 0 % charge;
  - 80 % foundry sand.

  The combination that leads to the best relationship between cost and flexural performance was also acceded. It is formed by:

  - 20 % (in mass) polyester resin;

- 0 % charge;
- 80 % foundry sand.

The obtained results of optimization process show that the Taguchi method and the analysis of variance ANOVA can be applied, with success, to polymer concrete materials' design.

The two optimized PM formulations were chosen as basis for sustaining the further objectives of present thesis. Both PM formulations will be submitted to an exhaustive characterization process, as described in chapters IV, V and VI, and their potential applications as construction materials, will be discussed and analyzed in the published papers presented in Appendixes A and B.

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IV. PHYSICAL AND STATIC MECHANICAL PROPERTIES OF PM FORMULATIONS

4.1 Introduction

Unlike conventional Portland cement concrete, there is not much information on the variability of properties in PC materials, especially on the variability of mechanical strengths (Mebarkia 1993). However, statistical information on PC and PM properties is a very important issue in the decision process of the minimum number of tests required to assure reproducibility.

As for traditional concrete, variation in properties for PC materials may be due to any of the following parameters:

- Variation in basic properties of the individual constituents (aggregates, polymers, catalyst system, and eventual additives);
- Variations in the environment conditions (temperature and moisture);
- Variation due to production techniques applied (mixing and casting procedures, compaction effort, and curing processes) (San José et al. 2002).
- And variation due to improper or inadequate testing methods, which may cause apparent or mistaken differences in PC properties (Richardson 1991).

In particular, strength test results may be specially affected by variation in the test parameters such as specimen geometry, specimen size, preparation of end surfaces, rigidity of testing equipment, and rate of application of stress. For this reason, testing should follow a single standard, with no departure from prescribed procedures.

4.1.1 Variability of Strength Properties

The strength of a brittle material such as concrete and PC cannot be described by an only average value: an indication of the variability of strength must be given, as well as information about the size and shape of the specimens. Whatever the test, the test results have to be interpreted in statistical terms. For instance, the mere fact that some test result is larger than some other result does not necessarily mean that the difference is 'significant' and not, instead, a chance consequence of the natural variability of values from the same source.

The variability in strength can be assessed by the standard deviation (SD). For a given mean strength, the SD characterizes fully the distribution (assumed to be of the normal type), as scattering data about the mean is a fixed function of SD. This is defined as the root-mean square deviation, *i.e.*

$$\mathrm{SD} = [\ \textstyle\sum (x-\mu)^2 / n\ ]^{\frac{1}{2}} \qquad (4.1)$$

where x represents the values of strength of all n specimens and μ is the arithmetic mean of these strengths. In practice, a limited number of specimens are computed, and their mean, the sample mean, is the estimation of the true population mean. In these cases, in the denominator of the expression, (n-1) is put, instead of n (Bessel´s correction).

Sometimes, it is convenient to express the scatter of results on a percentage basis. Hence, the coefficient of variation, COV ($\mathrm{COV} = \mathrm{SD}/\mu \times 100$), may be used for that purpose.

SD can also be used to determine the required average of strength that will provide the specified strength of the concrete, at a certain confidence level (Neville 1995).

4.1.2 Research Objective

In this chapter, the main physical and static mechanical properties of PM formulations are analyzed. Fresh state properties, setting behavior, specific weight, coefficient of thermal expansion, static compressive, bending and splitting-tensile strengths, deformation characteristics, and stress-strain relationships were determined and analyzed.

An effort was made in order to select the most adequate testing methods, regarding each property, so that reliable and comparable results could be obtained. The usual applied test methods were reviewed and discussed.

A special care was taken in maintaining both the production procedures, for all batches produced, and the environment conditions, during manufacturing and testing, in order to minimize induced variability on results.

Statistical variations of some of the analyzed properties were also investigated.

4.2 Physical Properties

4.2.1 Fresh State Properties: Workability, Consistency and Working Life

Although fresh concrete is only of transient interest, it should be noted that the strength of a particular concrete formulation is very seriously affected by the degree of its compaction. It is vital, therefore, that the consistency of the mix be such that the concrete mass can be placed, compacted and finished sufficiently easily and without segregation. This is particularly crucial in the case of PC formulations, where mixture workability and consistency are considerably time-dependent, and thus, the available time for a proper placement, compaction and finishing is significantly reduced. Therefore, working life of PC mixtures is also a physical characteristic of paramount importance in process technology of PC materials.

4.2.1.1 Definitions and usual test methods

i) Workability and consistency

Technical literature abounds with variations of definitions of workability and consistency but they are all qualitative in nature and they further reflect a personal viewpoint rather than a precise scientific meaning (Bartos 1992; Neville 1995).

The ASTM C 125 (2006) defines workability, in a qualitative manner, as the '*property determining the effort required to manipulate a freshly mixed quality of concrete with minimum loss of homogeneity*'. The ACI definition of *workability* is: '*that property of freshly mixed concrete or mortar which determines the ease and homogeneity with which it can be mixed, placed, consolidated and finished*' (ACI 116R-90). In the same reference, the definition of consistency is given as '*the relative mobility or ability of freshly mixed concrete or mortar to flow*', which is measured by slump. These terms have indeed specific meaning, but only under a set of certain circumstances and they can hardly be used as an objective and quantifiable description of a concrete mix.

There is no acceptable test which will measure directly the workability as given by any of the above definitions. Several attempts have been made to correlate workability with some easily determinable physical measurement, but none of them may be considered as fully satisfactory. However, they may provide useful information, in comparative terms, within a range of variation in workability.

Among the several methods developed to determine workability, the tests that measure the slump and the flow of concrete mixes, the penetration depth, the Vebe time and the compaction factor are the most widely used. However, it should be noted that no comparison is really possible between these different test methods as each one measures the behavior of freshly concrete under different test conditions. In addition, the particular use of each test depends upon of workability level of the given concrete mixture: while Vebe and compaction factor tests are more appropriate for low to medium workability mixes, slump and flow tests are more adequate for concrete mixtures with medium to very high workabilities (BS 1881-102; BS 1881-103; BS 1881-104; BS 1881-105).

In the investigation works carried out by Ohama et al. (1986; 1979), it was found that the workability and consistency of fresh polyester PC materials are remarkably affected by the binder content rather than the binder viscosity, regardless of the type of polyester resin binder. The same studies revealed that to determine workability and consistency of polyester PCs, the slump and flow tests are more adequate in the case of high binder contents, and the penetration test at low binder contents.

It is believed that above considerations are also generally applied to PC mixtures with other binders than polyester resins. Therefore, taking into account the relative high polymer content of epoxy and polyester mix formulations, the slump and flow tests were selected in the present study to assess workability and consistency of developed PM formulations.

ii) Working life

Working life of PC mixtures determines the available time for a proper mixing, placement, compaction and finishing of fresh PC materials. It can be defined as the elapsing time between adding the catalytic system to the liquid resin and the moment at which the mixture is no more workable. This moment is determined by different criteria according to the test method applied.

The working life of PC mixtures is very variable and it is affected by different factors, namely the pot-life of polymer binder, the polymer content, and the amount and type of catalytic system. For the same formulation, working life is also considerably affected by environmental conditions and total amount of concrete mass. Therefore, all test methods usually applied for determining working life of fresh PC mixtures define the environment conditions at which the test should be conducted (usually at temperature of 20±2ºC and a relative humidity of 70% or below), and the total amount of mixture that should be used for such determination.

Different criteria are used for determining the moment at which the fresh mixture is considered no more workable, depending upon the test method applied: the penetration resistance method, the pull-out method or the finger-touching method.

In the investigation work carried out by Ohama et al. (1981) concerning the working life of different formulations of polyester resin concretes, it was concluded that both the penetration resistance and the finger-touching tests are effective methods for determining the working life of fresh PC mixtures with a wide range of working life, consistency and mix proportions. It was also found that the reproducibility of the working life data by the tests is successfully obtained.

Attending to the above and taking into account that the finger-touching method does not require any special device, in the present study, this test method, as the simplest one, was chosen for determining the working life of PM formulations.

4.2.1.2 Experimental procedures and results

i) Workability and consistency

Workability and consistency of PM formulations were determined according to RILEM recommendation ‘Method of test for slump and flow of fresh polymer concrete and mortar’ (1995a). The tests were conducted in the laboratory maintained at a temperature of 20 ± 2ºC and a relative humidity of 65%. For each PM formulation, the slump and the flow were determined for two samples proceeding from different batches.

A steel cone with a top inside diameter of 50 mm, a base inside diameter of 100 mm and a height of 150 mm was used for the slump tests according to the specification. The cone, with the inside surfaces properly coated with release agent, was placed on a flat steel plate and then filled with the polymer mortar mass in two layers. Each layer was stroked 15 times with a standard tamping rod (straight steel rod with a diameter of 9 mm and a length of 300 mm, having the tamping end rounded to a hemispheric tip). After the top layer has been struck off, the cone was removed by raising it carefully in a vertical direction. All these operations were done within the maximum period of 3 minutes.

After cone removal, the slump was immediately measured by determining the vertical difference between the top of the cone and the displaced original center of the top surface of the PM. The flow was measured by determining the diameter, after the mortar has spread out, in the direction with larger diameter and in the direction at right angles to the former. The average value of these measures was taken as the flow of PM.

In all slump tests performed, a true slump (*i.e.* slumping evenly all round) was rather observed than a shear slump, and therefore they all were considered valid.

Obtained slump and flow test results are presented in Table 4.1 and, in Fig. 4.1, typical slump shapes of epoxy and polyester PM formulations are illustrated.

Table 4.1. Slump and flow test results of PM formulations (average of two samples).

PM Formulation		Slump Test		Flow Test	
Epoxy PM	Batch 1	55 mm	56 mm	126 mm	128 mm
	Batch 2	57 mm		129 mm	
Polyester PM	Batch 1	53 mm	52 mm	126 mm	125 mm
	Batch 2	50 mm		124 mm	

Fig. 4.1. Slump and flow tests of PM formulations: Cone removal (left) and typical slump shapes of epoxy and polyester PM formulations (center and right, respectively).

ii) Working life

Working life of PM formulations was determined by finger-touching test method, according to RILEM recommendation 'Determining methods for working life of fresh polymer concrete and mortar' (1995b). The tests were conducted in the laboratory maintained at a temperature of 20 ± 2ºC and a relative humidity of 60%. For each PM formulation, the working life was determined for two samples proceeding from the same batch.

Samples of fresh PMs of about 200 ml were packed and sealed in polyethylene film bags, and then the sense of touching through polyethylene film on them was inspected. Total time elapsing from adding the catalyst to polyester resin, or the hardener to epoxy resin, to the moment when a stiff feeling was felt for the first time was reported as working life. Obtained results, for both PM formulations are presented in Table 4.2.

Table 4.2. Working life of PM formulations (average of two samples).

PM Formulation		Working Life by Finger Touching Method	
Epoxy PM	Sample 1	42 min	42 min
	Sample 2	42 min	
Polyester PM	Sample 1	17 min	18 min
	Sample 2	18 min	

4.2.2 Setting Shrinkage

Setting shrinkage in PC materials can be quite large when compared to ordinary cement concretes. This undesirable feature is one of the most serious problems facing their precast and cast-in-place applications as large setting shrinkages may result in short-term troubles such as exfoliation, cracks and poor dimensional stability. Therefore, the examination of length change of resin mortar and concretes during setting bears considerable significance.

Shrinkage in PC materials occurs, basically, during the first hours due to polymerization process and it is generated by means of the interbreeding between polymer chains, which results on a volume lower than the initial one.

Generally, length change of PCs and PMs occurs in two different phases. In the first phase, at the start of polymerization (within the first 3-5 hours), a small expansion of PC takes place due to the exothermic nature of polymerization process. The initial opening of the bonds, which takes place along the crossing of polymeric chains, generates the heat that causes PC expansion as the incorporation of aggregates does not damper the exothermic process, which is associated with the polymeric reaction. After the exothermic peak has been reached, this effect quickly disappears due to crosslink process that shortens the distances between the long polymeric chains, leading to a general and steady reduction of material volume. In this stage, shrinkage process goes on until all polymeric reactions have been attained, converging to stable values after 24 hours after casting.

For the same matrix binder, final shrinkage of PC materials is significantly affected by resin content, catalyst and accelerator contents, environment temperature, and total amount of mass per batch. At higher catalyst and accelerator contents, the shrinkage increases through the curing time and the length change becomes nearly constant at an early curing time. Higher values of the later parameters also lead to increasing values of setting shrinkage on the final product (Letsch 1991; Ohama and Komiyama 1979).

4.2.2.1 Usual test methods for setting shrinkage of PC materials

At present, there is a lack of standards for setting shrinkage of PC materials, which led to the development of various internal methods by several researchers in the field, in order to fill this gap. Various techniques for measuring and monitoring the setting shrinkage of PCs and PMs have been proposed such as the use of many kinds of contact-type displacement meters, the use of mold gauges, and, more recently, the use of non contact-type measuring devices based on optical methods (Cano et al. 1998; Letsch 1991; Moriyoshi et al. 1997).

In the contact-type displacement meter method, resilience of its built-in spring can adversely affect the measurements. On the other hand, measuring process by mould gauges is unable to measure the strain of PC mass in its early stage of setting, when no adherence has yet been developed between the fresh material and the strain gauge.

The optical method based devices, as non-intrusive methods that do not confer any resistance to shrinkage deformations, seem to be the most satisfactory ones. This type of measuring systems consist of a mould with a bottom plate and side plates, lined with a Teflon sheet for reducing friction against the fresh PC material, an aluminum L-shaped end plates for measuring displacement, and a laser beam displacement meter. The bottom and side plates are assembled in advance and the L-shaped end plates are installed at both ends of the assembly to allow the contact to move freely, according to the expansion or shrinkage of the specimen. After the placing of the fresh material, displacement is measured with the laser beam displacement meter at given intervals. Some of these devices are further complemented with thermocouples and load cells that allow monitoring, respectively, temperature and internal stresses developed during setting.

Unfortunately, at the time, none of above measuring devices was available at INEGI lab. Therefore, alternatives methods were attempted in order to monitoring the setting shrinkage of PM formulations.

4.2.2.2 Applied test methods for setting shrinkage of PM formulations

In order to continuous monitoring setting shrinkage of PM formulations during the first hours, a first attempt was made using Fibre Bragg Grating (FBG) sensors embedded into PM specimens during casting.

FBG sensors system is a sensitive technique for health monitoring of structures with wide application in the field of Civil Engineering. This technique has a great potential as it gives in-real time data evaluation of measurements such as strains and temperature. The fabrication process of FBG sensors is based on the photosensitive mechanism, which is observed in Ge-doped optical fibres (Hill et al. 1993). If broadband light is traveling through an optical fibre containing such periodic structure, its diffractive properties promote that only a very narrow wavelength band is reflected back. The FBG resonance wavelength will vary accordingly with temperature or strain changes experienced by the fibre. Therefore, FBG sensor systems are enable to measure the internal strain state of a material into which they are embedded without influencing the stress of the specimen. Moreover, the dimensions of the optical fibres are very small so the sensors can be embedded in fresh concrete material during casting without damaging the host material, they can survive into the fresh material without any protective jacket, and they are immune to the influence of electromagnetic fields. An optical system apparatus connected by cables to the optical fibre can provide the in-real time monitoring of internal strains.

There are several successful FBG sensor related applications concerning traditional portland cement concrete structures (Shultz et al. 2001), but until now, no works have been done regarding their application in PC materials. This first experience, however, did not work out as well as it was expected. Some problems occurred related to both fibre embedding process and data acquisition system, which did not allow reliable readings. In spite of this, some qualitative information was obtained regarding the volumetric changes suffered by epoxy PMs during setting. More information related with this experience can be found in Novo et al. (Novo et al. 2005).

Attending to the failing of the above experience, in the present work, only the final shrinkage of PMs was determined. For that purpose, a conventional digital caliper was used for measuring length change of PM specimens 24 hours after casting. The accuracy of the method is not the most desirable one but it provides an estimate of the range of values of setting shrinkage that will be expected for these materials.

4.2.2.3 Experimental procedures and results

i) Continuous monitoring of setting shrinkage by FBG sensors

This attempt of monitoring setting shrinkage of PMs by embedded FBG sensors was only performed for epoxy PM formulation.

One single prismatic specimen with cross section of 30×10 mm^2 and 150 mm length was used in this study. A low thickness specimen allows the reduction of the effect of the variation of polymerization rate, as this parameter varies throughout the thickness of the specimen. Specimen dimensions were achieved by introducing a second silicon rubber mould in one of the steel cavities of the steel moulds usually applied for casting standard PM specimens (40×40×160 mm^3).

Immediately after specimen casting, a FBG sensor was embedded into the fresh PM specimen at 1 mm depth and a pre-tension was applied to keep it well aligned as shown in Fig. 4.2.

The optical fibre used in this study was a single mode fibre with an acrylate coating (SMF 28-Corning), with a fibre diameter of 250 μm and a 10 mm length Bragg grating (attenuation for 1550 nm: < 0.22 dB/km). In previous works, the results of strain and temperature measured by this type of optical fibres were validated by comparison with thermocouples and conventional strain gauges whose behavior is well known (Costa et al. 2003). The embedded optical fibre was extended by welding an optical cable that was connected to the optical system.

The optical system used for in-time real monitoring consisted of an erbium broadband source (Photonetics FIBREWHITE) to illuminate the FBG sensors, an optical spectrum analyzer (ANDO AQ6330) to view the Bragg wavelengths shifts, and a computer with data acquisition system (LabView®) for flexibility in data display, processing and storage of all information observed.

Strain variation of epoxy PM specimen during setting was monitored during 15 hours in a controlled environment. The obtained spectrum can be observed in Fig. 4.2. This curve is the result of volumetric variations of epoxy PM specimen during setting.

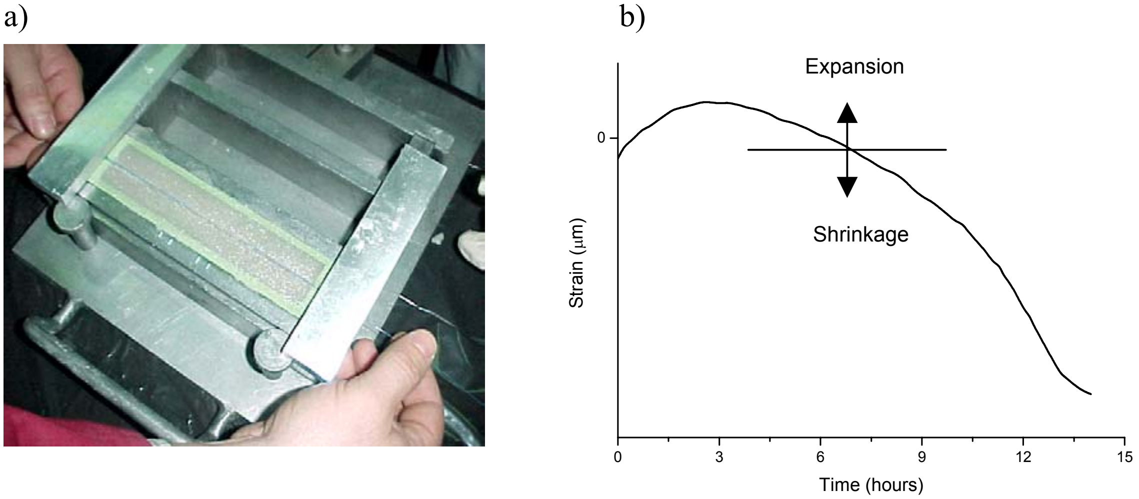

Fig. 4.2. a) Embedding process of optical fibre; b) Strain variation of epoxy PM specimen during setting.

Due to some troubles arisen from fibre embedding process, no reliable absolute strain values were obtained, therefore, strain variation as function of time is presented without strain scale. In spite of this incident, some useful information was achieved, concerning volumetric and thermal behavior of epoxy PMs during setting period, resumed in the following:

- During curing period, epoxy PM formulation reaches its exothermic peak within the range of 2.5 to 3 hours after mixing/casting process;
- Expansion phenomenon occurs within the first 3 hours, having its maximum value been estimated about 15% of the total value of shrinkage (obtained after 15 hours).
- After the first 3 hours, shrinkage process assumes higher significance, presenting positive values 6 hours after mixing.
- Shrinkage rate rises between the first 8 to 12 hours and tends to decrease after this period. Based on previous studies carried out by other researchers (Moriyoshi et al. 1997; San José 1996), it is reasonable to presume that shrinkage rate of epoxy PM would follow the same trend, decreasing progressively with time until a stable shrinkage value has been reached.

Experimental results illustrated the potential of the FBG sensors system for monitoring curing process of PC materials. Several issues, however, need further investigation in order to obtain reliable readings. In particular, the process to keep the optical fibre well aligned and under stress during polymerization must to be improved in order to avoid buckling due to PC expansion and shrinkage, as ill placement of the fibre leads to erroneous reading's interpretation.

Fibre Bragg Grating sensors are a new sensitive technique and their interaction with different materials such as PC materials must be studied and well understood before quality data can be obtained.

ii) Final setting shrinkage

Taking into account the impossibility to determine the absolute values of setting shrinkage of PM formulations, with basis on the results of the first experience, the basic method of measuring length variation by means of a digital caliper was applied.

Two PM specimens of each formulation, with square section of 20×20 mm^2 and 100 mm length, were casted in order to determine final setting shrinkage. A special silicone mould with two cavities was used for that purpose, as shown in Fig.4.3. The precise dimensions of these cavities, inside which PM specimens were casted, were known by means of the models used to produce the silicone mould.

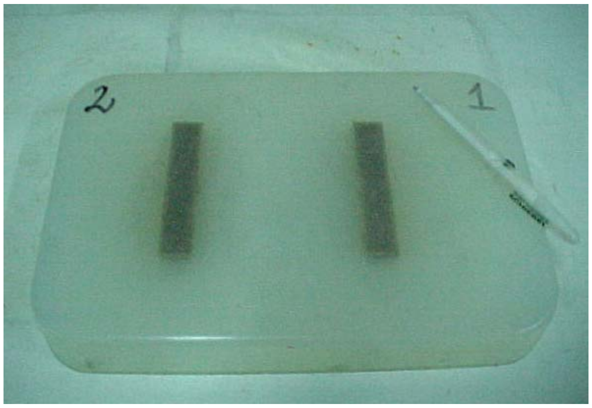

Fig. 4.3. Polyester PM specimens used for determination of final setting shrinkage.

The temperature (23ºC) and the relative humidity (60%) were maintained as constant as possible throughout all the steps of experimental work: mixing process, casting and setting period. One day (24 hours) after casting, the specimens were removed from the mould and their lengths were measured by means of a caliper to the nearest 0.01 mm. Relative variation lengths of both types of PM specimens, computed as final setting shrinkage of PMs at 24 hours, are presented in Table 4.3.

Table 4.3. Final setting shrinkage of PM formulations (average of two specimens).

PM Formulation		Final setting shrinkage (24 hours)	
Epoxy PM	Specimen 1	1.99 ‰	2.24 ‰
	Specimen 2	2.49 ‰	
Polyester PM	Specimen 1	5.49 ‰	5.99 ‰
	Specimen 2	6.49 ‰	

As it was expected, shrinkage value of polyester PM formulation is higher than epoxy based one and much higher than traditional cement concrete (0.35 ‰). For both formulations, obtained results are within the common range of values usually found for epoxy and polyester PMs with 20% of resin content (Letsch 1991; San José 1996).

4.2.3 Specific Gravity and Air Content

PC materials made with natural aggregate originating from hard rock have a density within a relative narrow range because the specific gravity of most rocks varies little. Further, the densities of common resins usually applied as matrix binders are very similar, which also contribute for the relative similarity of density values commonly found for these materials.

Although the volumetric content of the binder in the mix has a greater influence on the specific weight of this concrete material than in the case of conventional one, this feature too is not a major factor. Mixing and casting processes are the main contributing factors for the variability of densities on PC materials as different procedures lead to different air content entrainments. Thus, PC elements made according to the same formulation can attain different densities as function of mixing technique applied and compaction procedure.

4.2.3.1 Calculation procedure

Specific gravity and air content of epoxy and polyester PM formulations were determined with basis on RILEM specification PCM-4 (1995g). This recommendation covers the method of test for determining the unit weight and air content of freshly mixed polymer-modified mortars. Calculation procedures were adapted in order to determine the mentioned parameters for hardened PM formulations, taking advantage of the great number of both epoxy and polyester prismatic PM specimens produced during the experimental work of this thesis.

The unit weight (W) of each PM specimen, in kg/dm^3, was calculated according to the following equation:

$$W = W_1 / V \tag{4.2}$$

where W_1 and V are, respectively, the mass (kg) and the volume (dm^3) of PM specimens.

Accordingly, the air content (A) in percentage of each PM specimen was calculated from the following equations:

$$A = [\ (T-W) / T\ ] \times 100 \tag{4.3}$$

with

$$T = (W_b + W_a) / [(W_b / \rho_b) + (W_a / \rho_a)] \qquad (4.4)$$

where

- T is the unit weight of PM specimens calculated on an air-free basis (kg/dm^3);
- W is the unit weight of each PM specimen as given by equation (4.2);
- W_b, ρ_b are, respectively, the mass per batch (kg) and the specific gravity of resin binder (kg/dm^3);

and - W_a, ρ_a are, respectively, the mass per batch (kg) and the specific gravity of foundry sand (kg/dm^3).

4.2.3.2 Obtained results

Average results and correspondent standard deviation for specific gravity and air content of each PM formulation are presented in Table 4.4. Presented values correspondent to the average of several epoxy and polyester PM specimens of different batches, whose weights and volumes were measured throughout the experimental work of this thesis.

Table 4.4. Specific gravity and air content of PM formulations. Average results and correspondent standard deviations referred to 41 specimens.

PM Formulation	Specific gravity (Average ∣ St. Deviation) [kg/dm^3]	Air content (Average ∣ St. Deviation) [%]
Epoxy PM	1.799 ∣ 0.021	15.21 ∣ 0.98
Polyester PM	1.882 ∣ 0.022	8.33 ∣ 1.10

According to ACI 213R-87, both PM formulations can be classified into the category of structural lightweight concrete materials, as their densities are lower than 1.9 kg/dm^3 and their compressive strengths are higher than 17 MPa (ACI 1994).

Although the lower density of polyester resin (0.1 point less than epoxy system), polyester based mortars present higher density than epoxy based one. The high value of air content present on epoxy PMs, almost twice of polyester PM, is surely the responsible factor for this feature. The unexpected high content of accidental entrained air into epoxy PM formulation is probably due to the mixing process of both components of the resin system. Although the low viscosity of the hardener component (350 mPa.s), the epoxy resin base is very viscous (600 mPa.s), making hard the mixing process. The required thorough hand mix of the two components leads to the entrainment of a considerable amount of small air bubbles into resin system, which are hardly released during mixing and casting processes.

The higher values found for slump and flow of epoxy PM formulation, in spite of the higher viscosity of its resin binder, are certainly due to this great amount of air content, which has a considerable effect on workability and consistency of concrete mixes.

Air content of polyester PM formulation is within the range of values commonly found for polyester mortars (with similar resin contents), mixed in batch mixers without vacuum support, and casted without special compaction or vibration system devices (Gálan 2001).

4.2.4 Coefficient of Thermal Expansion

Coefficients of thermal expansion (CTE) are widely used for design purposes and to determine if failure by thermal stresses may occur when a solid body, composed of two different materials, is subjected to temperature variations.

Like most engineering materials, PC has a positive CTE but its value depends essentially on the composition of the mix. The influence of the mix arises from the fact that the two main constituents of PC, polymer binder and aggregate, have dissimilar thermal coefficients, and the coefficient of PC is a resultant of the two values. The linear coefficient of thermal expansion of polymers varies within a wide range of values, between 20 and 150 $\times 10^{-6}$ per ºC (Crawford 1990), and is higher than the coefficient of the aggregate, which varies, for the more common parent rocks, between 5×10^{-6} and 13×10^{-6} per ºC. As a result, depending upon PC formulation, the common range of values for the coefficient of thermal expansion of these materials is between 20×10^{-6} and 40×10^{-6} per ºC (for temperatures ranges between 10ºC and 40ºC).

As stated earlier, PC materials are often used to repair Portland cement concrete structures. From the previous chapter, it is already known, that PCs have in general higher coefficient of thermal expansion than Portland cement concretes as polymers have higher thermal coefficients than hydrated cement paste. In addition, the variation of thermal expansion of polymeric materials within the common temperature ranges is higher than that one that occurs for hydraulic concretes. Therefore, thermal behavior analysis of these repair materials, in terms of thermal expansion, is of crucial importance.

4.2.4.1 Usual test methods for CTE of PC materials

Different test methods, based on different standards, are being used to determine the linear coefficients of thermal expansion of PC materials, and it seems there is no consensus between them (ASTM:C:351 2000; ASTM:E:228 1989; RILEM 1995e). Applied procedure to measure length change, the specimen geometry and analyzed temperature range are the main discussion subjects.

The test method described on ASTM norm E 228, covers the determination of linear thermal expansion of solid materials over the temperature range of –180ºC to 900ºC, using vitreous silica dilatometers. This method can be applied to mortars and composites, among other solid materials. A transducer (dial gage or differential transducer) is commonly used for measuring the difference in length and a caliper is used to measure the reference length of the specimen. Length specimen is dependent of the transducer accuracy, and the tube and rod type of dilatometer apparatus determines the dimensions of the cross-section specimen. The accuracy of this method is strongly dependent of the precision of length and temperature measurements, as well as the calibration of the dilatometer. In addition, the method requires a special device, not commonly available on research labs, and the specified specimen geometry is not easily reached by casting process.

Recently, the ASTM standard test method for linear shrinkage and coefficient of thermal expansion of chemical-resistant mortars, grouts and monolithic surfaces, the ASTM C531, was adjusted in order to extend its application to polymer concretes. According to this method, thermal expansion of the material is evaluated by means of the average of coefficient of thermal expansion between room temperature and 100ºC. Length change is measured, through a micrometer, between special metal studs embedded in each end of the specimens (bars of square cross-section 25×25 mm^2 and 250 mm length). The measurements are performed after the conditioning of the specimens, for at least 16 hours, at each temperature level. The precision of this method has not yet been established. However, it is obvious that it will depend of user skill. The measurements at the highest temperature (100ºC) must be done very quickly, and the specimens must be removed, one at a time, at a rate that does not allow the temperature of the oven to drop below the established temperature. This method presents yet another drawback, which is the need to use special moulds that enables the moulding bars with the metal studs embedded at each end. On the other hand, the mean coefficient between 23ºC and 100ºC, determined by this method, gives only a rough idea of thermal expansion behaviour of resin concretes and mortars.

RILEM PC-13 norm, presented by Technical Committee 113: Test-Methods for Concrete-Polymer Composites, also specifies a test method for coefficient of thermal expansion of polymer concrete and mortar. In this method, lengths are measured by means of a length comparator, which must be capable of pressing on gage studs embedded on the sides of the specimens, at a gage length of 250mm. Prismatic specimens, with square cross-section of 100 mm and 400 mm length, are recommended.

Thermal expansion is analysed over the temperature range of 20ºC to 80ºC, with stepwise measurements of 20ºC. A thermostatic water bath, with sufficient capacity for the immersion of the specimens, is used to control the temperature. Water temperature is raised at a rate of 20ºC/h and held constant in each step for 2 hours. The mean coefficient of thermal expansion is calculated as the slope of the straight line that better expresses the relationship between thermal expansion and water temperature. This norm is not very clear about the way the measurements should be done: with the length comparator also immersed in the thermostatic bath, removing the specimens to make the measurements, or providing studs with enough length to allow the placement of the length comparator outside the bath. Regardless of this last remark, and considering all possible interpretations, this test procedure does not seem very practical.

Some researchers, based on existent standards applicable to ceramic tiles and cement pastes, developed their own methods for determination of the coefficient of thermal expansion of PC materials (Cano et al. 1998). However, these methods also present the shortcomings resulting from the mechanical process used to measure length changes of the specimens. Thermal strain of polymer concrete and mortars is normally not a linear function of temperature. Methods of measuring the expansion coefficient, by averaging the thermal strain over a large temperature range of many degrees, may result in failure to determine the variation in the coefficient of thermal expansion of these materials.

4.2.4.2 Applied test method for determining CTE of PM formulations

Previous studies, conducted by Wheat and co-workers (1995), showed that length change measurements, required to determine the coefficients of thermal expansion of PCs, could be made by electrical strain gages. This measuring process allows for a continuously monitoring thermal strain as function of temperature. Therefore, information on how coefficient of thermal expansion changes with temperature is obtained.

Ideally, a strain gage bonded to a test part would respond only to the applied strain in the part, and it would be unaffected by other surrounding variables. Unfortunately, the resistance strain gage, as all sensors in general, is somewhat less than perfect. The electrical resistance of the strain gage varies not only with strain, but with temperature as well. This temperature-induced resistance change is independent of, and unrelated to, the strain induced by mechanical and/or thermal stresses in the test object to which the strain gage is bonded. It is purely due to temperature change, and is thus called the thermal output of the gage.

Two concurrent and algebraically additive effects cause this phenomenon, sometimes referred to as *‘temperature-induced apparent strain’*. First, the electrical resistivity of the grid conductor is temperature dependent; and, as a result, the gage resistance varies with temperature. The second contribution to thermal output is due to the differential thermal expansion between the grid conductor and the test part or substrate material to which the gage is bonded. Because the grid is, by design, strain sensitive, the gage exhibits a resistance change proportional to the differential expansion. The errors due to thermal output can become extremely large as temperatures deviate from the arbitrary reference temperature (ordinarily, room temperature). Additionally to thermal output errors, the relation between strain and resistance change, the *‘gage factor’*, varies with temperature, inducing more measuring errors.

However, using self-temperature-compensated strain gages, which employ specially processed alloys, it is possible to minimize the thermal output over a wide temperature range, as long as they are applied to test materials with thermal expansion coefficients for which they are intended. Depending upon the test temperature, higher accuracy can be obtained making additional corrections, for the thermal output and gage factor variation, in the strain measurement. Engineering data sheet supplied in each package, series and lot of self-temperature-compensated strain gages, provides polynomial equations for the correspondent thermal output curve and gage factor variation with temperature. It should be noted that the thermal output data are only applicable to the strain gages of the designated lot number, applied to test material with the same coefficient of thermal expansion than the type of material used in determining the supplied thermal output curves.

To measure strains induced only by thermal effects, in a material not mechanically loaded, self-temperature-compensated strain gages indicated for test materials without thermal expansion, can be applied. This way, the effect of resistance change with temperature is compensated; the thermal expansion of grid conductor is also taken into account, but not the thermal expansion of the test part. Therefore, strain data obtained from tests are only due to the thermal expansion of test material.

Ordinary strain gages, not self-temperature-compensated, can however be applied to measure strains induced by thermal effects, as specified by Wheat et al (1995), and also recommended in ASTM D5335 (2000). However, this practice requires the use of compensate (dummy) gage bonded in a test material that has a known reproducible thermal expansion. On the other hand, this procedure yields less accuracy, as the thermal output error, due to the differential thermal expansion between the grid conductor and the test part, still remains.

In this research work, to measure the strains induced by temperature changes on epoxy and polyester PM formulations, strain gages with constant alloy in self-temperature compensated form for structural materials with coefficient equal to zero, were used. This process of length variation measurement provides more consistent and reliable results.

The variation of the CTE of PM formulations with temperature was also analyzed. It has been found that polymer concrete and mortars have lower coefficients of thermal expansion at lower temperatures than at higher temperatures. Plots of strains versus temperature are often bilinear, indicating a sharp change in the coefficient of thermal expansion (Wheat et al. 1995). To determine how this discontinuity varies for these two materials, specimens of both formulations were tested for several temperature ranges between –15ºC and 60ºC.

4.2.4.3 Experimental procedure

i) Specimens' geometry

Prismatic specimens, with square cross-section of 40×40 mm^2 and 100 mm length were used, but other geometries were possible as long as the specimens have the minimum dimensions (at least twice the length of the strain gages). All specimens were allowed to cure, for one day at room temperature and then post-cured at 80ºC for three hours, before being tested for thermal expansion.

ii) Length change measuring

Length changes measuring were made by strain gages, with constant alloy in self-temperature compensated form for structural materials without thermal expansion. Flexible gages with a cast polyamide backing, completely encapsulated, with 6.35 mm grid length, were used. Three specimens of each PM formulation were instrumented with one strain gage bonded longitudinally on one of their lateral faces.

In order to test the accuracy of the method for posterior validation, an aluminum alloy reference specimen (2017 4.0Cu-0.6Mg-0.7Mg-0.5Si), with a known coefficient of thermal expansion (mean coefficient of thermal expansion, between 20ºC to 100ºC, of 23.6 µm/mº C), was also instrumented and tested (ASM 1991).

Electrical strain gage data were recorded using two data loggers with continuous acquisition system (SPIDER-8) in eight channels. Strain gage data were registered with the gage factor setting of the strain indicator at 2.00. Corrections for the gage factor variation and for the thermal output were performed after data acquisition.

iii) Specimens' conditioning

Three instrumented specimens of each type of polymer mortar, as well as the aluminum alloy specimen, were placed in a climatic chamber at room temperature during eight hours. Strain indicator of data logger was then balanced for zero strain, in all channels. Afterwards, the temperature was lowered by steps of 12,5ºC to –15ºC, then it was increased in six increments until +60ºC, and finally, it was decreased by three steps to room temperature. The heating/cooling rate between temperature levels was approximately 0.28ºC/minute, and in each step, temperature was held constant for 7.75 hours in order to allow the specimens to reach thermal equilibrium. All specimens were subjected to a total of three of these cycles.

iv) Data treatment

Strain data used to determining the mean CTE, for each temperature range, was taken from the last strain measurement in each temperature level or step. At those points, the thermal equilibrium was already reached and the strain gage readings were constants. The obtained strain values were then corrected for the thermal output and gage factor variation according to the following equations:

$$\varepsilon = [\ \varepsilon_A - \varepsilon_{T/O}(T_i)\ ]\ .\ F^* / F(T_i) \tag{4.5}$$

$$\varepsilon_{T/O}(T_i) = A_0 + A_1.T_i + A_2.\ T_i^2 + A_3.\ T_i^3 + A_4.\ T_i^4 \tag{4.6}$$

$$F(T_i) = F_0\ .\ [1 + V_{\%}(T_i)/100\ ] \tag{4.7}$$

where:

- ε_A is the obtained strain, before any correction;
- ε is the strain magnitude corrected for both thermal output and gage factor variation with temperature;
- $\varepsilon_{T/O}(T_i)$ is the thermal output at temperature T_i;
- A_0, A_1, A_3 and A_4 are the polynomial coefficients of thermal output curve of gage strain;
- F* is the instrument gage factor set;
- $F(T_i)$ is the strain gage factor at temperature T_i
- $F_0$is the room temperature gage factor;

and - $V_{\%}(T_i)$ is the variation of gage factor for temperature T_i;

The coefficients of thermal expansion, for each temperature range, were calculated by first fitting straights lines between adjacent points of consecutive measurements of correct strain values and correspondent temperatures (Ei,Ti), and then, determining the respective slopes, as described in equation (4.8).

$$\alpha_{(Ti,\ Ti+1\ )} = [\varepsilon(T_{i+1}) - \varepsilon(T_i)\ ] / [T_{i+1} - T_i] \tag{4.8}$$

where:

- $\alpha_{(Ti,\ Ti+1\ )}$ is the mean coefficient of thermal expansion for temperature range between T_i and T_{i+1};
- $\varepsilon\ (T_i)$, $\varepsilon\ (T_{i+1})$ is the correct strain magnitudes at temperatures T_i and T_{i+1}, respectively.

For each polymer mortar formulation and for each temperature range, the mean coefficient of thermal expansion considered, corresponds to the average of eighteen values of $\alpha_{(Ti+1,\ Ti)}$ (2 values per cycle × 3 cycles × 3 specimens).

Dilatation-Temperature curves were obtained considering, for each temperature range, the expansion of an elementary volume of test material when temperature is raised from –15ºC to +60ºC. For each temperature range, the expansion was calculated considering the correspondent coefficient of thermal expansion, as described in equation (4.9).

$$\Delta V_{(Ti,Ti+1)}=3\left[\Delta T_{(Ti,Ti+1)}.\alpha_{(Ti,Ti+1)}\right]+3\left[\Delta T_{(Ti,Ti+1)}.\alpha_{(Ti,Ti+1)}\right]^2+\left[\Delta T_{(Ti,Ti+1)}.\alpha_{(Ti,Ti+1)}\right]^3 \quad (4.9)$$

where:

- $\Delta V_{(Ti,Ti+1)}$ is the expansion of an elementary volume of test material when temperature is increased from T_i to T_{i+1}.
- $\Delta T_{(Ti,Ti+1)}$ is the temperature variation between T_i and T_{i+1}.

4.2.4.4 Test results and discussion

i) Mean coefficients of thermal expansion

Strain data acquired by data logger throughout the three cycles, are plotted in Fig. 4.4, showing the different thermal behaviors of polyester and epoxy PMs when subject to temperatures changes. These data are not yet treated. In general, polyester mortars recover the equilibrium quite fast after temperature changes, while epoxy mortars require more time to stabilize and strain measurements present slightly more scatter.

For each type of PM, the variations of strain with temperature, during the three cycles, are shown in Fig. 4.5. Strain versus temperature data for specimens of the same formulation are very similar, and when plotted in the same graph become almost coincident. In order to make the obtained results more clear, only the strain-temperature curve of one specimen of each type is presented.

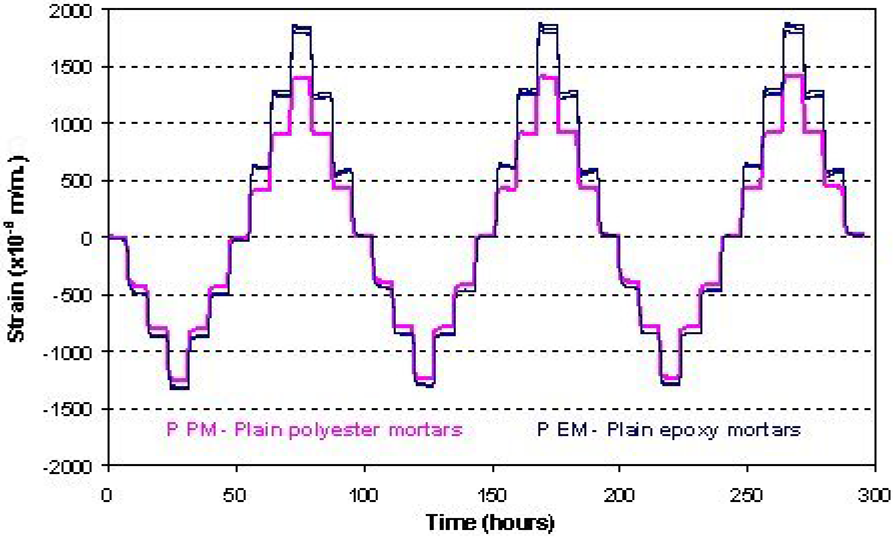

Fig.4.4. Strain data of PM formulations acquired by data logger throughout the three thermal cycles.

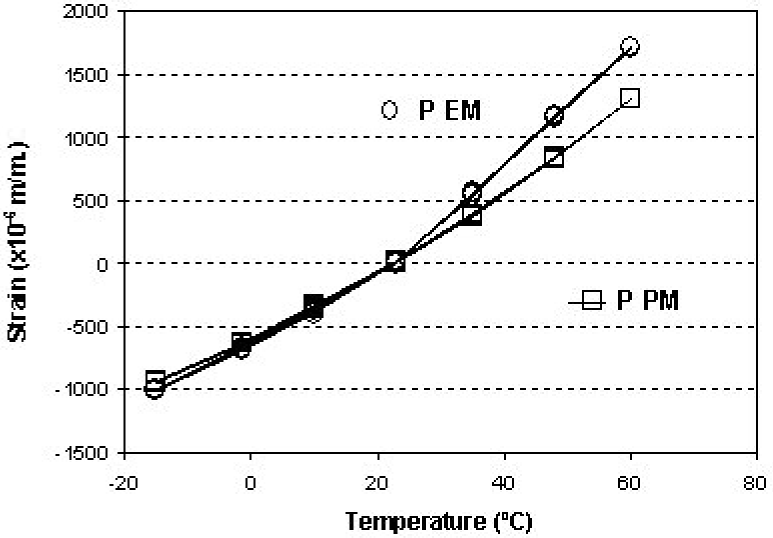

Fig. 4.5. Evolution of strains of epoxy (PEM) and polyester PM (PPM) specimens with temperature, during the three cycles.

Table 4.5 presents the mean coefficients of thermal expansion and correspondent standard deviations obtained for each temperature range, according to equation (4.8).

As expected, both formulations of PMs present higher coefficients of thermal expansion at higher temperatures. For temperatures between –15ºC and 10ºC, thermal expansion of

PMs are very similar, but above 10ºC, the increase rate of coefficient of thermal expansion of epoxy mortars is higher than that one that occurs for polyester mortars.

Table 4.5. Mean coefficients of thermal expansion of PM and aluminium alloy reference specimens.

Temperature Ranges [T_i , T_{i+1}]	Mean CTE α | St.Desviation (µm/m .ºC) AL Alloy 2017	Polyester PM	Epoxy PM
[-15ºC , -2ºC]	22.36 | 0.21	22.97 | 0.06	23.45 | 0.03
[-2ºC , +10ºC]	22.73 |0.26	25.39 | 0.64	26.39 | 0.76
[+10ºC , +23ºC]	22.36 |0.13	26.68 | 0.54	29.94 | 0.75
[+23ºC , +35ºC]	23.12 |0.09	30.86 | 0.09	44.45 | 1.50
[+35ºC , +48ºC]	23.10 |0.11	34.94 | 0.20	47.33 | 0.63
[+48ºC , +60ºC]	23.46 |0.10	39.08 | 0.38	45.89 | 0.62

ii) Dilatation-temperature curves

Dilatation-temperature curves are plotted in Fig. 4.6. These curves were determined considering the expansion of an elementary volume of test material when temperature is raised from –15ºC to 60ºC. An isotropic behavior for the test material was assumed. For each temperature range, expansion was calculated considering the correspondent coefficient of thermal expansion.

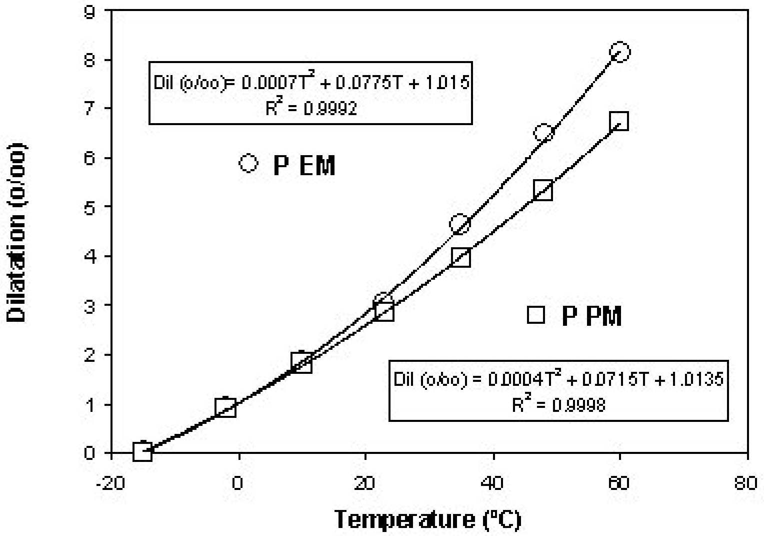

Fig. 4.6. Dilatation-temperature curves of both PM formulations: epoxy (PEM) and polyester PMs (PPM).

Dilatation-temperature curves of both PM formulations, between –15ºC and 60ºC, are more accurately predicted through an approximation to a parabolic law than a bilinear law. Considering these approximations, the variation of instantaneous coefficients of thermal expansion of both formulations with temperature, follow linear laws, as illustrated in Fig. 4.7.

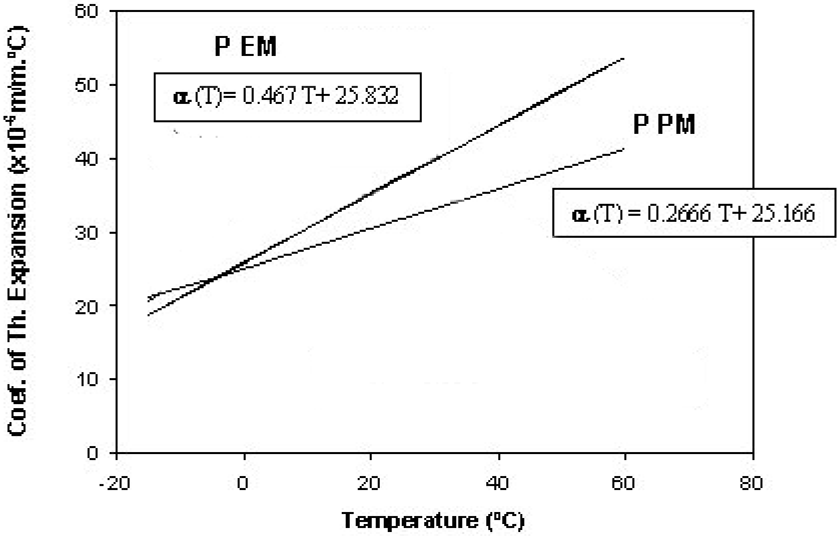

Fig. 4.7. Variation laws of instantaneous linear coefficient of thermal expansion with temperature of epoxy (PEM) and polyester (PPM) polymer mortars.

Regardless the above considerations, for practical uses, it can be considered that dilatation-temperature curves of both type of PMs follow bilinear laws, with discontinuity points both located at 23ºC. Corresponding mean coefficients of thermal expansion, for temperatures below and above these points, are presented at Table 4.6.

Table 4.6. Mean coefficients of thermal expansion of PM formulations considering a bilinear law for strain-temperature curves.

Temperature Ranges [T_i , T_{i+1}]	Mean Linear Coefficient of Thermal Expansion α (μm/m .ºC)	
	Polyester PM	Epoxy PM
[-15ºC , +23ºC]	25	27
[+23ºC , +60ºC]	34	46

iii) Validation of the method

Evolution of strains as function of temperature of the reference specimen used in this study, an aluminium alloy (1207), is plotted in Fig. 4.8. The known literature value of the coefficient of thermal expansion of this material is the mean coefficient between 20ºC and 100ºC: $\alpha_{(20^{\circ}C,\ 100^{\circ}C)} = 23.6\ \mu m / m.^{\circ}C$.

The measured values of strain and temperature (T_i, ε_i) throughout the thermal cycles were used to calculate, by inter and extrapolation processes, the expected values for $\varepsilon_{20^{\circ}C}$ and $\varepsilon_{100^{\circ}C}$. The correspondent slope of the straight line between the two points, (20ºC, $\varepsilon_{20^{\circ}C}$) and (100ºC, $\varepsilon_{100^{\circ}C}$), gave the expected value for the mean coefficient of thermal expansion of the aluminum alloy within the temperature range of 20ºC to 100ºC. The described calculation allowed assessing the accuracy of the applied method.

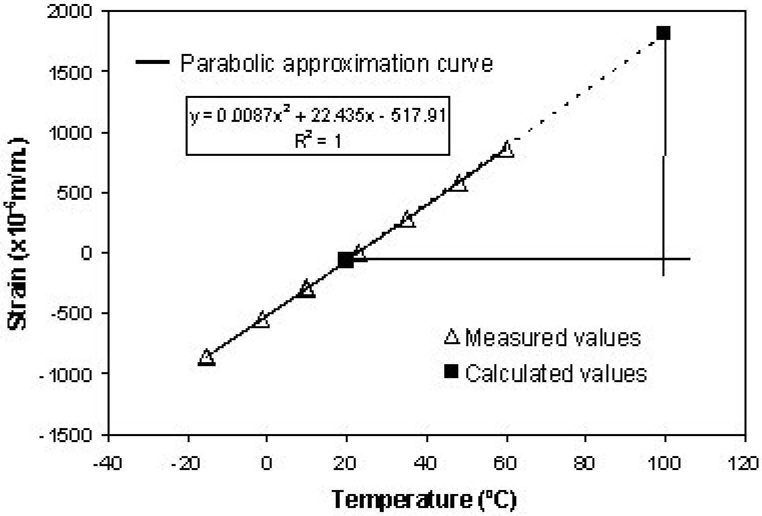

Fig. 4.8. Plot of strains versus temperature of aluminum alloy reference specimen. Calculation of expected value of its mean coefficient of thermal expansion between 20ºC and 100ºC.

Only a small difference of 0.5% was found between the literature value (23.6 μm/m.ºC) and the expected value obtained by this method (23.48 μm/m.ºC), which is a good indicator of the accuracy and precision of applied methodology for determining the thermal expansion of PC materials.

4.2.4.5 Conclusions

Based on test results, the following conclusions can be drawn:

- Both formulations of PMs present higher coefficients of thermal expansion at higher temperatures. For temperatures ranges between –15ºC and +10ºC, thermal expansion of both binder formulations are very similar, but above +10ºC, the increase rate of coefficient of thermal expansion of epoxy mortars is higher than the one found for polyester mortars.
- For both formulations, the variation of thermal expansion with temperature follows a polynomial law rather than a bilinear law. Therefore, it can be concluded that coefficients of thermal expansion of these materials vary continuously within the temperature range between -15ºC and +60ºC.
- For practical use, when a higher precision is not required, the following values for the mean coefficients of thermal expansion of epoxy and polyester PM formulations, may be considered: for temperatures ranges below room temperature, the coefficient values of 25 and 27 μm/mºC for polyester and epoxy mortars, respectively; and for temperatures ranges above this point, the correspondent values of 34 and 46 μm/mºC.

The method applied to determine the coefficient of thermal expansion of PM formulations is quite precise, with excellent accuracy for practical purposes. The method does not require any specific devices or special equipment, allows a higher freedom in terms of specimen geometry and it is very simple to implement, which make it a good alternative to the conventional methods.

4.3 Short-Term Mechanical Properties

4.3.1 Flexural Properties

In PC materials, the differences among the flexural parameters are higher than in the compression study. Therefore, flexural tests have been widely used for mechanically ranking the different PC types, in detriment of the compression ones, which are more adjusted for developing this purpose in conventional cement concretes (San José 2006).

According to this, throughout this thesis, flexural strength was systematically used for the assessment of PMs behavior under different environment conditions. This procedure enabled a great number of flexural test results (control specimens), which could now be used for a feasible statistical analysis.

4.3.1.1 Test and calculation procedures

i) Flexural strength

All flexural test results of control prismatic specimens of both formulations tested in three-point bending throughout the global present study were computed for this analysis.

All specimens were tested in bending up to failure at the loading rate of 1 $mm.min^{-1}$, with a span length of 100 mm, according to RILEM CPT PCM-8 test method (see chapter III for more information regarding test procedure and testing set-up).

The specifications of RILEM standard, in terms of specimen geometry and span length, are similar to those specified in ASTM C348-02, standard test method for flexural strength of hydraulic cement mortars (2002). In both standards, shear effect is not taken into account on calculation procedure of flexural strength. Despite the very short span length compared with specimen thickness, shear effect is disregarded. Concrete and mortars are assumed as isotropic materials and the theory of plane cross sections is used. Flexural strength, considered as the strength under normal stresses, is determined applying equation well known from the strength of materials.

Nevertheless, corrections could be made but obtained results could not be compared to those obtained on other studies on cement or polymer mortars, which usually apply the above standards. On the other hand, analytical research shows that the effect of shear on the stress distribution over the height of a bar is considerably less than the effect on deflection. According to Tarnopol'skii and Kincis (1984), for sufficient practical accuracy, the deviations of the normal stress distributions from linear, and tangential stresses from parabolic, can be disregarded if parameter *k* is less than 1.2, where *k*, for isotropic materials is given by the following expression:

$$k = \pi \frac{\mathrm{h}}{2\,\mathrm{l}} \sqrt{2\ (1+\mu)} \qquad (4.10)$$

where *h* is the specimen height, *l* is the span length and μ is the Poisson's ratio.

In this particular case, for Poisson' ratio values around 0.22 to 0.26 (values obtained experimentally), *k* values between 0.98 and 1.00 were found. Thus, flexural strength, considered as the strength under normal stresses, was determined applying equation (3.1) from the strength of materials.

i) Flexural elasticity modulus

Load-deflection curves obtained from flexural tests were used to determine secant elasticity modulus in accordance with the procedure described in the ASTM C580-02, standard test method for flexural strength and elasticity modulus of chemical-resistant mortars, grouts and polymer concretes (2002).

According to this standard, once again, shear effect is not considered in the calculation procedure. Deflections are assumed to be small and the theory of plane cross sections is used. For a simply supported prismatic specimen, with a concentrated load *P* in the middle of span *l*, and without allowance for shear, elasticity modulus (*E*) is easily calculated only by means of the testing variables, load *P* and deflection at midspan w_{max}, by:

$$\mathrm{E} = P\, l^3 / 48\ \mathrm{I}\ w_{max} \qquad (4.11)$$

where *I* is the second moment of area of the cross section of the specimen ($I = bh^3/12$).

However, modulus of elasticity determined by equation (4.11) is fictitious since it does not reflect the effect of shear stress, which is so much higher as greater the height to span ratio (*h/l*). Therefore, and taking into consideration that shear has a larger effect on deflection than on the distribution of stresses, shear effect was here taken into account on calculation procedure of flexural elasticity modulus, through Timoshenko simplified approach for the deflection at midspan of a rectangular bar with allowance for shear (Tarnopol'skii and Kincis 1984):

$$w_{\max} = w^*_{\max} \left[1 + \alpha \, (h/l)^2 \, E/G \right] = w^*_{\max} \, (1 + 0.486 \, k^2) \tag{4.12}$$

where $w^*_{\max}$ is the maximum deflection of the bar without allowance for shear (see equation 4.11); h is the height of the bar; α is a coefficient depending on cross-sectional of the bar (α=1.2 for a rectangular cross section); and k is the coefficient given by equation (4.10).

In the above expression, elastic to shear modulus ratio was obtained considering polymer mortars as isotropic materials.

4.3.1.2 Test results and discussion

i) Flexural strength

The distributions of the flexural strength of both types of test specimens are represented, graphically, by the histograms shown in Fig. 4.9. The data are also depicted in a probability scale in Fig. 4.10.

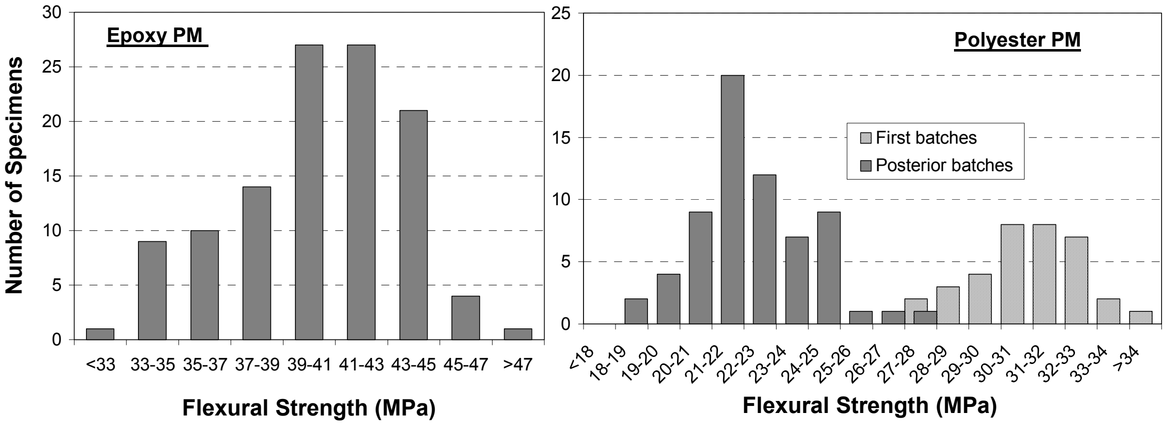

Fig. 4.9. Histograms for flexural strength distributions of epoxy (at left) and polyester (at right) PM formulations.

For polyester PM formulation, two different distributions are presented. During the experimental plan of this thesis, polyester PM specimens were produced with unsaturated polyester NESTE 226E proceeding from different drums. This resin was very popular at INEGI lab and it was also used by other researchers for different end-uses than this one described here (polymer mortar binder). It has been found that the first batches, proceeding from the first drum, and which were used on the optimization process and, partially, on the chemical resistance program, presented in general, a considerable higher flexural strength than posterior batches did. No explanation was found for this variability. Posterior batches were also made with polyester binder proceeding from different drums and no significant differences were noticed on flexural test results of control specimens. Taking into account the discrepancy of results, between the first batches (from the first drum supply) and all the others, it seems reasonable in this statistical analysis to separate flexural strength data into two different distributions.

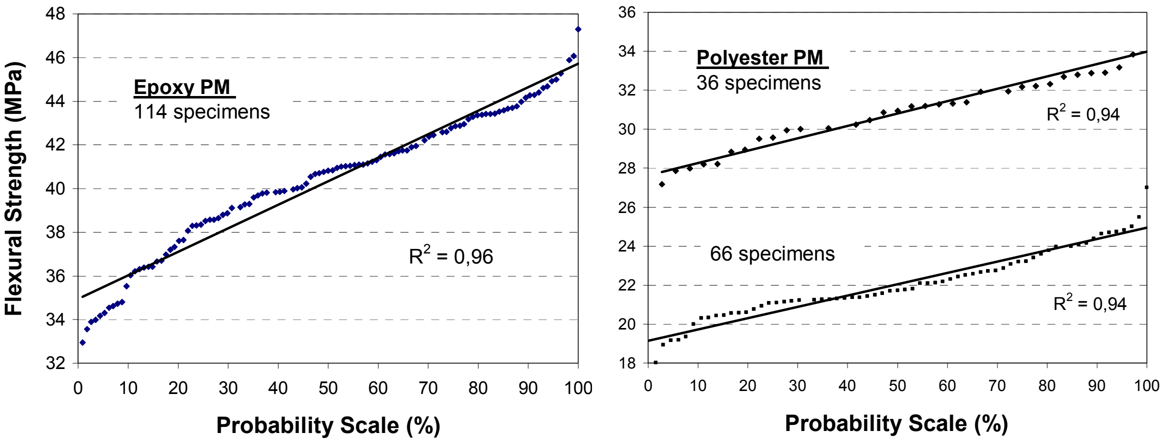

Fig. 4.10. Normal probability plots for flexural strength data of epoxy (at left) and polyester (at right) PM formulations.

From normal probability plots, showed in Figs. 4.10, it can be assumed that all three 'types' of tests follow a normal or Gauss distribution, as linear approximations are obtained. The means may be estimated as the flexural strength at the 50% level on the probability scales, and the standard deviations may be estimated by noting that for a normal distribution, one standard deviation above the mean occurs at a probability level of 84.13%. Thus, one standard deviation in strength is defined by the increment between the 50% and 84.13% levels.

With 95% confidence, it may be predicted that the correct estimates of the mean flexural strength, f_{fl}, is in the range of 39.7 to 41.0 MPa for epoxy PM formulation, and between 21.5 and 22.6 MPa for polyester based formulation (assuming the posterior batches). The latter values were computed from the following relationships:

$$f_{\mathrm{fl}} = \mu \pm \mathrm{t}\,[\,\mathrm{SD}/\,(n)^{1/2}\,] \tag{4.13}$$

where μ is the average strength, n is the number of specimens and t = 1.96 for 95% confidence level.

The mean, standard deviation (SD) and coefficient of variation (COV) of flexural strength data of both types of PM formulations are summarized in Table 4.7. Minimum, maximum and average values of coefficient of variation within batches are also presented. Estimated values for the population obtained through linear approximation of probability function are also showed.

Table 4.7. Statistical analysis results of flexural strength data of PM formulations.

Flexural Strength Statistical Parameters	Epoxy PM	Polyester PM	
		First batches	Posterior batches
SAMPLE			
Sample size	114	36	66
Arithmetic Mean	40.40 MPa	30.36 MPa	22.10 MPa
SD - Standard Deviation	3.18 MPa	1.69 MPa	1.76 MPa
COV- Coef of Variation	7.87 %	5.56 %	7.96 %
Range of COV within batches	[0.81% , 6.99 %]	[0.30% , 6.30 %]	[1.40% , 9.56 %]
Average of COV within batches	3.44 %	4.06 %	5.16 %
POPULATION			
Linear approximation	y=0.1077x +34.98	y=0.0635x+27.626	y=0.0581x+ 19.137
Arithmetic Mean	40.36 MPa	30.80 MPa	22.04 MPa
SD - Standard Deviation	3.68 MPa	2.36 MPa	2.16 MPa
COV- Coef of Variation	8.36 %	7.66 %	9.80%

Average flexural strength of epoxy PM formulation is rather near the upper limit of the common values found for this type of mortar, which are usually within the range of 15 MPa to 45 MPa, as function of binder content. This feature reinforces the assumption that a high quality PM has been developed.

Relatively to polyester PM formulation, average flexural strength is within the range of values commonly found for these types of resin based mortars (between 13 MPa and 40 MPa). Nevertheless, the mean flexural strength obtained for the first batches of polyester PMs was unusually high for mortars with 20% in weight of polyester binder.

In order to determine whether the two sets of data corresponding to polyester PM flexural test results were the 'same' or 'different', the means were compared by using the 't test' based on the student's distribution. The T-test revealed that the two sets of data were in fact, statistically speaking, largely different and could not be considered the same system. In testing the null hypothesis at the 5% level of significance, t-test value was considerably above the critical value. Some explanations could be advanced for the occurrence, but none of them is certain. Poor quality control system of the producer? Lack of styrene or accelerator in the posterior drum supplies? Deficient mixing of the drum before pouring the required resin? Nevertheless, the occurrence did not compromise the present research work as all conclusions were made with basis, mostly, on relative results and not on absolute values.

Hereinafter, for polyester PM formulation, the distribution with the larger number of specimens will be assumed as more representative of material's behavior.

The variability of flexural strength data of PM formulations, assessed by correspondent coefficient of variations, are quite good taking into account that no support system was used during casting process for compaction and vibration. Until now, there is not much available information on the variability of strength properties of PC materials to use as comparison basis. Mebarkia (1993) reported a coefficient of variation of 5% for the flexural test data of polyester PC formulation with a sample size of 15 specimens; Hsu (1984) found the COV value of 8% for the same type of test data of MMA based PC, but with a larger sample size (39 specimens). Both studies revealed that the coefficient of variation depends on the type of testing, as similar trends were observed regarding the variation of COV with the type of strength test data. Highest coefficients were found for splitting tensile tests (16% and 12% for, respectively, polyester and MMA PCs) and lowest for compression tests (4% and 5%, for the same PC formulations). One of the few studies on PC materials in which uniaxial tensile tests were performed, reported a COV of 11% for the test data of seventeen MMA based PC specimens (Kim 1986). Nevertheless, irrespectively of the testing type, COV value will always be strongly related with the reproducibility of the manufacture technology applied.

ii) Minimum number of tests required

In order to determine, for each formulation, the minimum number of future tests required to ensure that the committed error in average measured value, with 95% confidence, is kept below 5%, the following relationship was used (Soroushian et al. 1993):

$$N = t^2 \, COV^2 / Er^2 \tag{4.14}$$

where N is the minimum number of test specimens; *t* is the value of student's distribution for the specified confidence level (t=1.645 for large sample size at 95% confidence level); COV is the coefficient of variation; and *Er* is the maximum error in the average measured value (5%).

For the coefficient of variation (COV) of the 'samples', a minimum number of 7 test specimens was found for both formulations. However, if the average values of COV within batches is computed instead of COV of global distributions, the minimum number of tests decreases for 2, as variability within batches is lower than in the global distribution. This result sustain the reliability of the experimental work done throughout this thesis, as, in all the experiments involving flexural resistance, a minimum number of 3 flexural test results was computed for material assessment behavior. Moreover, in each part of the experimental program, specimens belonging to same batch were used.

iii) Flexural elasticity modulus

Secant elasticity modulus of both PM formulations, determined by means of load-defection curves, is presented in Table 4.8. Standard deviation and correspondent coefficient of variation are also presented. Statistical analysis was performed for minor set of data than those used for flexural strength analysis. The reason for the different criterion is related with the treatment data required by each test, which is very time consuming, as described in the following:

Firstly, an initial correction of the original load-defection curves is required to eliminate the initial small slope branch, characterized by high deflection to load ratios, caused by specimen accommodation to nose supports.

Then, a second adjustment is necessary to remove the typical stepwise of the curve, at approximately 3.5 kN to 4.0 kN load level. The likely reason for this ‘stair’ effect on flexural curve might be related to a slight indentation on specimen surface. Prismatic specimen surfaces generally tend to be richer in resin content, and consequently, less tough than core material. Thus, this systematic bump in the curve does not reflect a material characteristic; instead, it rather reflects a surface material characteristic. The same effect was already noticed in other research works. For large size specimens, this effect is not noticeable and can be disregarded.

Al the above procedures require a minutiae data treatment taking into account that each load-deflection curve contains more than one hundred points.

Table 4.8. Statistical analysis results of flexural elasticity modulus of PM formulations.

Elasticity Modulus Statistical Parameters	Epoxy PM	Polyester PM*
Sample size	6	6
Arithmetic Mean	3.92 GPa	3.21 GPa
SD - Standard Deviation	0.06 GPa	0.13 GPa
COV- Coef of Variation	1.5 %	4.0 %

* Test results of specimens proceeding from posterior batches.

The results obtained for flexural elasticity modulus of both PM formulations are largely behind the expected range of values. Even considering the corrections for allowance in shear, obtained values are very low and do not seem plausible. It is not reliable that PMs have stiffness in the same order than the resin binders, even considering their high content. Since introduced simplifications induce to large errors, this procedure is not suitable for the determination of elasticity modulus. Another approach must be thought in order to determine this parameter, either by bonded gages in the outer surface of the specimens, to directly measure the tensile strains in a four-point bending test (see section 4.3.3.1), or by increasing the span to height ratio in order to reduce the shear effect. Until then, obtained results must be disregarded.

4.3.2 Compressive Properties

The most common of all tests on hardened conventional concrete is the compressive strength test, partially because it is an easy test to perform, and partially because many of the desirable characteristics of concrete are quantitatively related to its compressive strength.

Although flexural strength test has been considered as the most relevant one for PC materials, as more indicative of the strength characteristics of these materials, compressive test is also of major significance, mainly because of the intrinsic importance of material's compressive strength in structural design.

The complete stress-strain relationships in axial compression are also important to better understand material's behavior, being an important tool for accurate prediction of deflection, toughness and dynamic response.

4.3.2.1 Test and calculation procedures

i) Compressive strength, compressive elasticity modulus and Poisson's ratio

In order to determine compressive strength of PM formulations, two types of compression tests were performed: compression tests on cylinder specimens, with 50 mm diameter and 100 mm height, and compression tests on broken parts of standard prismatic specimens ($40\times40\times160$ mm^3) tested in bending. A universal mechanical testing machine INSTRON, shown in Fig. 3.7, with a load cell of 300 kN was use for that purpose.

Prior testing, the end surfaces of cylinder specimens were ground on a geological rock grinder until they were smooth, flat and perpendicular to the axis of the specimen. All specimens were allowed to cure at room temperature during one day, and post cured at 80ºC during three hours, before being tested in compression.

Cylinder PM specimens were tested in compression at the loading rate of 1.25 mm.min^{-1} according to RILEM PC-5 test method (1995c). With the purpose of determining secant elasticity modulus, three specimens were instrumented with wire strain gages bonded to two diametrically opposite gage lines parallel to the axis of the specimen, in accordance with procedures described in RILEM PC-8 and ASTM C 469 standards (ASTM:C469-94 1994; RILEM 1995f). In order to obtain Poisson's ratio, one specimen of each series was also instrumented with two bonded strain gages mounted circumferentially at diametrically opposite points at the specimen mid-height. Longitudinal and circumferential strains, as well as LVDT (Linear Voltage Differential Transducer) data, were recorded through a data logger with a continuous acquisition system (Spider 8).

Prismatic PM specimens were tested in compression at the same loading rate of 1.25 mm.min^{-1}, following procedure described in UNE 83821: 1992 test standard (1992).

Both testing set-ups are illustrated in Fig. 4.11.

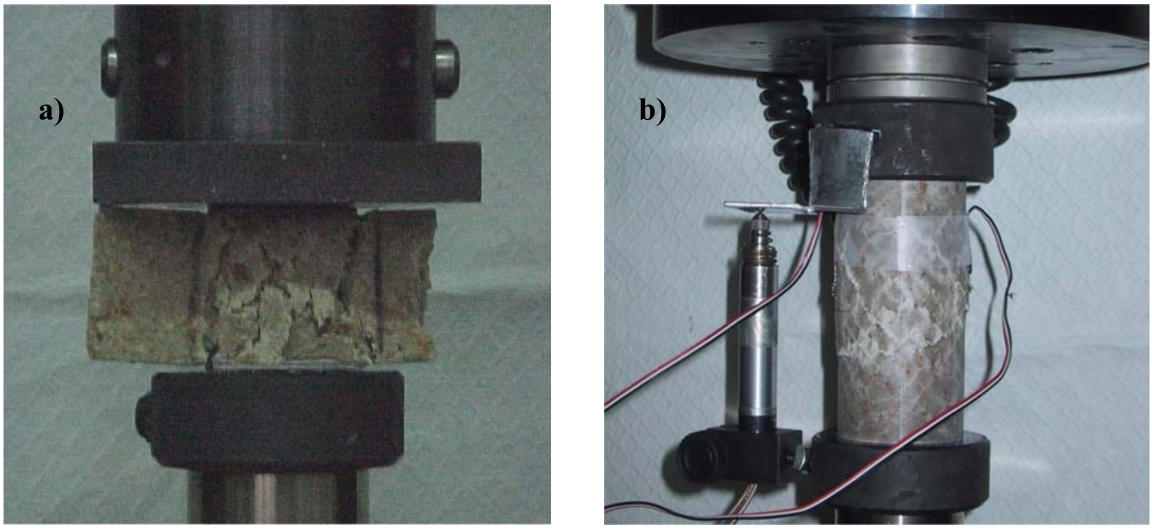

Fig. 4.11. Test set-ups of compression tests performed on a) broken parts of standard prismatic PM specimens tested in bending, and b) cylindrical PM specimens.

For all specimens, compressive strengths were calculated by dividing the maximum applied load by the initial cross section area of the cylinder specimens, or load surface area of prismatic specimens (40×40 mm^2).

Secant elasticity modulus in compression and Poisson's ratio were calculated according to the following equations:

$$E = \frac{S_2 - S_1}{\varepsilon_2 - 0.000050} \qquad (4.15)$$

where E is the chord elasticity modulus; S_2 is the stress corresponding to 40% of maximum load; S_1 is the stress corresponding to a longitudinal strain of 50 millionths; and ε_2 is the longitudinal strain produced by S_2.

$$\nu = \frac{\varepsilon_{t2} - \varepsilon_{t1}}{\varepsilon_2 - 0.000050} \tag{4.16}$$

where ν is the Poisson's ratio, and ε_{t2} and ε_{t1} are the transverse strains at mid-height of the specimen, produced respectively by stresses S_2 and S_1.

iii) Stress-strain relationships

Experimental stress-strain curves were obtained by means of load-strain data recorded during compression tests performed on instrumented cylinder PM specimens.

The ascending part of the stress-strain curve in axial compression is easier to obtain experimentally than the descending part. The difficulties arise from the fact that the shape of the softening branch is dependent not only on the concrete material but mainly on the test conditions. Specimen height to diameter ratio, control mode of testing machine (displacement or load control mode), strain or load rate, type of strain gage and gage length are some of the influencing factors.

Several empirical relationships have been developed to fit the experimental stress-strain curves. In general, all of them are function of three experimental parameters: peak stress f_c , strain at peak stress ε_c , and initial tangent elastic modulus E_0. Additional constants, obtained by means of experimental data, are usually introduced to fit the steep of descending branch.

The usual empirical relationships can be categorized into three main classes.

- The first class consists of two separate relations, one for the ascending part and the other for the descending part. One example of this type of empirical relationship can be found in research work carried out by Zhang et Guo (1987), concerning the tensile behavior of conventional portland cement concrete.
- The second category consists of one equation but with two sets of constants, for the ascending and the descending curves. Fanella et Naaman (1985) purposed an empirical relationship of this type to describe the compressive stress-strain curves of fiber reinforced cement mortars, which was also applied, with success, by Mebarkia (1993) to feet the compressive stress-strain curves of glass fiber reinforced polymer mortars

- The third category is represented by one equation with the same constants for the complete stress-strain curve. An example of such equation may be as follows (Carreira and Chu 1985):

  $$Y = X / [\ q + (1\text{-}q)\ X^{1/(1\text{-}q)}\ ] \qquad (4.17a)$$

  with Y and X given by the following expressions:

  $$Y = \sigma / f_c \qquad (4.17b)$$

  $$X = \varepsilon / \varepsilon_c \qquad (4.17c)$$

  $$q = E_c / E_0 \qquad (4.17d)$$

  where σ and f_c are, respectively, the stress and the peak stress; ε and ε_c are, respectively, the strain and the strain at peak stress; and q is the ratio of secant elasticity modulus at peak stress (E_c), to initial elastic modulus (E_0); and reflects the nonlinear pre-peak behavior of the stress-strain relationship.

  The above equation (4.17a) has one parameter q. A two-parameter relationship, which constitutes one of the most interesting general expressions, was proposed by Sargin (1979) and may be written as:

  $$Y = [\ k\,X + (k'\text{-}1)\ X^2\ ] / [\ 1 + (k\text{-}2)\ X + k'X^2\ ] \qquad (4.18)$$

  where X and Y are defined by Eqs. (4.17b) and (4.17c); the parameter k is the ratio of initial elasticity modulus (E_0) to secant elasticity modulus at peak stress (E_c), *e.g* $k = 1/q$, with q defined by Eq. (4.17d); and the second parameter k', which allows to adjust the steep of post-peak curve, is determined by the least-squares fit of the predicted to the experimental data points.

In order to fit the obtained experimental stress-strain curves, both empirical relationships described in Eqs. (4.17) and (4.18) were applied.

4.3.2.2 Test results and discussion

i) Compressive strength, compressive elasticity modulus and Poisson's ratio

For both PM formulations, obtained results of compression tests performed on cylinder and prismatic specimens are presented throughout Table 4.9.

Stress-strain curves obtained from compression tests performed on cylinder PM specimens are plotted in Fig. 4.12. Typical failure modes are also illustrated in Fig. 4.13.

Table 4.9. Statistical analysis results of compressive test data of PM formulations.

Compressive Properties Statistical Parameters	Epoxy PM	Polyester PM
COMPRESSIVE STRENGTH -CYLINDERS		
Number of specimens	9 (3 batches)	9 (3 batches)
Arithmetic Mean	70.16 MPa	64.13 MPa
SD - Standard Deviation	6.74 MPa	1.43 MPa
COV- Coef of Variation	9.61 %	2.24 %
Range of COV within batches	[0.61 % , 2.50 %]	[0.23 % , 1.17 %]
Average of COV within batches	1.33 %	0.69 %
COMPRESSIVE STRENGTH -PRISMATIC		
Number of specimens	18 (3 batches)	18 (3 batches)
Arithmetic Mean	75.23 MPa	65.03 MPa
SD - Standard Deviation	3.15 MPa	3.09 MPa
COV- Coef of Variation	4.19 %	4.76 %
Range of COV within batches	[1.02 % , 3.99 %]	[2.12 % , 2.64 %]
Average of COV within batches	2.44 %	2.43 %
ELASTICITY MODULUS -CYLINDERS		
Number of specimens	3 (1 batch)	3 (1 batch)
Arithmetic Mean	12.60 GPa	11.57 GPa
SD - Standard Deviation	0.32 GPa	0.17 GPa
COV- Coef of Variation	2.57 %	1.50 %
MAXIMUM STRAIN -CYLINDERS		
Number of specimens	3 (1 batch)	3 (1batch)
Arithmetic Mean	10.45 ‰	15.99 ‰
SD - Standard Deviation	0.24 ‰	0.35 ‰
COV- Coef of Variation	2.26 %	1.59 %
POISSON'S RATIO -CYLINDERS		
Number of data	2 (1specimen)	2 (1 specimen)
Arithmetic Mean	0.26	0.22

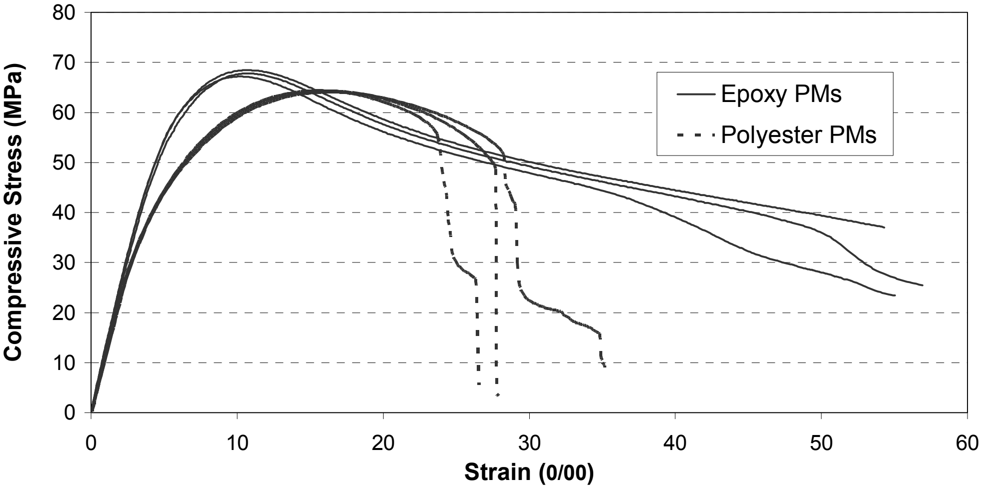

Fig. 4.12. Stress-strain curves obtained from compression tests (cylinder specimens).

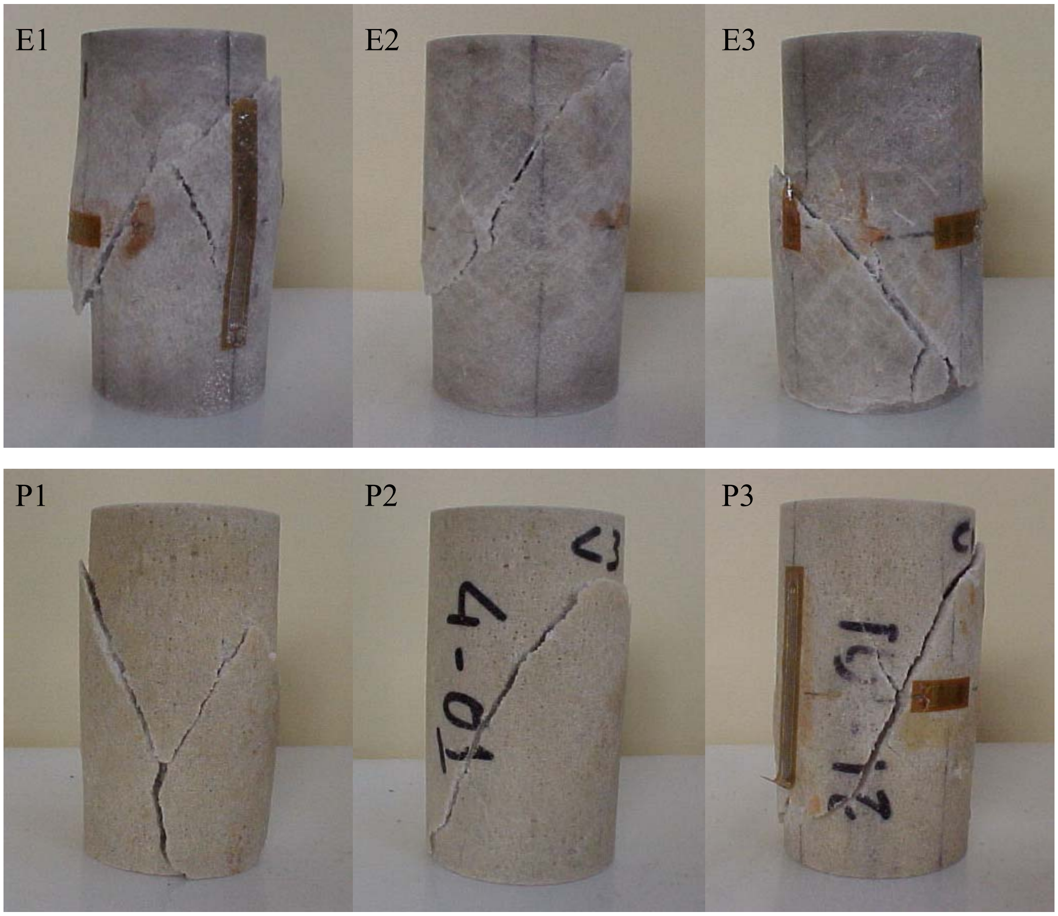

Fig.4.13. Typical failure modes of cylinder PM specimens tested in compression: epoxy PM specimens (E1, E2 and E3) and polyester PM specimens (P1, P2 and P3).

Failure Mode:

For both formulations, cylinder test specimen failed, mostly, in shear (eight of the nine epoxy PM specimens and seven of the nine polyester based ones). Examples of this type of failure are illustrated in Fig. 4.13, namely through images E2, E3, P2 and P3.

The angle that the crack pattern makes with the horizontal (bottom of the specimen) defines the type of failure. A cone-type failure is observed if the angle is between 0º and 45º, a shear failure if the angle is between 45º up to 70º-80º and a splitting failure if upper angle values occur. In general terms, it was observed that the angles' failure of polyester PM specimens were higher than those found for epoxy PM specimens: the other two polyester PMs failed in splitting (see image P1 of Fig. 4.13) and the last epoxy PM had a cone-type failure (see image E1 of Fig 4.13). Moreover, the disintegration of the core of tested specimens was more notorious on epoxy PM specimens than on polyester based ones. Additionally, a crosslink of micro shear cracks, oriented at 45% with reference to specimen end-surfaces, was noticed in all epoxy PM specimens immediately after the maximum load has been reached (see images E1, E2 and E3 of Fig. 4.13).

As noticed by other researchers, the polymer content, the aggregate type, the test conditions in terms of specimen confinement, and the specimen height to diameter ratio, have a great influence on the type of failure (Mebarkia 1993; Wang 1981). As these parameters were the same for both types of specimens, material characteristics, such as Poisson's ratio, material friction angle and cohesion, seem to be the single factors accountable for the differentiated observed failure mode.

Compressive Strength:

As it was expected epoxy PMs present higher compressive strength than polyester based mortars. However, this difference (9% and 15% higher for, respectively, cylinder and prismatic specimen) is not so outstanding as in the case of flexural strength, which is almost two times higher. This is in accordance with the assumed premise that flexural resistance is a better parameter for the mechanical assessment of PC materials.

Flexural to compressive strength ratios of 0.57 and 0.34 were found for, respectively, epoxy and polyester PM formulations. These ratios are much higher than similar parameters found for conventional cement concretes (around 0.2), mainly due to the great flexural resistance of PMs, especially of epoxy based ones.

Obtained compressive strengths of PM formulations were within the usual range of values obtained for polyester and epoxy PMs.

Cylinder/Cube Strength Ratio:

For both formulations, compressive tests performed on 'modified cubes' of prismatic specimens led to slight higher values of compressive strength (around 7.5% and 1.5% higher than compressive strength values of, respectively, cylinder epoxy and polyester mortar specimens). A higher difference was expected taking into account the following:

- The restraining effect of the platens of the testing machine, which extends over the entire height of the cube but leaves unaffected a part of the test cylinder, generally leads to higher ultimate strengths on compression tests of cube specimens;
- The different equivalent sizes of the specimens (it would be expected that a cube with 4 cm height had an ultimate strength higher than the equivalent cube with 10 cm height);
- The restraining effect of the overhanging parts of the 'modified cube', which, is reasonably to assume, that would have a slight increasing effect on the ultimate strength.

Nevertheless, considering the small size of the samples and the high scatter of data found for epoxy cylinder specimens tested in compression, no reliable conclusions could be made regarding the cylinder/cube strength ratio of PM formulations. However, the obtained results allow that, in the future, compression test of 'modified cubes', jointly with flexural tests, could be used as a comparative test to assess and/or control the quality of PM batches. No different specimens (cylinder) are required and the same control prismatic specimens used for bending tests can be reused for compressive tests.

Elasticity Modulus:

Secant elasticity modulus of epoxy PM specimens is slight higher than polyester based mortars. The same pattern was observed for initial tangent elastic modulus. Both obtained values are closer to the lower limit of the common range of values found for PC materials.

Several formulas have been derived from which the compressive modulus of elasticity can be calculated for composite materials when the moduli of the component materials are known. With the purpose of comparing the theoretical limits of the elasticity modulus with the experimental data, the expression purposed by Hansen (1965) was applied:

$$E = 1 / [(V_1/E_1) + (V_2/E_2)]^{-1} \tag{4.19}$$

where E is the elasticity modulus of the two-phase material; E_1 and E_2 are the elasticity modulus of component materials; and V_1 and V_2 are the respective fractional volumes.

Equation (4.19) is based on the assumption that the average stress in a two-phase material is the same in the matrix and in the particles, conversely to the rule of mixtures (Kevin-Voigt model), which assumes that the average strain in the material is the same in the components. Neither the approximation of uniform strain nor of uniform stress is in fact correct, but the former leads to an upper limit and the latter, in principle, gives a lower limit. It would expect that Eq. (4.19) is more adequate to PM since its matrix has a much lower modulus of elasticity than does its aggregates.

Assuming an elasticity modulus between 45 GPa and 65 GPa for foundry sand, which is a common range of values given in the literature for silica aggregates (Neville 1995), the lower and upper limits found for the elasticity modulus of PM formulations were within the following ranges:

- Epoxy PM: [7.2 to 7.4 GPa; 25.2 to 36.0 GPa]
- Polyester PM: [10.2 to 10.7 GPa; 27.0 to38.4 GPa]

The lower elasticity modulus of epoxy resin and the higher air content of epoxy PM formulation are probably the major factors accountable for the lower theoretical limit values found for this formulation.

A higher lateral to longitudinal compressive strain ratio was found for epoxy based mortars comparatively to polyester based ones. The value for the latter is within the range of values usually found for conventional concrete materials (between 0.15 to 0.22).

Stress-strain curves:

As it can be observed through stress-strain curves plotted in Fig. 4.12, a higher stiffness is shown by epoxy PM specimens than by polyester based mortars. The determined secant elasticity moduli (at 40% of peak stress) do not reflect this large difference in stiffness of the two materials. The ascending branch of stress-strain curves of epoxy PM specimens is not only steeper, but also almost linear up to 60% of maximum stress, whereas polyester based mortars present rather a more ductile behavior, with corresponding ascending branches approximately linear only up to 40% of peak stress.

As in the case of ordinary concrete, the deviation from linearity indicates the propagation of bond microcracks at the interface between the matrix binder and the aggregates. As a result, there is a reduction in the effective area resisting the applied load, so that the local stress is larger than the nominal stress based on the total cross-section of the specimen. These changes cause that the strain increases at a faster rate than the nominal stress, and so stress-strain curve bends over, and becomes increasingly non-linear. Viscoelastic nature of polymer binder may also contribute to increase the non-linearity of stress-strain curve as polymer chain slipping, in addition to chain coiling (bending of bond angles), cause plastic deformation in the polymeric phase of PMs. Thus, it seems that microcracks propagation and/or polymer chain slipping phenomena start earlier in polyester based mortars than in epoxy based ones.

With increasing applied stress, matrix cracks, connecting to bond cracks, begin to form much more extensively. The development of this continuous crack system, reducing progressively the number of load carrying paths, leads to the stress-strain curves bend to an increase rate until the ultimate strength of the specimen is reached. Until this point, polyester PM specimens withstand much more strain than epoxy mortars do (an average strain at peak stress of 16‰ was found for polyester PMs against 10.5‰ for epoxy based mortars).

Post-peak behavior is also very distinct for both PM formulations. Descending branch of polyester PM formulation is almost symmetric to the ascending part, but it has a limited extension as a brittle failure occurs at compressive strains around 25‰ to 30‰ (approximately at 80% of maximum capacity load). Conversely, softening branch of epoxy PM specimens is less steep than the ascending part and greatly larger than in the case of polyester based mortars. Furthermore, no brittle failure was observed. Instead, a progressive and steadily loss of load capacity occurs as compressive strain increases.

For this last formulation, it is difficult to define a criterion for failure. Ultimate strain has been defined as the strain at which, for above corresponding stress, Poisson’s ratio increases sharply. This is caused by extensive vertical cracking, and at this stage (collapse stage), concrete is no longer a truly continuous body and its behavior is similar to a soil

(Neville 1995). In terms of stress-strain curve, for lightweight concrete, it is usual to associate this discontinuity moment to the point, above which, descending branch becomes convex, with reference to strain axis, tending to a horizontal line (Arnould and Virlogeux 1986). As shown in Fig. 4.12, no point with the above description can be found. After inflexion points, slopes of descending branches tend to stabilize, becoming almost constants. In face of the above, and taking into account that no transversal strain data was available after peak stress, ultimate strain was considered around 35‰, as the strain above which, a significant change in the slope of at least one of the descending branches occur.

ii) Stress-strain relationships

Empirical relationships, correspondent to Eqs. (4.17) and (4.18), versus experimental test data, are plotted in Fig. 4.14 for both formulations.

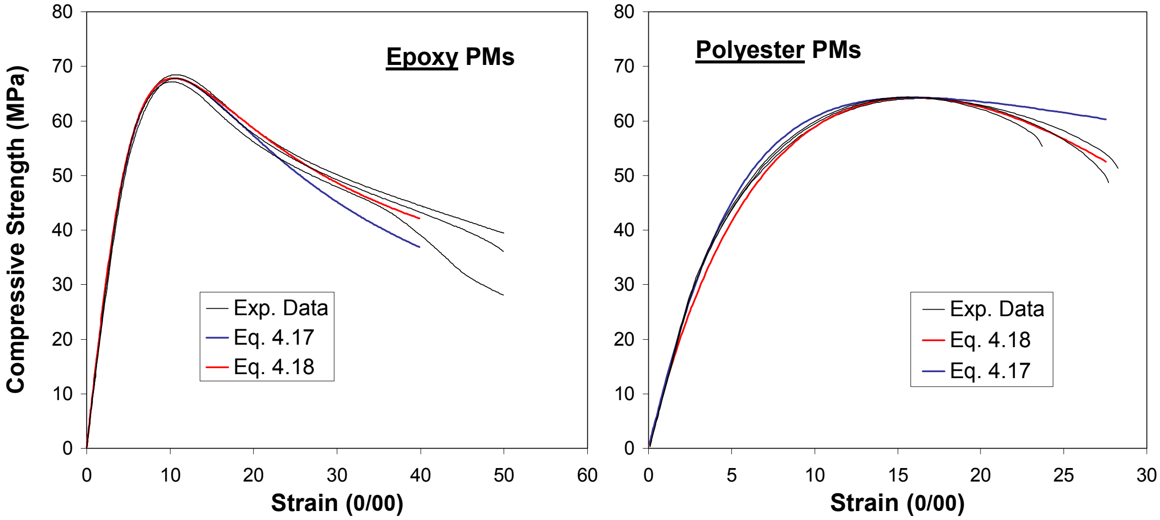

Fig. 4.14. Comparison of stress-strain empirical relationships to the experimental data.

The parameters and constants of applied equations that better fit experimental data are shown in Table 4.10. The average values of compressive strength, strain at peak stress, secant elasticity modulus at peak stress ($E_c = f_c / \varepsilon_c$), and initial tangent elastic modulus were used to determine the parameters q and k. Initial tangent elastic modulus was determined through experimental strain-stress curves (average values of 13.93 GPa and 12.36 GPa were found, respectively, for epoxy and polyester PM formulations).

Table 4.10. Parameters of the empirical stress-strain relationships.

Parameters of equations		Epoxy PM	Polyester PM
CARREIRA ET CHU	EQ. 4.17 – q	0.465772	0.325151
SARGIN	EQ. 4.18 – k	2.146114	3.075494
	EQ. 4.18 – k'	1.331114	0.000494

As shown in Fig. 414, the two-parameter relationship purposed by Sargin, defined by Eq. (4.18), shows the best agreement with the experimental data, for both types of PM specimens.

For conventional cement concrete, experimental studies show that the theoretical curve that best fit experimental data is always between the two curves correspondent to $k' = k-1$ and $k'= 0$. The former is representative of the compressive behavior of ductile cement concretes with weak resistances, whereas the later (symmetric parabola) is rather representative of brittle concrete materials with high resistance (Arnould and Virlogeux 1986).

The above statements concerning the relationship between k' value and stress-strain behavior are, partially, in agreement with obtained results, as explained in the following:

- On one hand, stress-strain curves of polyester PMs are clearly representatives of ductile materials with pseudo-plastic behavior, with soft bending curvatures near the peak, either for the ascending part or for the descending branch. In the same manner, for epoxy PMs, the ascending curves and the first parts of the descending branches, immediately after peak stresses, being steeper, are rather characteristics of stiffer materials. These features are in disagreement with the physical mean of k' values found for both formulations.
- On the other hand, polyester PMs present a brittle failure. Collapse does not occur immediately after peak stress, but it is clearly a brittle failure, with total loss of capacity load, which is in agreement with value found for k' parameter($k' \cong 0$). In the same manner, descending branch of epoxy PMs, after the initial post-peak drop,

become progressively smoother and less steeper, with the strains increasing a faster rate than the nominal applied stress. This is also in agreement with the physical mean of *k*' value found for this formulation (*k*'= *k*-0.82).

Regardless of the validity, or not, of physical mean of *k'* parameter when applied to PC materials, Sargin empirical stress-strain relationship, with the determined *k* and *k*' parameters (Table 4.10) and average values of cylinder compressive strength and strain at peak stress given in Table 4.9, can be applied with success to modelling compressive stress-strain behavior of PM formulations.

iii) Overall comparison with ordinary concrete materials

In the global sense, similarities in fact exist between stress-strain behavior of PC materials and conventional concretes. However, significant differences also coexist. PC materials withstand much more strain than ordinary concretes do, and this feature is greater the lower the loading rate. Strains corresponding to peak stress as high as 8‰ to 14‰ are commonly found in PC materials, which is four to seven times more than the usual values observed in ordinary concretes. This implies that polymer based concrete is a more ductile material than Portland cement concrete. This characteristic arises from the viscoelastic nature of matrix binder.

The overall stress-strain behavior of PC materials may be considered, as this way, as governed majority by two distinct phenomena:

- Crack growth in the composite structure, which is presumed to be at some extent similar to crack growth in ordinary concrete;
- The elastic and plastic deformation of polymeric binder matrix, which is presumed to be analogous to that of the plain polymer. Coiling and slipping of polymeric chains are here considered as the main mechanisms accounted for those deformations.

Thus, some of the PC material's behavior can be understood by considering the known behavior of regular concrete, and some of its behavior can be understood by examining the behavior of polymers.

4.3.3 Tensile Properties

There are three types of test for strength in tension: direct tension test, flexure test, and splitting tension test.

A direct application of a pure tension force, free from eccentricity, is very difficult to obtain. To avoid secondary stresses such as those induced by grips or embedded studs is a complicated and complex process that is not easily reached most of the times. On the other hand, these tests usually require special shapes for the test specimens not easily obtained by casting. In consequence of this, direct tensile tests are rarely used to determine tensile strength of concrete materials. Instead, indirect tensile tests such as flexural or splitting-tension tests are preferred.

The splitting tensile test is simple to perform, does not require unusual specimen types and gives more uniform results than direct tensile tests. The strength determined in the splitting test is believed to be closed to the direct tensile strength of the concrete, being 5% to 12% higher (Neville 1995). However, some studies indicate that, in the case of mortar and lightweight aggregate concrete, the splitting test yields to low a result (Hannant et al. 1973).

In flexure tests, the maximum tensile stress reached in the bottom fibre of the test specimen also gives an indirect measure of tensile strength. The four-point bending test, with the load points spaced at one-third of the span, offers some advantages over the three-point bending test. The former is considered to be more reliable and realistic in the sense that more elements are subjected to the critical stress (Hammant 1971; Tarnopol'skii and Kincis 1984). Under four-point bending, one-third of the length of the bottom fibre is subjected to the maximum stress, so that the probability of a weak element occurring is higher than in the case of centre-point loading, in which, only the elements of the extreme fibre, immediately behind the load line, are subjected to the maximum stress. It follows that modulus of rupture given by three-point bending tests are usually higher than those determined by four-point bending, being both higher than direct tensile strength.

There are additional possible reasons, besides the influence of loading arrangement, why the modulus of rupture test gives a higher value of strength than a direct tension test made on the same material. First, the issue already mentioned in point 4.3.2.1, the modulus of rupture is determined with basis on the elastic beam theory, in which the stress-strain relation is assumed to be linear; however, in tension, the departure from linearity of the stress-strain relation occurs at stress/strength ratios of around one-half (Neville 1995). Second, in the flexural test, the maximum stress reached may be higher than in direct tension because the less-stressed fibres, nearer the neutral axis, hinder the propagation of eventual cracks.

Comparative experimental studies showed that the correct value of tensile strength for concrete materials is around 75% of the theoretical modulus of rupture given by the four-point bending test (Raphael 1984).

In the present study, tensile strength of PM formulations was assessed by both indirect tensile tests: splitting tensile test and four-point bending test. Additionally, flexural-tensile elasticity modulus was also determined, directly, by means of stress-strain curves obtained from flexural tests.

4.3.3.1 Test and calculation procedures

i) Splitting tensile test

The splitting tension tests were conducted on cylinder specimens, with 50 mm diameter and 100 mm height, according to RILEM PC-6 test method (1995d). All test specimens, three for each formulation, received the usual curing treatment before being tested in splitting at room temperature. Prior to testing, the end surfaces of the test specimens were trimmed with a diamond-blade saw to make it easier to measure the length.

The tests were performed in a Universal testing machine INSTRON, with a load cell of 300 kN., shown in Fig. 4.15, at LABEST facilities (Laboratory of Civil Engineering Structures of Faculty of Engineering of Porto). The specimens were placed horizontally at the centre of the bearing plates to prevent any eccentricity in loading, and the lower and upper bearing plates were maintained parallel during loading. Load was then applied, in load-control mode, at a constant rate of 0.7 kN/s until failure.

Splitting tensile strength, $f_{\mathrm{sp,t}}$, was determined by the following equation:

$$f_{\mathrm{sp,t}} = 2P / \pi DL \tag{4.20}$$

where P is the maximum load recorded; D is the specimen diameter and L is the specimen length.

In the splitting tensile tests, immediately under the line load, a high compressive strength is induced and in practice, in order to assure that failure in compression does not take place, the related standards prescribe that narrow strips of a packing material are interposed between the cylinder and the platens (ASTM C496-90; BS 1881 117:1983). Without packing strips, the recorded strength is lower, typically, by 8%. Since no packing strips were applied, obtained results were rectified by an increment of 8.7%.

ii) Four-point bending test

In order to determine the modulus of rupture, four-point bending tests were performed on standard prismatic specimens (40×40×160 mm^3) of both PM formulations, following the procedures described in RILEM PC-7 test method (1995e). The universal testing machine INSTRON with a load cell of 100 kN was used for that purpose. Load points were spaced at one-third of the span with an overall length of 100 mm. Load was applied in displacement control mode at the loading rate of 1 $mm.min^{-1}$. All specimens, three for each formulation, received the usual curing treatment before being tested in four-point loading at room temperature.

In order to determine an accurate and reliable value for flexural elasticity modulus (see section 4.3.1.2), specimens were instrumented with one wire strain gage bonded at the mid-span of the outer tensile surface. Strain, deflection and load data were recorded through a data logger with a continuous acquisition system (Spider 8).

The modulus of rupture was determined according to equations (4.21) or (4.22), as function of fracture position: inside or outside the load points.

$$f_{\mathrm{fl,t}} = \mathrm{PL} / \mathrm{bd}^2 \tag{4.21}$$

$$f_{\mathrm{fl,t}} = 3\mathrm{Pa} / \mathrm{bd}^2 \tag{4.22}$$

where $f_{\mathrm{fl,t}}$ is the flexural strength; P is the maximum load recorded; b and d are, respectively, the width and the depth of the beam; and a is the distance of the fracture from the near support (average distance measured on the tension surface).

Secant elasticity modulus was determined through stress-strain curves calculating the stress to strain ratio at 50% of maximum deflection.

4.3.3.2 Test results and discussion

i) Splitting tensile strength

Splitting tensile test results (without rectification) are presented in Table 4.11. Obtained load-displacement curves are also plotted in Fig.4.15.

Table 4.11. Splitting tensile test results of PM formulations.

Splitting Tensile Strength Statistical Parameters	Epoxy PM	Polyester PM*
Arithmetic Mean	17.44 MPa	12.07 Mpa
SD – Standard Deviation	0.53 Mpa	0.37 Mpa
COV- Coef of Variation	3.0 %	3.1 %

* Test results of specimens proceeding from posterior batches.

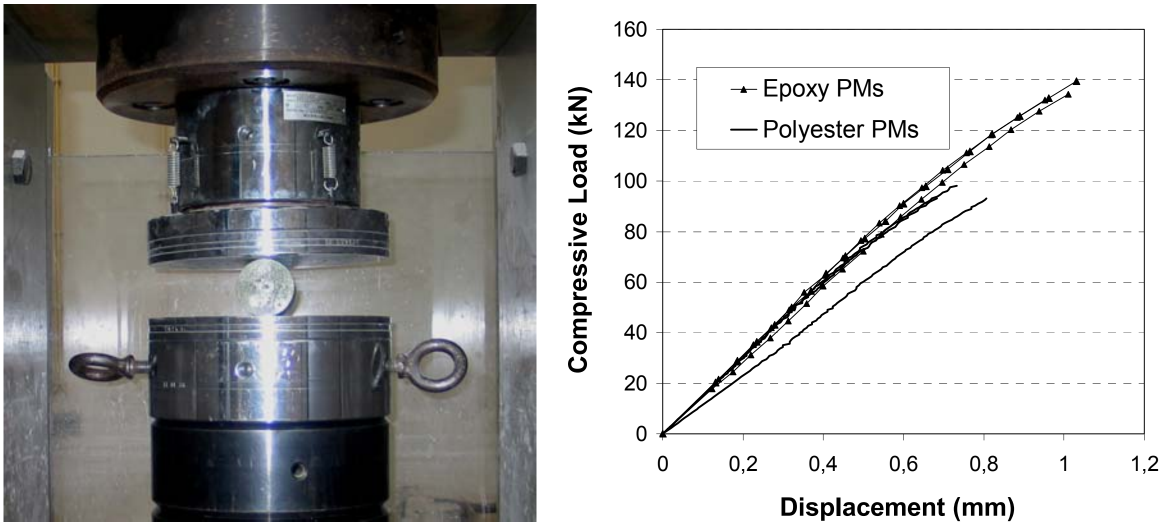

Fig. 4.15. Splitting tensile test set-up (at left) and load-displacement curves obtained from correspondent tests performed (at right).

ii) Four-point bending strength

Four-point bending test results, in terms of modulus of rupture, maximum tensile strain, and secant elasticity modulus, are presented in Table 4.12. In Fig. 4.16, correspondent stress-strain curves are plotted.

For all tests performed, fracture occurred inside the load points, therefore, modulus of rupture was determined according to Eq. (4.21).

Table 4.12. Four-point bending test results of PM formulations.

Flexural Properties Statistical Parameters	Epoxy PM	Polyester PM*
FLEXURAL STRENGTH		
Arithmetic Mean	25.82 Mpa	16.99 Mpa
SD – Standard Deviation	1.07 Mpa	0.81 Mpa
COV- Coef. Of Variation	4.2 %	4.8%
MAXIMUM TENSILE STRAIN		
Arithmetic Mean	3.08 ‰	3.74 ‰
SD – Standard Deviation	0.08 ‰	0.22 ‰
COV- Coef. Of Variation	2.6 %	5.8 %
SECANT ELASTICITY MODULUS		
Arithmetic Mean	9.82 Gpa	9.74 Gpa
SD – Standard Deviation	0.48 Gpa	0.51 Gpa
COV- Coef. Of Variation	4.9 %	5.2%

* Test results of specimens proceeding from posterior batches.

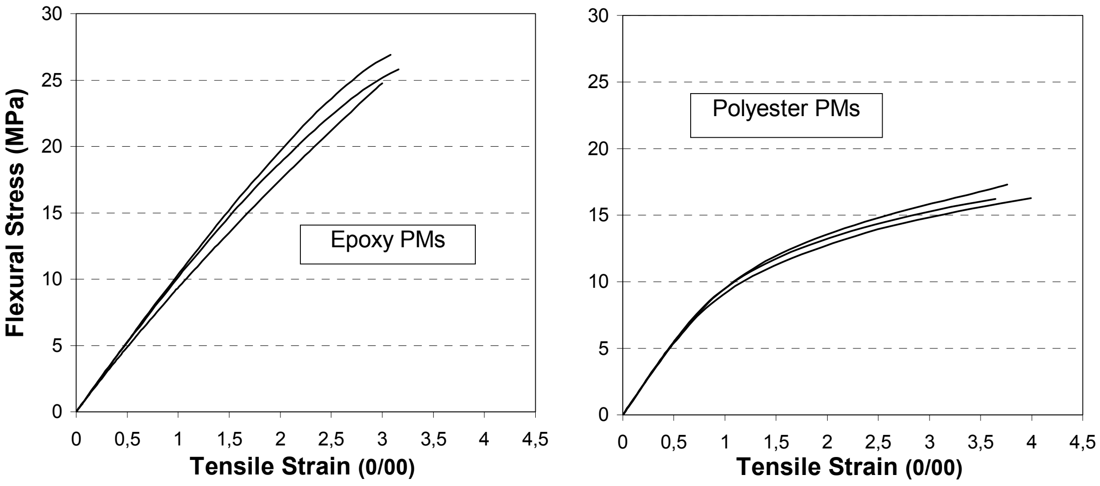

Fig. 4.16. Stress-strain curves obtained from third-point loading tests performed on instrumented prismatic specimens of both PM formulations.

As in compression tests, a higher stiffness is shown by epoxy PM specimens than by polyester based mortars, as it can be observed through stress-strain curves plotted in Fig. 4.16.

Once again, the determined flexural elasticity modulus does not reflect this distinct behavior. Departure from linearity of the stress-strain relations occurs at similar stress/strength ratios for both formulations, between 45% and 50%, but, after this point, the stress-strain curves of polyester based mortars bend drastically comparing with those of epoxy PMs. In spite of the higher flexural-tensile strength reached by epoxy mortars, a higher tensile strain is sustained by polyester based mortars until failure.

Flexural-tensile elasticity modulus values, obtained directly from stress-strain curves, are coherent with material composition as well as with determined compressive elasticity modulus. Therefore, hereinafter they will be assumed as the 'correct' ones.

iii) Tensile strength

With basis on both indirect tensile test results, the following relationship could be used to estimate the average direct tensile strength, f_t, of PM formulations:

$$f_t = [\alpha\, \beta\, f_{sp,t} + \beta'\, f_{fl,t}] / 2 \tag{4.23}$$

where $f_{sp,t}$ and $f_{fl,t}$ are, respectively, the average splitting tensile and four-point bending strength values, presented at Tables 4.11 and 4.12; α is the correction parameter for the effect of the lack of packing strips on splitting test (α=100/92); and β, β' are the correlation factors between direct tensile strength and, respectively, splitting tensile and four-point bending strengths (β = 1/1.12 to 1/1.05 and β'= 0.75).

Obtained estimating results are presented at Table 4.13.

Table 4.13. Estimation of direct tensile strength of PM formulations.

Direct Tensile Strength	Epoxy PM	Polyester PM
By means of splitting strength	16.92 to 18.05 MPa	11.71 to 12.49 MPa
By means of four-point bending strength	19.36 MPa	12.74 MPa
Arithmetic Mean	18.14 to 18.70 MPa	12.22 to 12.62 Mpa

The obtained indirect tensile strengths and the correspondent estimated direct tensile strengths are within the range of values usually obtained for these materials. The higher strength values found for epoxy based mortars are in accordance with the higher bond capacity and greater adhesion to mineral aggregates of epoxy resin binder.

Estimated tensile to cylinder compressive strength ratios between 0.26 and 0.27, and between 0.19 and 0.20 were found, respectively, for epoxy and polyester PM formulations. For ordinary concrete, the same ratio varies in general between 0.07 and 0.11. The relative high ratio of tensile to compressive strength of PM formulations (and PC materials in general) is mainly due to the tighter bonding between the polymeric binder and the aggregates, since the cracking of ordinary concrete is usually initiated from the interfaces of cement paste and aggregates.

However, it is interesting to note that, the same way as for ordinary cement concretes, the ratios of the nominal tensile and compressive strengths vary in a similar manner than the Poisson’s ratios and between approximately the same limits. The higher the Poisson’s ratio, the higher the tensile to compressive strength ratio.

For cement concrete materials, there are strong indications, that is not a limiting compressive strain, but a limiting tensile strain that determines the strength of concrete under compressive static loading. It has been found that, at the point of initial cracking, the strain on the tension face of a beam in flexure and the lateral tensile strain in a cylinder in uniaxial compression are of the same magnitude (Neville 1995). It is, therefore, possible that compressive failure is governed by the lateral strain induced by Poisson’s ratio, since for elements sufficiently removed from the platens of the testing machine, lateral strain can exceed the ultimate tensile strain of concrete. Failure occurs then by splitting, at right angles to the direction of the load, and this has been frequently observed, especially in specimens whose height is greater than their breadth (Yin et al. 1989).

In the case of epoxy and polyester PM formulations, lateral tensile strain induced by Poisson’s ratio in the cylinder specimens during compression tests, was estimated as equal, respectively, to 89% and 94% of correspondent ultimate tensile strains. It follows that the conditions of tensile failure were not achieved before the limiting compressive strain of PM specimens has been reached. However, concrete failure is a complex process not yet well understood, even for ordinary cement concretes. Several mechanisms are involved, and therefore the hypothesis that some PM specimens failed in compression tests due to tensile strains induced by Poisson’s ratio cannot be disregarded, especially in the case of polyester PM specimens.

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V. DURABILITY STUDY OF PM FORMULATIONS

5.1 Introduction

5.1.1 General

Durability is one of the most important features of a construction material.

Neville defines this attribute as the '*ability of the material to withstand the processes of deterioration to which it can be expected to be exposed'* (Neville 1995). Until recently, there was a wrong assumption that 'strong material is a durable material' and as a result, the developments in construction material technology have concentrated on achieving higher and higher strengths. It is now known, that, for many conditions of exposure of building materials, especially of those with structural role, both strength and durability have to be considered explicitly at the design stage. However, it will be a mistake to replace overemphasis on 'strength' by overemphasis on 'durability'.

It is essential that every construction material should continue to perform its intended functions, *i.e*. it should maintain its required strength and serviceability during the specified or traditionally expected service life.

Polymeric composite materials are one of the youngest construction materials and the ones that are appearing time after time, with new and changed properties, as new combinations and formulations are developed. Therefore, long-term behavior of these materials cannot be deduced from experience with the material over the expected lifetime or from long-time tests (Letsch 2001a). Regardless of their significant advantages over conventional construction materials, mechanical and durability properties are highly susceptible to the type of polymer and reinforcement (or aggregate) employed, as well as to the content of both components (Pardo et al. 1995).

The number of possible formulations (ingredients and proportions) that can be used to produce polymer composite materials is limitless. Therefore, the results of previous research are often applicable only to that particular material. Even if certain consistencies may exist, they always must be verified.

Hence, it is necessary to study the rate of degradation of each specific PC formulation when subjected to different aggressive environments, as this rate varies as function of the matrix type (and content), is strongly affected by the adhesion between matrix and aggregates at interface, and it is also dependent of the nature and packing level of aggregates.

Considering this, the various aspects affecting the durability of developed PM formulations are the subject matter of the present chapter.

5.1.2. Causes of deterioration

Inadequate or poor durability manifests itself by deterioration, which can be due either to external factors or to internal causes within the material itself. The various actions can be physical, chemical, or mechanical.

Mechanical damage can be caused by impact, abrasion or erosion. The later will be considered towards the end of present chapter, as an effect of wind, one of the components of weather that cause degradation.

Chemical (acid and alkalis) attacks occur mainly through the action of aggressive ions, such as chlorides, sulfates, or of carbon dioxide, as well as many natural or industrial liquids and gases. This topic is discussed in section 5.2.

Physical causes of deterioration include the effects of high temperatures, freezing and thawing, thermal shocks, and also the effects of differences in thermal expansion of aggregates and of the binder matrix. The influence of these thermal factors is also analyzed in this chapter, throughout section 5.3.

Another important cause of physical damaging is fire. Behavior under fire is of paramount impact, and hence it will be discussed in chapter VI.

As emphasized by Neville (1995), it should be observed that the mechanical, physical and chemical processes of deterioration could act in a synergetic manner, as it occurs in weathering processes. Deterioration of concrete materials is rarely due to one isolated cause, and that's why, it is sometimes very difficult to assign damage to a particular factor. In section 5.4, the main components of weather that cause degradation, which include sunlight, temperature, moisture, wind, dust and pollutants, are discussed. The influence of outdoors exposure to natural weathering on material mechanical properties is analyzed. Additionally, a comparative analysis with the effects caused by accelerated artificial weathering, in salt fog and arc-xenon chambers, is also done.

At this point, a special mention must be done to a particular material characteristic, which has been considered as the main cause of material deterioration: permeability. Indeed, with the exception of mechanical damage, all the adverse influences on durability involve the transport of fluids through the material. Concrete durability largely depends on the ease with which fluids, both liquids and gases, can enter into, and move through concrete, (which is commonly referred to as permeability of concrete). For this reason, consideration of durability requires an understanding of the mechanisms involved.

In the strict sense of the word, permeability refers to flow through a porous medium. However, the movement of various fluids through concrete takes place not only by flow through the porous system but also by diffusion and sorption, so the phenomenon involved is in fact (prior to) lied to penetrability of concrete. Nevertheless, the commonly term *permeability* will be used to designate the overall movement of fluids into and through concrete.

Often permeability is misunderstood with porosity. In the pore system of concrete, there are pores of different types, some of which contribute to permeability and some of do not, and it is this feature that allows to distinguish between porosity and permeability. According to Neville (1995), *porosity* is a measure of the proportion of the total volume of concrete occupied by pores, and is usually expressed in percent. If the porosity is high and the pores are interconnected, they contribute to the transport of fluids through concrete, so its permeability is also high. Conversely, if the pores are discontinuous or otherwise ineffective with respect to transport, then the permeability of the concrete is low, even if its porosity is high.

The effect of PM permeability on its mechanical behavior is also approached throughout this chapter.

Physical limitations do not allow the present study of being extensive and exhaustive enough as it would be desirable, either in terms of the exposure times either in terms of the number of aggressive environments analyzed. Nonetheless, some of the more relevant durability issues, listed above, are here considered in the present chapter.

5.2 Chemical Durability

5.2.1 Introduction

5.2.1.1 Overview

There have been several publications on deterioration of Portland cement concrete when exposed to corrosive chemical agents (Attiogbe and Rizkalla 1988; Fattuhi and Hughes 1988; Hendrik and Orbison 1987; Kurashidge and Uomoto 2001), however, little information is available concerning the resistance of polymer concrete and mortars to those aggressive environments, especially over a long period of time.

Previous literature on polymer-metal composites showed that one of the most common aggressive environments is water (Kinlock 1987). Within this scope, Ohama (1977) studied the resistance of polyester PC to hot water as found in the construction works in hot spring areas or chemical plants. Cylindrical PC specimens, with five different polyester matrixes, were immersed in boiling water for up to 1 year before being tested in compression and splitting tension. He concluded in general, that with additional immersion time, the erosion depth of polyester PC specimens tends to increase, and the compressive and tensile strengths tend to decrease, with no remarkable appearance or weight change.

Mebarkia and Vipulanandan (1995) also investigated the behavior of polyester PC and polyester polymer when exposed to water, over a maximum period of 1 and 3 years respectively. After one-year immersion, a strength decrease of more than 30% was observed on PC specimens. On the other hand, immersion of polyester polymer specimens in water for 3 years resulted in less than 5% decrease in strength. It was concluded that water diffusion into the PC affected the interface rather than the polymer.

The limited studies on PC have shown, in general, the superior chemical resistance of this kind of material over Portland cement concrete when subjected to a wide range of chemical environments, such as acids, alkalis, and petroleum products.

Yammamoto (1987) immersed Portland cement and polyester resin mortar specimens in 10% hydrochloric acid and 10% sulphuric acid solutions for a period of 28 days. No loss in weight was observed for the polymer mortars; however, cement mortar specimens lost about 50% of their initial weight.

Mebarkia (1993) analyzed the changes in compressive and splitting tensile strength of polyester PC, after one-month immersion, in chemical solutions with various pH levels . It was observed that the strength of PC decreased with the increase in pH level of the chemical solutions.

Ohama and co-workers (1986a) also investigated the effect of 11 typical reagents for industrial uses in the compressive strength of polymethyl methacrylate concrete. Test results showed that this kind of material is seriously attacked by acetone and toluene, and slightly attacked by hydrochloric, sulfuric and acetic acids. Conversely, it shows good resistance to tap water, alkali, salts, kerosene and rapeseed oil.

Chawalwala (1996) studied the application of vinyl and polyester PC, with basalt aggregates, as a wear overlay surface for a composite bridge deck. The behavior of these PCs when exposed to water and chemicals, such as motor oil and antifreeze solutions, was investigated. Test results showed that basalt based PC systems were particularly affected by water (water immersion and diluted antifreeze), and property losses were primarily due to the weakness of the interface between the aggregate and the polymer matrix phases, which depends on the absorbed water content.

Griffiths and Ball (2000) conducted a research work on degradation processes of glass-fibre-reinforced polyester PC (GFR PC). The deterioration of flexural strength of GFR PC specimens after immersion in several chemical solutions for varying periods was evaluated. Exposures to water, gasoline, diesel fuel, engine oil, saline, alkalis and acid solutions were considered. No measurable degradation of polyester PC occurred after three weeks exposure to water and petroleum products, and furthermore, no visible signs of deterioration were noticed. On the other hand, exposure to acids and alkalis resulted in moderate to severe strength losses, particularly in those specimens immersed in alkaline solutions. Attack of the resin/aggregate/fibre interface and deterioration of polyester matrix itself were identified as the principal mechanisms of chemical degradation.

All the above investigation works indicated that the degradation of PC materials, after exposure to water or chemical agents, is either due to weakening of the matrix material or due to the degradation of the interface. But as metioned by Chawalwala (1996), the former is likely only one part of the problem, since plain resin materials exposed to similar conditions usually degraded at a significantly lower rate than correspondent PC materials.

The contact of polymer composite materials with aggressive liquid media is accompanied by a complex range of physical and chemical processes, such as the absorption and diffusion of the medium and also the dissociation of the macromolecules. These complex processes are indubitably related to the particular nature of each material. Therefore, it is necessary to study the rate of degradation of each particular PC formulation when exposed to different chemical agents, as this rate, as stated earlier, depends on polymer binder matrix, aggregate type and on the interface between these two components.

5.2.1.2 Objective

In this subchapter, the effect of a variety of chemicals and water on the performance and durability of developed PM formulations is analyzed. For this purpose, specimens of both formulations were immersed for various periods of time, up to 12 weeks, in several liquid media simulating various environmental conditions. The liquids included water, sodium chloride, sulphuric acid and sodium hydroxide solutions. The choice for these chemical reagents is justified by the increasing use of PM and PC structures near seawater and residual waters. Chemical resistance was evaluated through the variation of bending strength and variation of mass, after immersion in test solutions. The rate of degradation with exposure time was also evaluated.

5.2.2 Experimental Program

5.2.2.1 Test specimens

The study was conducted on prismatic specimens (40×40×60 mm^3) of both formulations in analysis. For each kind of PM formulation, four batches with 18 specimens each (3 control specimens + 15 test specimens) were produced. All the specimens were allowed to cure for one day at room temperature and then post-cured at 80ºC for three hours.

5.2.2.2 Chemical resistant tests procedure

The cured specimens were tested for chemical resistance at room temperature in accordance with RILEM recommendation PC-12 TC113: 'Method of test for chemical resistance of polymer concrete and mortar' (1995b). Used test solutions were as follows:

10 % sulphuric acid	$H_2\,SO_4$	pH = 0.5
10% sodium hydroxide	Na OH	pH = 13.5
10% sodium chloride	Na Cl	pH = 7.0

A control solution of distilled water was also used according to the above specification (pH = 7). The pH levels of test solutions and water covered a wide range, from 0.5 to 13.5. Test specimens, after record of their weight, were soaked in above solutions for periods of time of 1, 7, 21, 56 and 84 days. After each immersion period, the appearance of three test specimens was visually checked, cleaned by running tap water, quickly dried by blotting they with a paper towel, and their weight was measured. Finally, they were submitted to three-point bending tests according to RILEM PCM-8 recommendation (1995c). Test results were compared with those obtained from flexural tests of the three control specimens. The test program is summarized in Table 5.1.

Table 5.1. Summary of chemical resistant test program.

Nº and Type of Specimens	Test Solutions	Immersion Periods
18 Epoxy PM specimens 18 Polyester PM specimens	10 % $H_2\,SO_4$ Solution 10 % Na Cl Solution 10 % Na OH Solution Distilled Water (Control Sol.)	0, 1, 7, 21, 56 and 84 days

5.2.2.3 Calculation procedure

Mass and flexural strength change of the specimens, after each immersion period, were calculated by equations (5.1) and (5.2), as follows:

$$\text{Mass change} = [(M_f - M_i) / M_i] \times 100 \tag{5.1}$$

where M_i is the mass (g) of the specimens before immersion; and M_f is the mass (g) after immersion period.

$$\text{Flexural strength change} = [(F_f - F_i) / F_i] \times 100 \tag{5.2}$$

where F_i is the flexural strength (MPa) of control specimens; and F_f is the flexural strength (MPa) of test specimens after each immersion period.

Accordingly, relative mass change and relative flexural strength change of the specimens, after each examination period, were calculated by equations (5.3) and (5.4):

$$\text{Relative mass change} = (M_{oi} / M_{ow}) \times 100 \tag{5.3}$$

where M_{oi} is the mass change of the specimens, after immersion in each test solution, for each examination period (%); and M_{ow} is the mass change of the specimens, after immersion in control solution of distilled water, for the same examination period (%).

$$\text{Relative flexural strength change} = (F_{oi} / F_{ow}) \times 100 \tag{5.4}$$

where F_{oi} is the flexural strength change of the specimens, after immersion in each test solution, for each examination period (%); and F_{ow} is the flexural strength change of the specimens, after immersion in control solution of distilled water, for the same examination period (%).

5.2.3 Test Results

Test results, in terms of mass change and flexural strength change (average values), for each test solution and for each kind of PM formulation, as function of immersion period, are shown in Figs. 5.1 and 5.2.

Additionally, in Fig. 5.3, flexural strength retained by PM specimens after the longest immersion period, as function of test solution is also presented.

The relative changes of mass and flexural strength, for the same immersion period, are presented in Table 5.2.

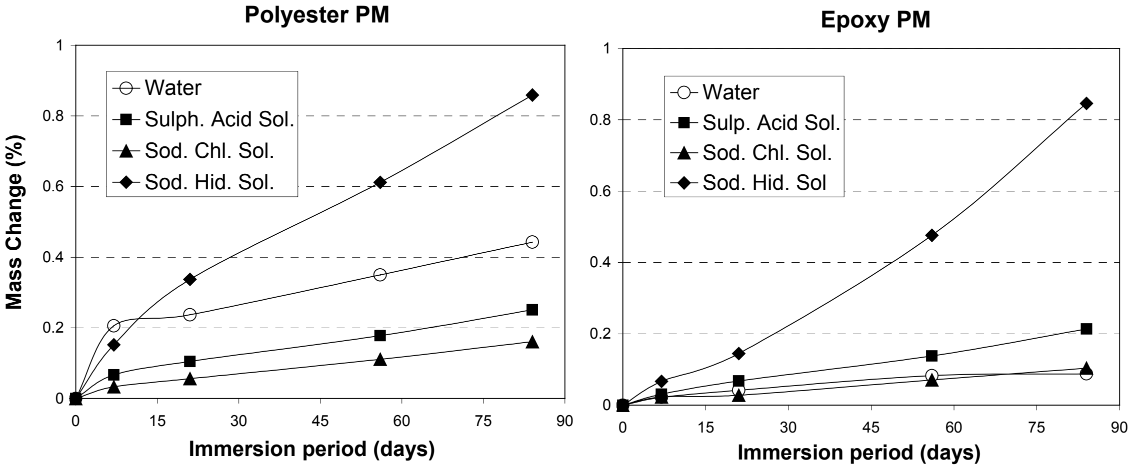

Fig. 5.1. Mass change (%) of polyester and epoxy PM specimens as function of immersion period and test solution.

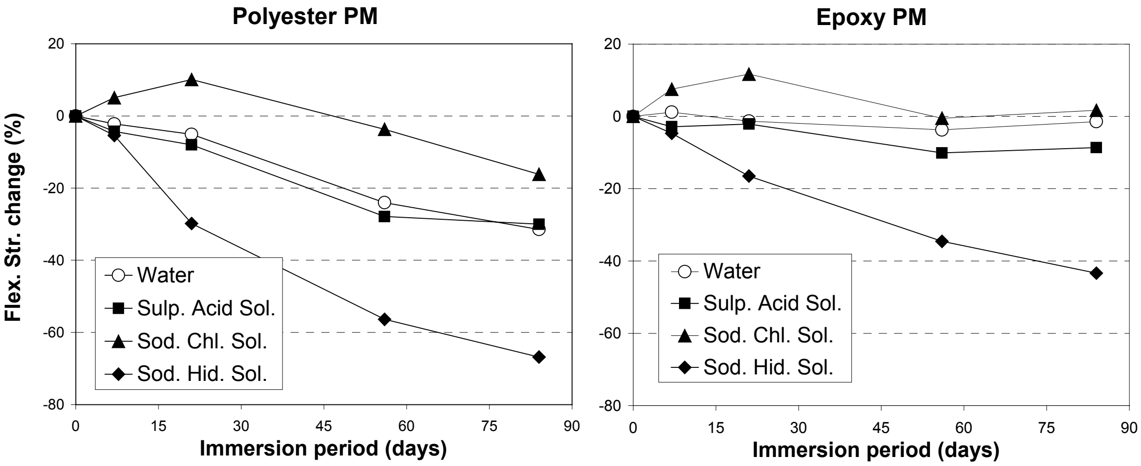

Fig. 5.2. Flexural strength change (%) of polyester and epoxy PM specimens as function of immersion period and test solution.

Table 5.2. Relative mass change and relative flexural strength change of both PM formulations after 84 immersion days in chemical test solutions.

Test Solutions	Polyester PM Relative Mass Change (%)	Relative Flexural Strength Change (%)	Epoxy PM Relative Mass Change (%)	Relative Flexural Strength Change (%)
$H_2 SO_4$	57	95	243	591
Na Cl	36	51	118	-114
Na OH	222	212	961	3271

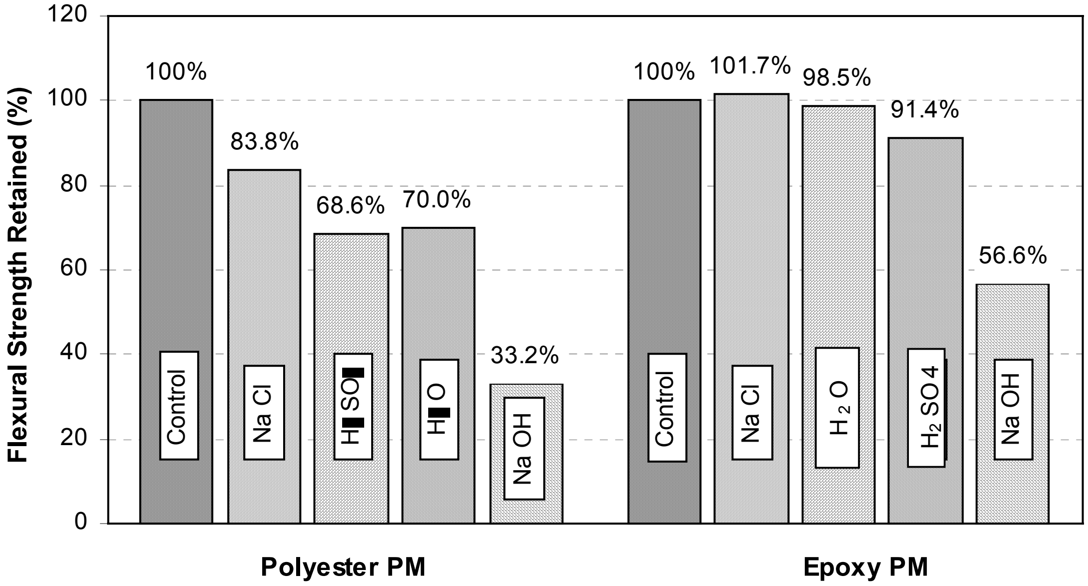

Fig. 5.3. Flexural strength retained by polyester and epoxy PM specimens after 84 immersion days in the various liquid solutions.

Other than the specimens of epoxy PM formulation immersed in sodium chloride solution, no notorious visible changes were observed after removing the specimens from the test solutions. Nevertheless, after being tested in bending, the failure surface of almost test specimens, especially polyester based ones, revealed an eroded rim or color-faded caused by water diffusion, which became larger as the immersion period increased.

The appearance change, on the exterior and failure surfaces of test specimens, after each examination period, is described in Table 5.3. The more relevant changes are illustrated in Figs. 5.4 to 5.6.

By an X-Ray microanalysis (EDS/WDS) and a scanning electronic microscopy (SEM) analysis on samples of attacked surface, it was possible to determine the chemical nature of the incrustations that appeared in the surface of some epoxy PM specimens immersed in sodium chloride solution.

The photographic record of the density map of an affected sample, obtained by scanning electronic microscopy, is illustrated in Fig. 5.7.

Table 5.3. Appearance change of PM specimens after immersion in test solutions.

Time (days)		**Polyester PM**			
		Control Solution	H_2 SO_4 Solution	Na OH Solution	Na Cl Solution
1	ES[1]	No change	No change	No change	No change
	FS[2]	No change	No change	No change	No change
7	ES	No change	No change	No change	No change
	FS	No change	No change	Slight erode rim (3 mm)	No change
21	ES	No change	No change	No change	No change
	FS	Marked erode rim (1 mm)	Slight erode rim (2 mm)	Marked eroded rim (6 mm)	Slight erode rim (1 mm)
56	ES	No change	No change	No change	No change
	FS	Marked erode rim (3 mm)	Marked erode rim (3 mm)	Marked erode rim (10 mm)	Slight erode rim (2 mm)
84	ES	No change	No change	No change	Fair whitening
	FS	Marked erode rim (5 mm)	Marked erode rim (4 mm)	Marked erode rim (15 mm)	Slight erode rim (3 mm)

Time (days)		**Epoxy PM**			
		Control Solution	H_2 SO_4 Solution	Na OH Solution	Na Cl Solution
1	ES	No change	No change	No change	No change
	FS	No change	No change	No change	No change
7	ES	No change	No change	No change	Small chestnut incrustations
	FS	No change	No change	No change	No change
21	ES	No change	Slight whitening	No change	Small chestnut incrustations
	FS	No change	No change	Slight erode rim (0.5 mm)	No change
56	ES	No change	Slight whitening	No change	Small chestnut incrustations
	FS	No change	No change	Slight erode rim (1 mm)	No change
84	ES	No change	Slight whitening	No change	Small chestnut incrustations
	FS	No change	No change	Slight erode rim (2 mm)	No change

[1] ES- Exterior surface; [2] FS- Failure surface

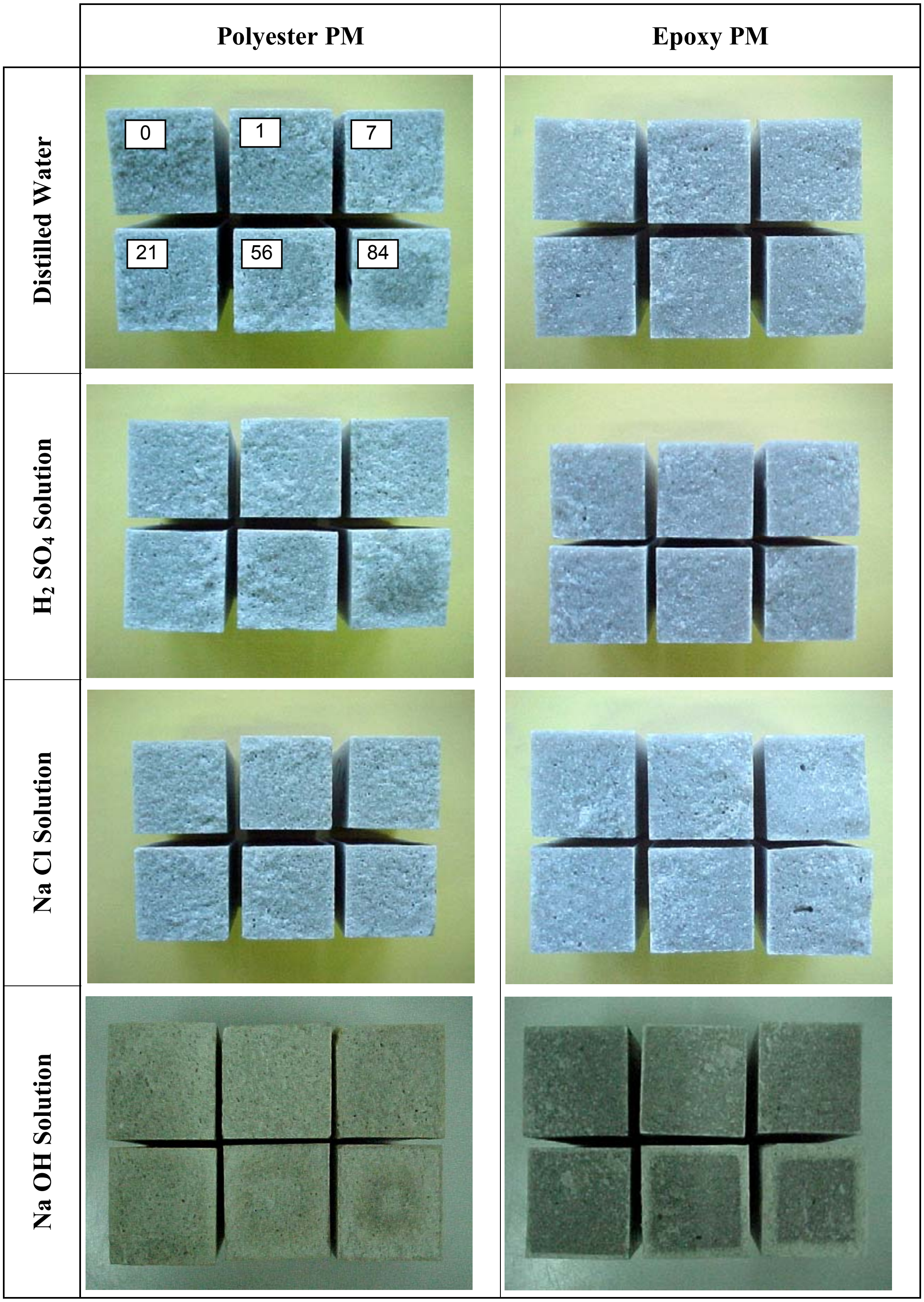

Fig. 5.4. Failure surface of control (0) and test specimens for the successive immersion periods in test solutions (1, 7, 21, 56 and 84 days).

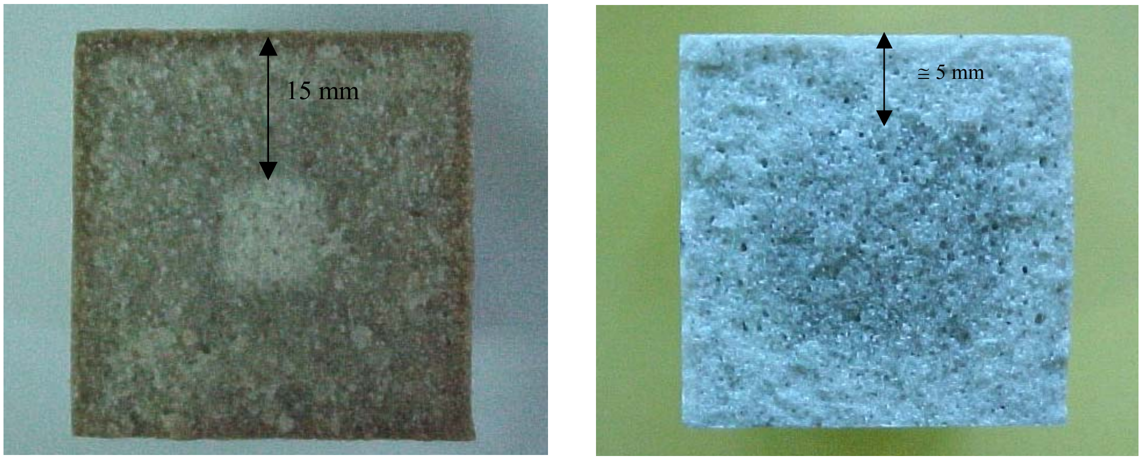

Fig. 5.5. Detail of failure surfaces of polyester PM specimens immersed for 84 days in the alkalis solution (left) and distilled water (right), where the erode rim caused by liquid medium diffusion is notorious.

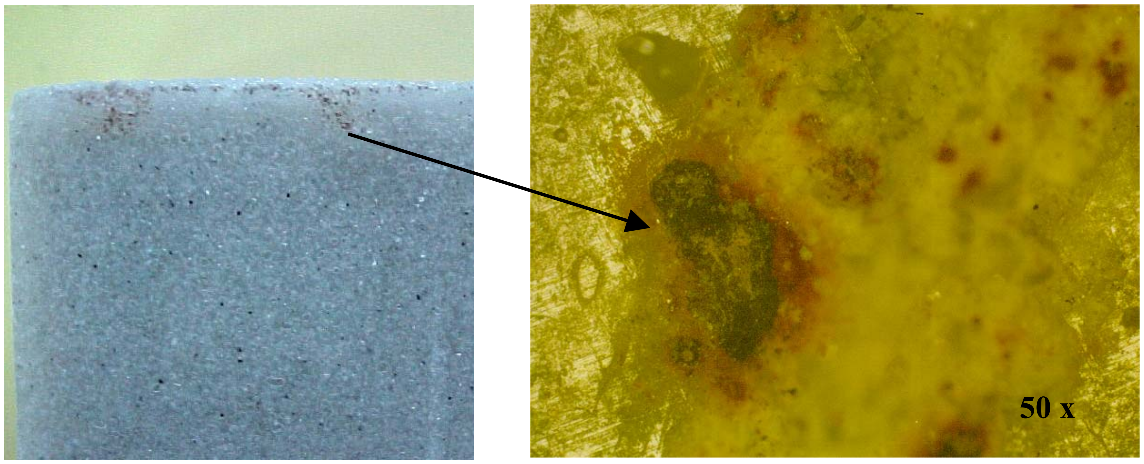

Fig. 5.6. Incrustations dark chestnut that appeared in the exterior surface of epoxy PM specimens immersed in sodium chloride solution, and correspondent record photographic obtained by optical microscopic (50x).

The chemical specters or elementary distribution profiles, obtained by X-Ray microanalysis of three different points of that sample, are also shown in Fig. 5.7:

- One point corresponding to a smooth surface of the sample (Profile I);

- Another point corresponding to an area where there was a slight detachment of concrete mass caused by demoulding process, but without chemical attack signs (Profile II);
- And finally, a third point in the edge of that detachment area in which incrustations were located (Profile III).

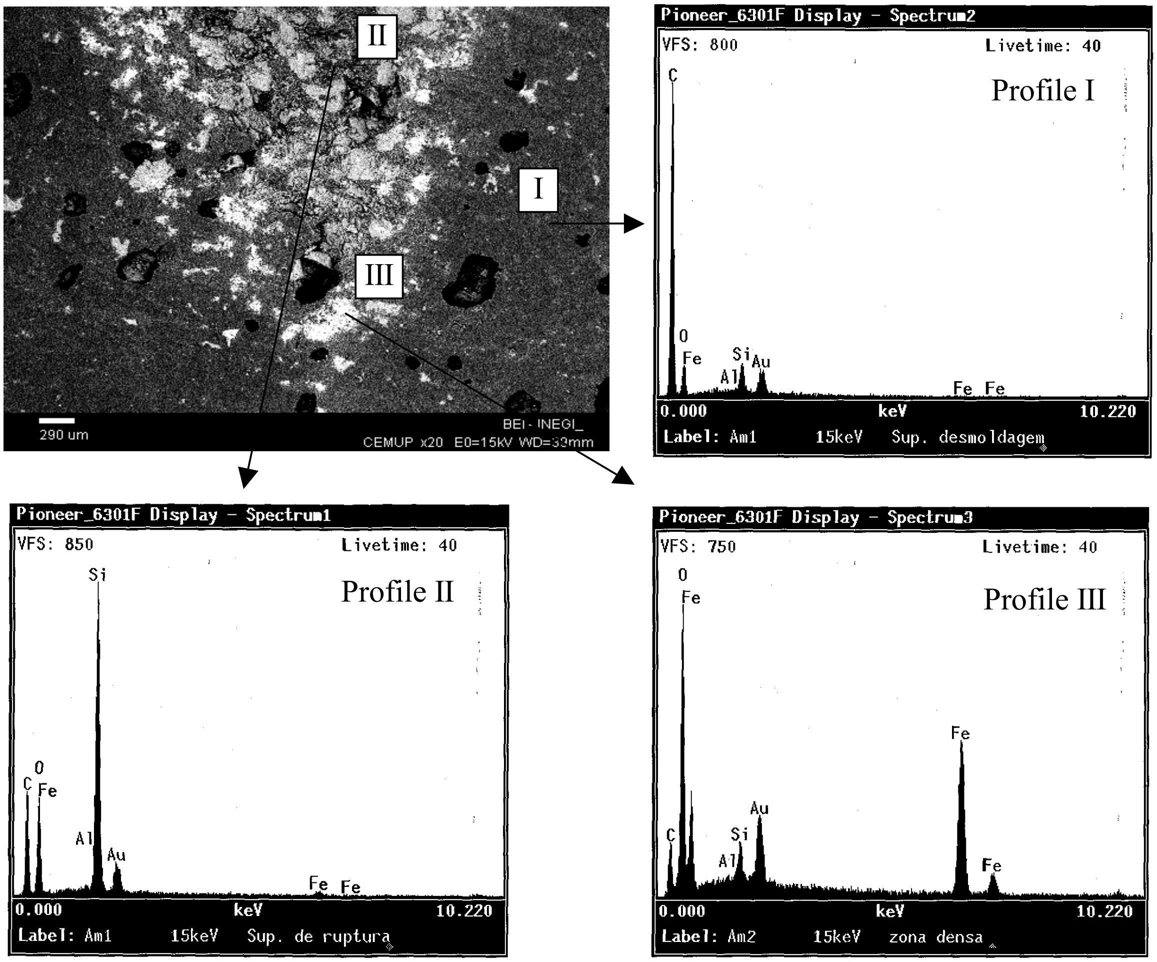

Fig. 5.7. Density map (SEM) of an affected sample of epoxy PM specimen immersed in sodium chloride solution, and elementary distribution profiles of three different points of that sample obtained by spectroscopy.

Attempting to high pattern of iron oxide present in profile III, it was concluded that the formations dark chestnut were, unequivocally, little rust incrustations. The appearance of these incrustations is probably related to the presence of iron trioxide in foundry sand constituents (0.1%). This compound, despite its little content, is unstable in alkali environments, and is reduced to iron (II) oxide, the stable form when pH increases.

Zones with slight detachments are suitable for the occurrence of this phenomenon, as in these zones, sand grains are not totally recovered with polymer binder due to abrasion process. The presence of free amine in those places, proceeding from epoxy resin hardener, creates a favorable alkali environment to oxidation process.

5.2.4 Discussion of Results

5.2.4.1 Mass variation

No scaling surfaces were noticed and no sediments were found inside solutions containers. It can therefore be concluded that weight change of all test specimens was only due to water uptake.

Other than epoxy PM specimens immersed in sodium hydroxide solution, the weight changes of this kind of PM specimens were very small and always smaller than those for polyester based specimens. The divergence of values was more significant in relation to control solution of distilled water: for 84 days immersion period, average mass change of epoxy mortar specimens was 0.09 % against 0.44 % for polyester mortar specimens.

Weight gains of polyester specimens immersed in control solution were, indeed, higher than those occurred for acid and salted solutions. It seems that the presence of acid and salt in water hinders, somehow, the sorption-diffusion process into polyester based PC materials. This phenomenon was already noticed by Aniskevich et al. (2003), who studied the influence of sorbed liquid and temperature on polyester PC creep behavior. Based on experimental results, they concluded that the presence of acid in water hampers the sorption-diffusion processes. This effect gets more expression, as the acid concentration gets higher.

For both formulations, a very high mass change occurs for specimens immersed in sodium hydroxide solution: after 84 immersion days, weight gains by polyester and epoxy mortar specimens were, respectively, up to 2 and 9 times higher than corresponding weight gains in control solution; (relative mass changes of polyester and epoxy mortar specimens were, respectively, 222 % and 961 %).

For both types of formulations, PM specimens that underwent a lesser water diffusion process were those immersed in salt solutions. An explanation for this feature may be advanced with basis on osmotic mechanisms and on the research carried out by Ashbee and co-workers (1967; 1969). They have found that disc-shape cracks, or internal microvoids, form in both epoxy and polyester resins after as little as 3 days' immersion in water at 100ºC, or 16 weeks' immersion at 60ºC. These voids have been shown to contain water and after drying out, a small amount of soluble matter is deposited in the cavity. Ashbee et al., therefore, proposed that the voids are formed by diffusion water dissolving salt impurities in the resin, and exerting osmotic pressure from within. Evidence to support this was the fact that if a salt solution was used as an immersion fluid, instead of pure water, a small amount of cracks occurred.

5.2.4.2 Flexural strength variation

Residual flexural strength of both types of PM is drastically reduced when exposed to sodium hydroxide solution. After 84 days of immersion, flexural strengths of polyester and epoxy specimens fall, respectively, 66 % and 43 %. As polyester is weakly acidic, the acid-base interaction may explain the greater reduction on flexural strength of polyester based PMs. This result was not unexpected. Previous research works on deterioration of polyester PC materials have shown the highly aggressive character of alkaline solutions. Mebarkia (1993) registered a decrease of 28 % on compressive strength of polyester PC after one-month immersion in 10 % sodium hydroxide solution. Similarly, Griffiths and Ball (2000) recorded a loss of 38 % on bending strength of glass fibre reinforced polyester PC after two weeks exposure to the same chemical environment.

For the other chemical test solutions, flexural strength variation was clearly smaller, especially for epoxy PMs. For the longest exposure period, flexural strength changes occurred in this type of PM were approximately –8 % (H_2 SO_4 Sol.) and +2 % (Na Cl Sol.), against –30 % (H_2 SO_4 Sol.) and –16 % (Na Cl Sol.), in the case of polyester PM.

The higher permeability of polyester PM, denoted by higher weight uptake values after immersion, and indicated equally by the marked visible erode rim in failure surfaces, could be the main factor for the higher decrease in flexural strength showed by this type of PM.

For both types of mortar, the specimens immersed in salt solution showed the smallest flexural strength decrease after 84 immersion days. Moreover, for the first examination periods (1, 7, and 21 days), even an increase in the flexural strength occurred. This increase in flexural resistance could be irrelevant, but it also could be indicative of little representation of control specimens. (The control specimens, chosen among all the specimens proceeding from the same batch, could be precisely those, which had smaller flexural strength).

The rust incrustations that appeared in the surface of some epoxy PM specimens immersed in salt water, did not affect their flexural strength. It is a located and superficial phenomenon, and even for longer immersion periods, it is not expected it becomes influential in the mechanical strength of the material.

5.2.4.3 Correlation between mass and flexural strength variations

There is a positive correlation between mass change and flexural strength reduction.

This correlation is very clear in the case of polyester PMs immersed in distilled water, alkalis and acid solutions, as shown in Fig. 5.8.

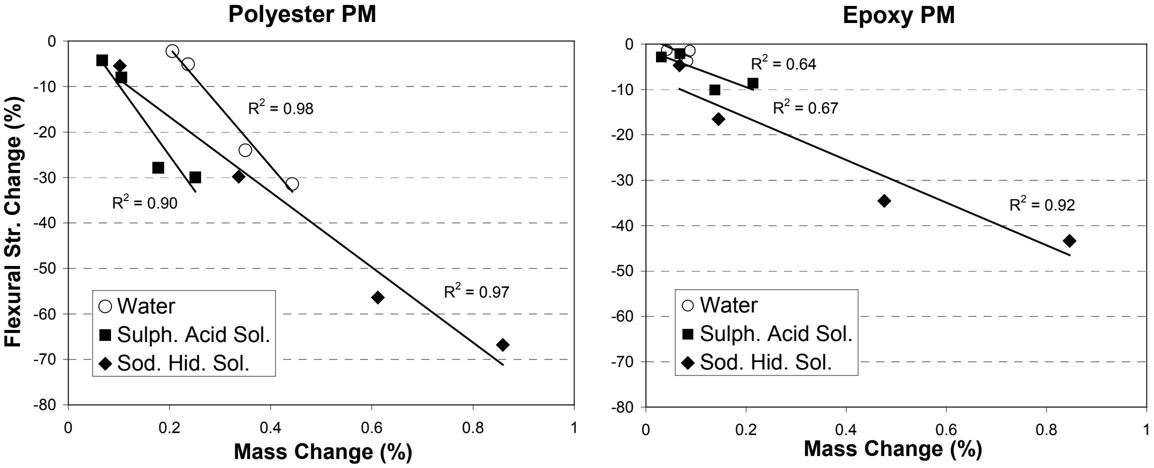

Fig. 5.8. Correlation between water uptake (mass change) and flexural strength reduction for both formulations of PM immersed in water, acid and alkalis solutions.

The linear correlation coefficients obtained were, respectively, 0.98, 0.97 and 0.90. In relation to epoxy PM specimens, the correlation is not so strong: for the same test solutions, the coefficients obtained were 0.64, 0.92 and 0.67.

The correlation between these two parameters was already expected, as mentioned in previous works carried out by several researchers (Chawalwala 1996; Mebarkia 1993; Mebarkia and Vipulanandan 1995; Ohama et al. 1986a).

It is very important in composite materials that good adhesion is maintained across the interfacial region. This is because, in most multiphase composites, the load is transferred from one phase to another through a shear mechanism at the interface. Previous studies showed that polymers did not react or dissolve in water, and their strength is not affected by immersion up to 3 years in water (Davis and Sims 1983; Kinlock 1987; Mebarkia 1993). Hence, it can be concluded that the most predominant factor causing the reduction in strength is the degradation of the interface due to water diffusion into PM.

In the case of the test specimens (both types) that have been immersed in salt solution, it was not possible to establish a positive correlation between water uptake and strength reduction due to flexural strength increases in the first examination periods.

5.2.5 Conclusions

The effects of sodium chloride, sodium hydroxide and sulphuric acid solutions on the bending strength and mass of epoxy and polyester PM formulations were investigated in various periods, from 1 to 84 immersion days. A comparative analysis with the effect of water immersion was also done.

Based on experimental results, the following conclusions are proposed:

- Polyester and epoxy PM formulations are markedly attacked by sodium hydroxide solutions. A deeper study, with longer immersion times, is needed to evaluate the significance and the level of strength reduction.
- Epoxy PMs are hardly affected by sulphuric acid and sodium chloride solutions, which is an indicator of the excellence chemical resistance of this kind of material to these aggressive chemical environments. It seems that the natural heterogeneity

among specimens is, likely, the main reason of the small differences recorded for the flexural strengths obtained for consecutive examination periods.

- Flexural strength decrease of polyester PMs with immersion time in water, sodium chloride and sulphuric acid solutions is not irrelevant, specially in the last one, and it cannot be attributet to the natural variability among specimens proceeding from the same batch. Another experimental program, with longer immersion periods, would be needed to determine the trend decrease.

5.3 Thermal Durability

5.3.1 Introduction

As mentioned earlier, durability is one of the most important properties for a material to be used in the building industry. The relevant literature commonly reports the chemical durability in various aggressive environments. However, thermal durability, *i.e.* the ability of a component to retain its physical-mechanical properties during and after exposure to severe thermal conditions, is also very important (Oshima et al. 2001).

Building components, during their lifetime, are often subject to changing temperatures. These temperatures can change from well below zero up to about 80ºC in direct sunlight, depending on geographical location and on the color of the surface, and it can be much higher than the temperature of the surrounding air (Letsch 1987). Therefore, thermal sensitivity is an important subject that must be taken into account in the evaluation of durability and service life of construction materials.

One of the foremost problems related with polymeric composite materials, arises from the viscoelastic properties of the polymer, which results in creep and high sensitivity to high temperatures (Cano et al. 1998; Tavares et al. 2002). Mechanical properties of polymers undergoing temperature variation change considerably, especially within the glass transition temperature range. Glass transition temperature (Tg) takes place over a wide temperature range, which lies for many resins used in Civil Engineering between 20ºC and 80ºC. This means that during the service lifetime of the material the glass transition can occur (Letsch 2001a). Hence, thermal durability becomes one of the most important factors in the assessment criteria of a polymeric composite material, as a potential construction material.

5.3.1.1 Overview

Previous works on the mechanical behavior of hydraulic concrete materials when subjected to severe thermal conditions, can be found in Sun et al. (2001; 1999), Balendran et al. (2001), Komonen and Pantalla (2001), and Shao and Jiang (2001). However, in spite of the previous explanation, there appears to be only a very limited amount of work done on the performance of polymer concretes and mortars under the same conditions. Furthermore, most of the related literature is restricted to a limited temperature range and to a certain type of polymer. Traditional approaches are usually focused on temperatures above room temperature, which is understandable taking into account that typical polymer concrete resins present glass transition temperatures above this value. However, resistance to very low temperatures, depending upon polymer concrete application, could also be a very important and even crucial subject.

Letsch (2001b) conducted a research work on the mechanical behavior of a polyester PC at temperatures of 23ºC, 40ºC and 60ºC. He concluded that the presence of higher temperatures resulted only in a small decrease in compressive strength, but a relatively large decrease in flexural strength and a very large increase in creep deformation.

A similar study was carried out by Vipulanandan and Paul (1990). The compressive and splitting-tensile behavior of epoxy and polyester PCs were studied under various test temperatures: 22ºC, 60ºC and 80ºC. In the same way as Lestch, they observed that increasing temperatures causes only slight decreases in compressive strengths of both PC formulations, while splitting-tensile strengths are severely affected by the same temperature conditions.

A comparative study of the influence of temperature on the mechanical strength of three different PCs (epoxy, polyester and acrylic based ones), had also been carried out by Pardo and co-workers (1995), with the aim of establishing a criterion to determine the safety factor for precast structures. Concrete specimens were tested in bending and compression, after conditioning at different temperatures, from 20ºC to 200ºC. The test results showed that, when the specimens were tested at room temperature, after tempering, no important reduction in strength occurred. However, when the specimens were tested at aging temperature, a significant decrease of both flexural and compressive strength characteristics took place.

The same research team also analyzed the mechanical behavior of polyester PC after exposure to 100 thermal fatigue cycles (San José et al. 1998). Six different thermal cycles have been considered: 30 minutes at 20ºC followed by 3 hours at 40º, 60º, 80º, 120º, 140º and 160ºC, respectively for each cycle. After 100 thermal cycles, three specimens of each series were tested at room temperature, and the other specimens were tested at the maximum cycle temperature. They concluded that thermal fatigue does not affect strength if PC is taken back to its initial conditions, and as long as polymer decomposition temperatures are not exceeded. However, the combination of mechanical and thermal actions up to 60ºC implies the obligation of applying the thermal partial safety coefficients, depending on the type of resin and load (live or permanent).

Gálan (2001) also used thermal fatigue cycles to evaluate thermal durability of binder formulations of unsaturated polyester PMs. The aim of her research work was to analyze the viability of application of ‘*Polialbero*’ as local construction material. Polialbero was the designation given by the research to PM prepared with a specific aggregate called Albero. This aggregate can only be found in the province of Sevilla (Spain), and its use is widespread in the Andalusia region. In order to simulate local weathering conditions (temperature and moisture fluctuations), polialbero specimens were exposed to distinct thermal fatigue cycles. Temperature and humidity ranges, simulating Spring/Summer and Autumn/Winter season conditions, were defined according to the maximum and minimum values recorded locally for these parameters in the last years. After 360 cycles, corresponding to one year of outdoor exposure, no significant influence was observed on mechanical strength of polialbero specimens.

A different approach was used by Oshima et al. (2001) to analyze thermal sensitivity of epoxy and polyester PCs. Tests were performed on temperature-dependent mechanical properties such as dynamic Young’s modulus, logarithmic decrement, creep coefficient, compressive and flexural strengths. The study was conducted in order to determine the temperature inflexion points in the respective properties where the temperature dependency became dominant. Tests results showed that the inflection points were related to the heat distortion temperature (HDT) of the resins used, rather than the glass transition temperature (Tg). Furthermore, it was found out that the temperature inflexion points were not affected by the resin content.

Only a few papers focused on freeze-thaw resistance of polymer mortars and concretes have been written until now. The absence of moisture in the matrix of this kind of concrete material, which is the principal cause of the relative vulnerability of ordinary hydraulic concretes to freeze-thaw actions, is probably the main reason for this lack of data.

However, frost resistance is also related with the material porosity and with its coefficient of water absorption, and as a result, depending upon these characteristics, frost durability could also be an important feature to taken into account.

Chawalwala (1996) conducted a research work on freeze-thaw durability of vinyl and polyester PC. The aim of his study was to assess the viability in applying these materials as a wear overlay surface for a composite bridge deck. PC specimens were exposed to controlled humidity freeze-thaw cycles, ranged from +15 ºC to –10 ºC, up to 500 cycles. Flexural tests were then conducted in order to evaluate strength retention after environmental exposure. It was observed that dry freeze-thaw cycling had practically no effect on flexural properties of PC, while freeze-thaw cycling conducted under high humidity conditions (90%) showed significant strength degradation.

Bhutta and co-workers (2001) studied the durability, including the freeze-thaw resistance, of a polyester PM formulation with waste iron aggregates for counterweight purposes. The tests were conducted in a temperature range of +5 ºC to –18 ºC. Freeze-thaw durability was evaluated through the relative dynamic modulus of elasticity and mass change of the specimens at every 30 cycles in a total of 300 cycles. At the end of the experimental program, all the specimens were tested in compression. Throughout the cycles, the measured relative dynamic modulus of elasticity of counterweight specimens was practically the same, and moreover, no significant mass change was found. However, after 300 cycles, the compressive strength of PM specimens was slightly influenced by the alternating freeze-thaw actions.

When wet aggregates are used in PC formulations, as it is sometimes required in field applications, their deterioration due to freeze-thaw actions can be more pronounced due to misture. Under this perspective, Ohama et al. (1986b) analyzed the freeze-thaw durability of a polyester PC formulation made with wet aggregates. Polyester PC specimens were prepared with various moisture contents, from less than 0.1% up to 5%, and tested for freeze-thaw cycling in water in a temperature range of –17.8 ºC to +4.4 ºC. Freeze-thaw durability was evaluated through the weight change and the relative dynamic modulus of elasticity measured at every 50 cycles up to 600 cycles. It was noticed, from the durability factor data, that the freeze-thaw resistance of polyester PC with aggregate moisture content of 1%, or less, is excellent, while that of polyester PC with aggregate moisture contents of 3% and 5% is very poor. Test results were attributed to the complex effect of the strength reduction, due to the hydrolysis of polyester resin matrix during curing process, together with the volume expansion caused by the freeze-thaw cycling action.

The same research team conducted a posterior study, in order to improve the freeze-thaw durability of polyester and methyl methacrylate PC made with wet aggregates (Ohama et al. 1987). Moisture absorptive additives, such as zeolite and ordinary Portland cement, a silane coupling agent and steel fibres were added to PC formulations in order to achieve the intended purpose. It was concluded, from the test results, that the use of the mentioned admixtures with wet aggregates causes a great deal of improvement in the freeze-thaw durability of polyester and metyl methacrylate PCs, although their moisture contents reaches about 5%. In particular, in the case of polyester PC, they realized that the use of the ordinary Portland cement concrete as a moisture absorptive additive could be recommended because of its hydraulic property.

5.3.1.2 Research objective

Following all the above studies, the work presented in this subsection aims to analyze and quantify the strength degradation process occurring in the developed PM formulations as a consequence of different thermal effects.

For this purpose, specimens of both formulations were exposed to the following thermal conditions: conditioning at constant temperatures, for temperature levels between –20ºC and +100ºC; positive thermal fatigue cycles (+20ºC / +100ºC); and wet and dry freeze-thaw cycles (-10ºC / +10ºC).

Residual flexural strengths, during and after exposure to these severe thermal conditions, were obtained.

The analysis of flexural strength degradation process allowed the assessment of material thermal durability.

5.3.2 Experimental Program

5.3.2.1 Test specimens

The study was conducted on prismatic specimens, 40x40x60 mm, of both formulations in analysis. For each kind of PM formulation, five batches with 18 specimens each (3 control specimens + 15 test specimens) were casted.

All the specimens were allowed to cure for one day at room temperature and then post-cured at 80ºC for three hours, before being exposed to the defined environmental conditions.

5.3.2.2 Thermal durability tests procedure

A climatic chamber, shown in Fig. 3.6, was used to submit the test specimens to the different thermal conditions defined in the following. Flexural tests were carried out according to RILEM recommendation (RILEM 1995c).

i) Conditioning at constant temperature

To determine the influence of temperature on flexural strength of PM formulations, two types of study were carried out:

- In the first one, specimens were heated or cooled to the different test temperatures in the climatic chamber (three specimens for each temperature level), and after that, they were immediately tested in bending at aging temperature (conditioning temperature). Heating/cooling rates were respectively, +5 ºC/min. and –2 ºC/min. Temperature test was maintained for 3 hours in order to establish a steady state condition of heat transfer.
- The second study was carried out as the first one, but the specimens were quickly tempered, by immersion in water, before being tested in bending at room temperature. Test specimens were kept in the water bath for at least 3 hours.

ii) Thermal fatigue cycles

To evaluate the flexural strength deterioration of PM induced by repeated thermal actions, specimens of both formulations were also exposed to the following thermal fatigue cycles:

- Positive thermal fatigue cycles, between +20 ºC and +100 ºC: 2 hours at 100 ºC followed by 6 hours at 20 ºC; heating/cooling rate of 0.67 ºC/min.; moisture content of 50 % (during the temperature level of 20 ºC).
- Freeze-thaw cycles between –10 ºC and +10 ºC: 2 hours at 10 ºC followed by 2 hours at –10 ºC; heating/cooling rate of 0.17 ºC/min. This experimental program was divided into two series: in the first series, test specimens were heated and cooled by air (dry cycles); in the second one, in order to accelerate degradation process, test specimens were frozen and thawed in water (wet cycles).

Bending tests were performed, at room temperature, after 50 and 100 cycles (three specimens for each cycle period and for each cycle type). The weight of the specimens that were subjected to freeze-thaw cycles was recorded prior to and after exposure to thermal cycles. Both thermal fatigue cycles, positive and freeze-thaw cycles, are schematically described in Fig. 5.9.

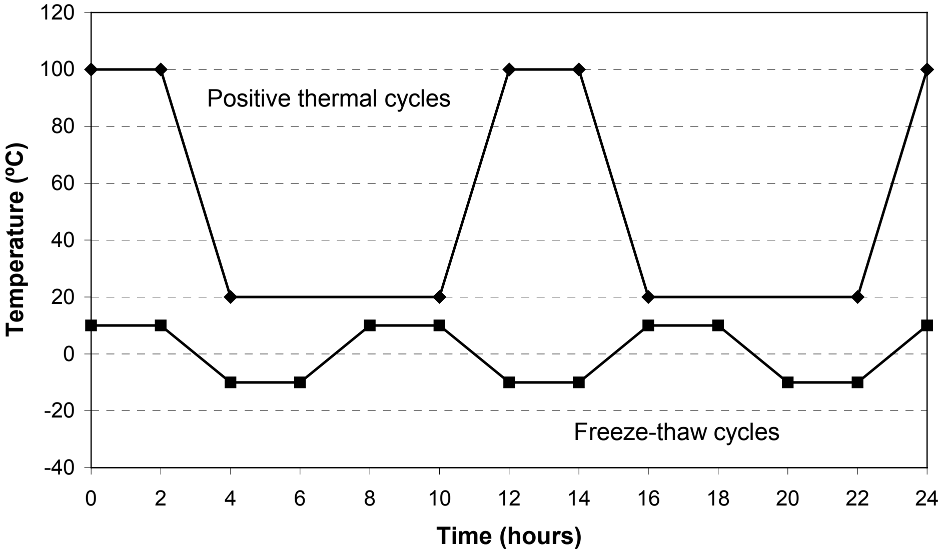

Fig. 5.9. Thermal fatigue cycles that were subject specimens of both PM formulations.

At this point, a special remark must be done concerning the different criteria commonly used for the assessment of the resistance of concrete to freeze-thaw attack and, in a certain way, to justify the criterion used in the present study.

Generally, in the case of Portland cement concrete, the criteria are the course of scaling during the attack and the overall amount of scaling after the attack. However, only by means of the amount of scaling, it can be hardly assessed how far the microstructure has really been damaged (Dimming et al. 2001). Especially, in the case of PC and PM, the consideration of scaling alone is questionable.

Another common method to assess concrete deterioration is to measure the change in the dynamic modulus of elasticity of the specimen. The reduction in the modulus after a number of cycles of freezing and thawing expresses the deterioration of the concrete. With the ASTM method (ASTM C666/C666M-03 2003) it is usual to continue freezing and thawing for 300 cycles or until the dynamic modulus of elasticity is reduced to 60% of its original value, whatever occurs first. Durability factor can then be calculated as function of the total number of the cycles, the number of cycles at the end of the test, and the relative dynamic modulus of elasticity. There are no establish criteria for acceptance or rejection of concrete in terms of the durability factor; this parameter is thus primarily useful in a comparison of different concretes. These methods, using the measurement of the dynamic elasticity modulus, indicate damage before it has become apparent, either visually or by other methods, although there are some doubts about the interpretation of the decrease of the modulus after the first few cycles (Neville 1995).

The effects of freezing and thawing can also be assessed from measurements of the loss of compressive or flexural strength, or from observations of the change in length or in the mass. A large change in length is indicative of internal cracking. The measurement of mass change is more appropriate when damage takes place mainly at the surface of the specimen, but is not reliable in cases of internal damage. Loss of load carrying capacity gives a straight measure of strength deterioration of concrete, but requires a superior number of test specimens as a destructive assessment method.

It can be seen that a number of tests and of means of assessing freeze-thaw durability are available, and thus, the interpretation of test results may become quite difficult. The ideal would be to use all of them, in order to make possible a consistent comparison with other concrete materials or other studies, but this procedure would not be reasonable, neither in terms of time, nor in terms of the number of specimens required.

As a straight assessing methodology of the damage, and also in order to maintain a uniform criterion throughout this thesis, the assessment of freeze-thaw durability of PM formulations was based on loss of flexural strength. Nevertheless, the experimental program could be complemented and improved with the measurement of the changes in dynamic elasticity modulus. Unfortunately, the unavailability of resonance vibration equipment, necessary to measure the fundamental transverse frequency, hindered the determination of this parameter.

The range of temperatures, heating/cooling rate and periods of time under the same temperature level were chosen among usual values recommended by the norms (ASTM C666/C666M-03 2003; EN 1340 2003; JIS A-6204 2000) and reported in previous literature. A previous control test was performed in order to check if the chosen parameters met the required conditions.

In spite of the number of cycles prescribed by ASTM test method (300 freeze-thaw cycles), only 100 cycles were carried out in this experimental program. Limitations of time and availability schedule of climatic chamber were the restrictive factors that conditioned this option. Nevertheless, it can be stated that some accelerated freeze-thaw tests may result in destruction of concrete materials that in practice could behave satisfactory. The ability of a concrete material to withstand a considerable number of laboratory freeze-thaw cycles (say 100-150) is a probable indication of its high degree of durability under service conditions (Neville 1995).

5.3.3 Experimental Results and Discussion

5.3.3.1 Influence of temperature on flexural strength

Flexural test results (average flexural strength and correspondent standard deviation) are presented at Table 5.4. Relationships between conditioning temperature and flexural strength of both formulations of PMs, for each test condition, are shown in Figs. 5.10 and 5.13. In order to access test temperature effect on ductility and stiffness of PM formulations, typical shapes of stress deflection curves obtained from flexural tests were determined and plotted in Figs. 5.11 and 5.12.

Table 5.4. Flexural test results after exposure to different test temperatures.

<table>
<tr><th rowspan="3">Test Temp.
(ºC)</th><th colspan="2">Epoxy PM</th><th colspan="2">Polyester PM</th></tr>
<tr><th colspan="2">Flex. Strength | St. Deviation (MPa)[b]</th><th colspan="2">Flex. Strength | St. Deviation (MPa)[b]</th></tr>
<tr><th>Aging Temp.</th><th>Room Temp.</th><th>Aging Temp.</th><th>Room Temp.</th></tr>
<tr><td>-20</td><td>51.30 | 2.32</td><td>41.35 | 1.78</td><td>20.22 | 0.97</td><td>22.50 | 0.44</td></tr>
<tr><td>-10</td><td>48.10 | 1.45</td><td>-</td><td>19.67 | 2.61</td><td>-</td></tr>
<tr><td>0</td><td>45.66 | 0.82</td><td>40.97 | 2.20</td><td>20.02 | 1.26</td><td>22.90 | 2.05</td></tr>
<tr><td>+10</td><td>41.92 | 2.21</td><td>-</td><td>20.29 | 2.19</td><td>-</td></tr>
<tr><td>+20</td><td>41.26 | 0.73</td><td>-</td><td>20.89 | 2.08</td><td>-</td></tr>
<tr><td>+23 (Ref.)[a]</td><td>41.09 | 1.24</td><td>42.64 | 0.79</td><td>20.33 | 0.26</td><td>23.80 | 2.05</td></tr>
<tr><td>+30</td><td>33.48 | 0.51</td><td>-</td><td>18.98 | 0.85</td><td>-</td></tr>
<tr><td>+40</td><td>18.37 | 0.78</td><td>42.25 | 0.68</td><td>18.87 | 0.46</td><td>22.98 | 1.95</td></tr>
<tr><td>+50</td><td>6.86 | 0.43</td><td>-</td><td>15.21 | 0.25</td><td>-</td></tr>
<tr><td>+60</td><td>3.09 | 0.13</td><td>41.72 | 0.81</td><td>12.89 | 0.20</td><td>23.32 | 2.32</td></tr>
<tr><td>+80</td><td>1.26 | 0.52</td><td>-</td><td>6.92 | 0.18</td><td></td></tr>
<tr><td>+100</td><td>0.80 | 0.61</td><td>45.48 | 0.44</td><td>2.44 | 0.19</td><td>24.26 | 1.21</td></tr>
</table>

a) Control specimens.

b) Average values of three specimens.

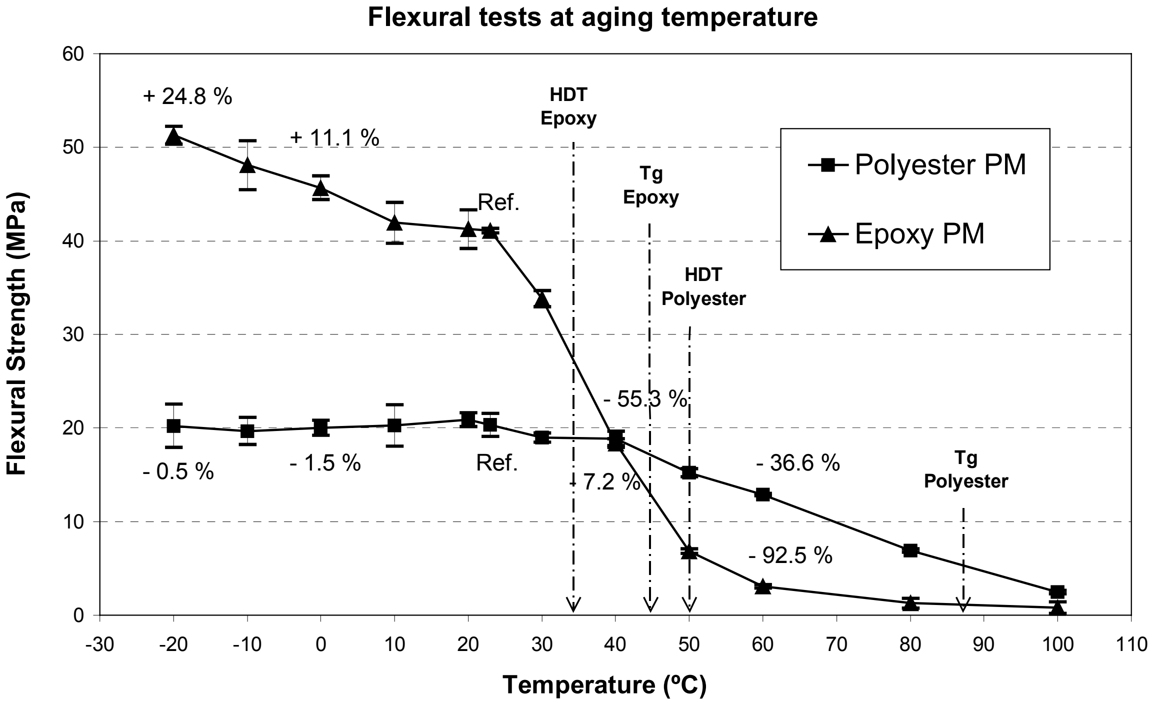

Fig. 5.10. Flexural strength of epoxy and polyester PMs as function of test temperature.

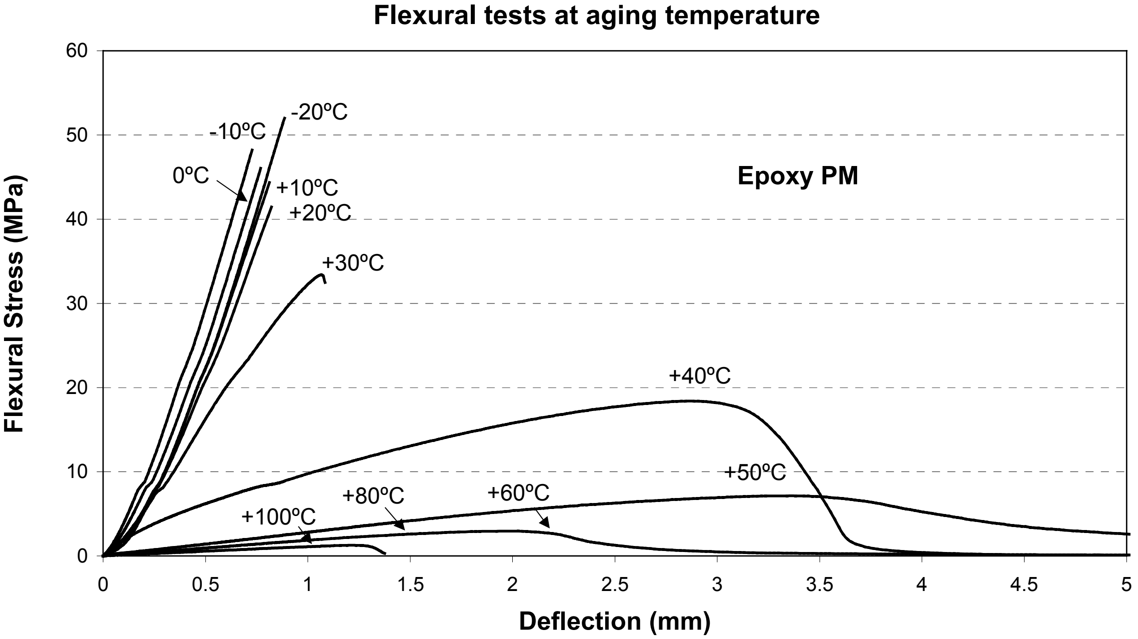

Fig. 5.11. Stress-deflection curves of epoxy PM specimens obtained from flexural tests carried out at aging temperatures.

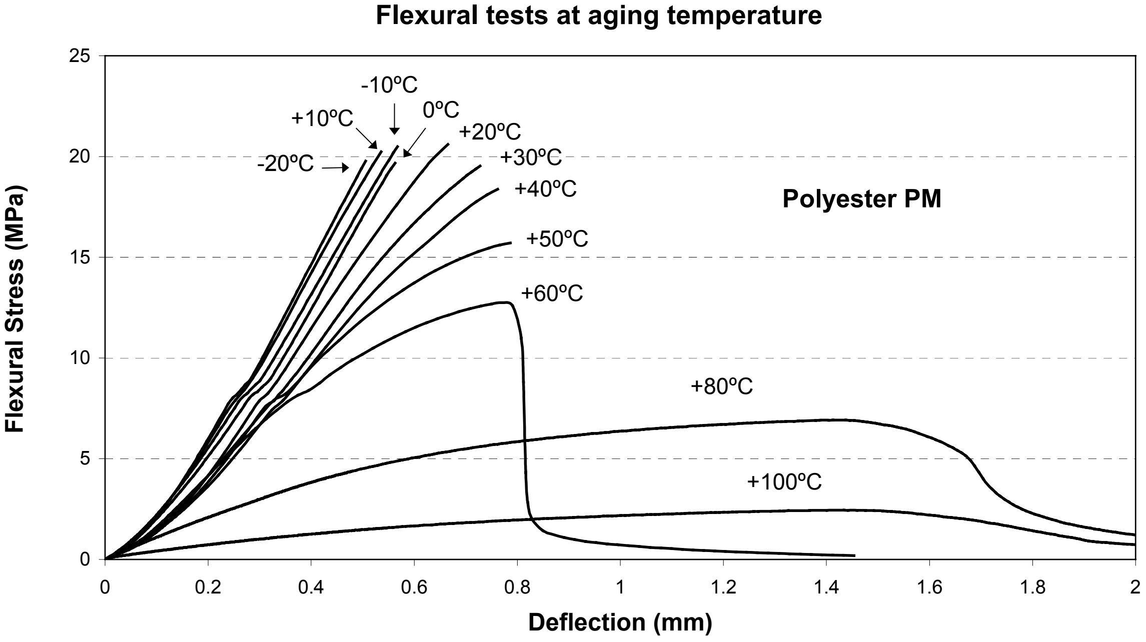

Fig. 5.12. Stress-deflection curves of polyester PM specimens obtained from flexural tests carried out at aging temperatures.

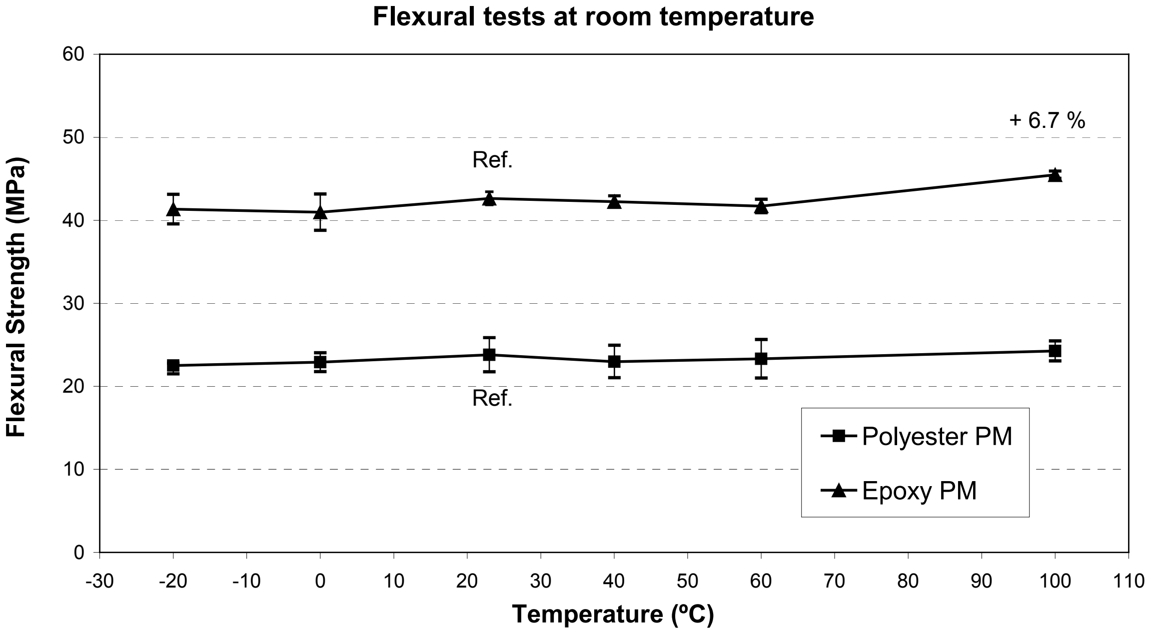

Fig. 5.13. Flexural strength of epoxy and polyester PMs, after tempering, as function of conditioning temperature.

i) Flexural tests carried out at aging temperature

As shown in Fig. 5.10, flexural strength of epoxy mortars presents a strong and marked temperature dependency. The characteristic value of flexural resistance remains stable just within a limited range of temperatures, approximately between +10 ºC and +23 ºC. For temperatures above room temperature, flexural strength of this particular mortar decreases drastically: between +23 ºC and +50 ºC, a decrease of 85% of its initial resistance occurs, and at +100 ºC, the load carrying capacity becomes almost insignificant.

On the other hand, for temperatures below +10 ºC, bending strength tends to increase as the temperature test decreases. This trend is very clear, and it appears to indicate, that for lower temperatures than –20 ºC, a higher increase of flexural strength should be expected. Relatively to polyester mortar formulation, it seems that its flexural strength is not significantly affected by environmental temperature within temperature range between –20 ºC and +40 ºC. For higher temperatures, a gradual decrease of flexural strength occurs, but the decrease rate is lower than the one that occurs for epoxy binder formulation.

For both mortar formulations, the loss of load bearing capacity with increasing temperature is associated with a progressive loss of material stiffness, as shown in Figs. 5.11 and 5.12. As temperature test increases, the flexural elasticity modulus decreases and failure mode becomes more ductile, and less brittle.

The temperature values of the inflection points, when temperature dependency becomes dominant, are related to the heat distortional temperatures (HDT) of the resins used in each mortar formulation, rather than the correspondent glass transition temperatures (Tg), as can be seen in Fig. 5.10. These points, named by other researchers (Oshima et al. 2001) as ‘heat distortional temperatures of polymer mortars’, are both located around 10 ºC lower than HDT values of resins used (40ºC and 24ºC respectively, for polyester and epoxy PM formulations). Although the inflection points of the temperature dependency of the flexural properties of PM formulations are well related to HDT of resins used, the flexural properties are not related to HDT, which are mainly the characteristics values of the deformation property of resins.

ii) Flexural tests carried out at room temperature after specimens tempering

According to test results presented in Fig. 5.13, conditioning temperature during exposure time had no significant influence on flexural strength of both formulations, as long as specimens were taken back to their initial environmental conditions and tested at room temperature. A slight increase on flexural strength of epoxy mortar specimens that have been exposed to the highest conditioning temperature was observed, possibly due to a post-curing phenomenon. A similar behavior was found by Pardo and co-workers (1995) on a epoxy PC formulation subjected to the same conditions.

Similarly, no noteworthy differences induced by temperature conditioning were observed on the flexural elasticity modulus and failure mode of mortar specimens.

The recovering of initial flexural properties observed on both formulations could be explained, partially, by molecular mobility of polymeric chains. This mobility increases with temperature, and is associated to local motions of the less hindered groups around their equilibrium position. As temperature reaches the glass transition temperature, molecular mobility strongly increases leading to configuration rearrangements of the polymer chain backbones. The loss of mechanical strength is one consequence of this process. However, when polymers are tempered, there is not enough energy to maintain this mobility, and therefore, initial cohesion between polymeric chains is recovered.

5.3.3.2 Influence of thermal fatigue cycles on flexural strength

Average flexural test results of mortar specimens that have been subjected to thermal fatigue cycles are presented in Table 5.5. The weight change of mortar specimens submitted to freeze-thaw cycles is also presented. Residual flexural strengths of both formulations after 50 and 100 exposure cycles, for each different thermal cycle, are shown in Figs. 5.14 to 5.16.

In addition, in Fig. 5.17, failure surface of both types of PM specimens that were submitted to 100 freeze-thaw cycles in water is also shown.

Table 5.5. Flexural test results after exposure to positive fatigue cycles and freeze-thaw cycles.

Thermal Fatigue cycles	Epoxy PM		Polyester PM	
	Flex. Str. | St. Dev. (MPa)[a)]	Mass change (%)[a, b)]	Flex. Str. | St. Dev. (MPa)[a)]	Mass change (%)[a, b)]
+20ºC / +100ºC				
- 0 cycles	40.70 | 0.27	-	20.33 | 1.24	-
- 50 cycles	34.75 | 2.58	-	19.17 | 1.28	-
- 100 cycles	30.82 | 1.66	-	19.49 | 1.63	-
-10ºC / +10ºC (dry)				
- 0 cycles	40.85 | 1.11	0	22.11 | 0.96	0
- 50 cycles	40.56 | 2.69	0.010	23.20 | 0.83	0.031
- 100 cycles	39.18 | 1.86	0.017	23.19 | 0.30	0.052
10ºC / +10ºC (wet)				
- 0 cycles	40.85 | 1.11	0	22.11 | 0.96	0
- 50 cycles	38.27 | 0.61	0.094	23.40 | 0.20	0.240
- 100 cycles	38.66 | 1.66	0.137	22.11 | 0.63	0.355

a) Average result of three specimens.
b) Mass change was determinate in accordance with RILEM TC113/PC-11 (RILEM 1995a).

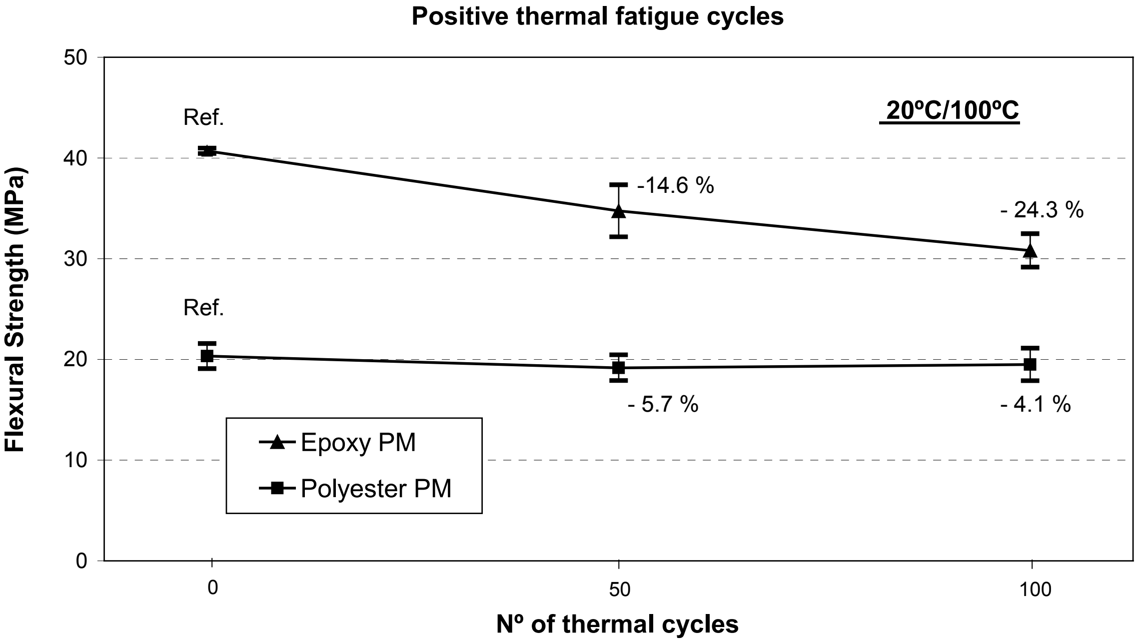

Fig. 5.14. Residual flexural strength of epoxy and polyester PMs after exposure to 50 and 100 positive thermal fatigue cycles.

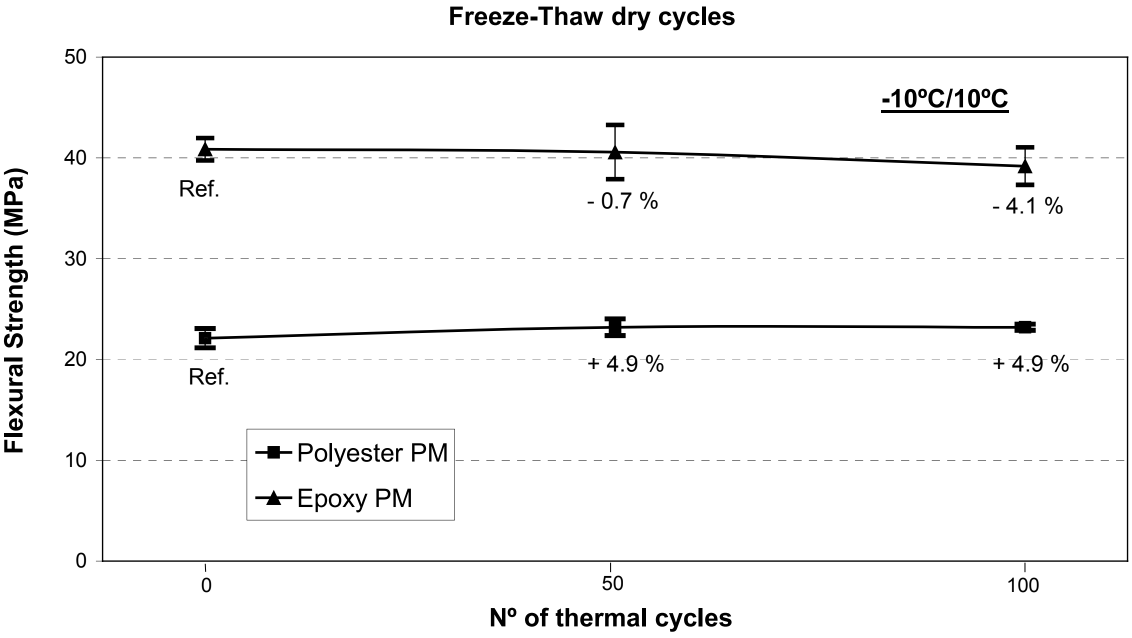

Fig. 5.15. Residual flexural strength of epoxy and polyester PMs after exposure to 50 and 100 freeze-thaw dry cycles.

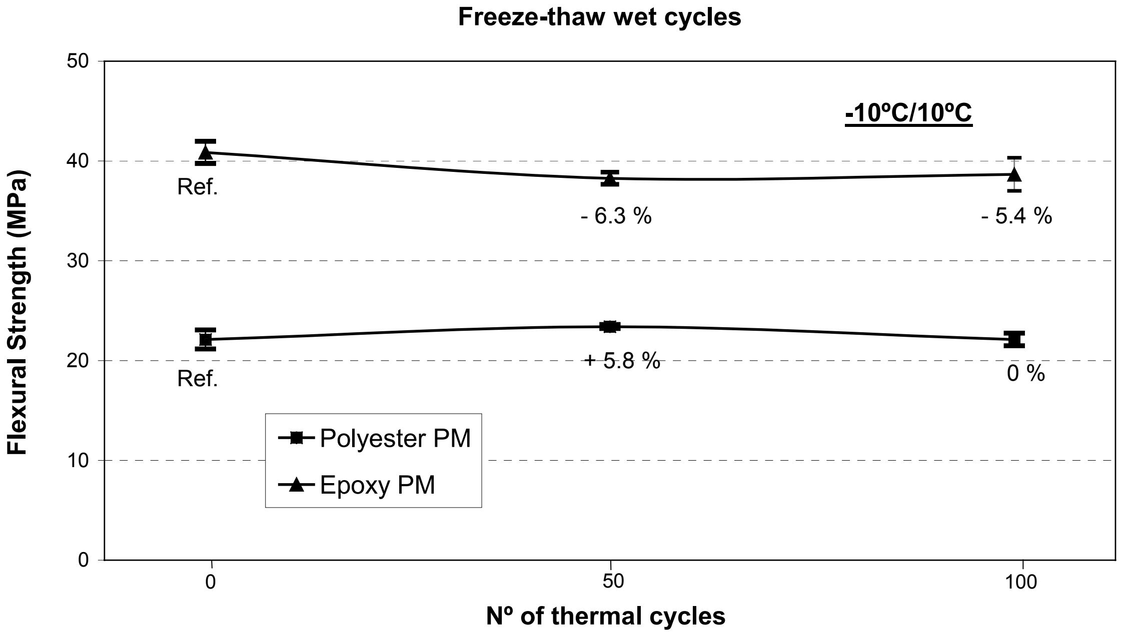

Fig. 5.16. Residual flexural strength of epoxy and polyester PMs after exposure to 50 and 100 freeze-thaw wet cycles.

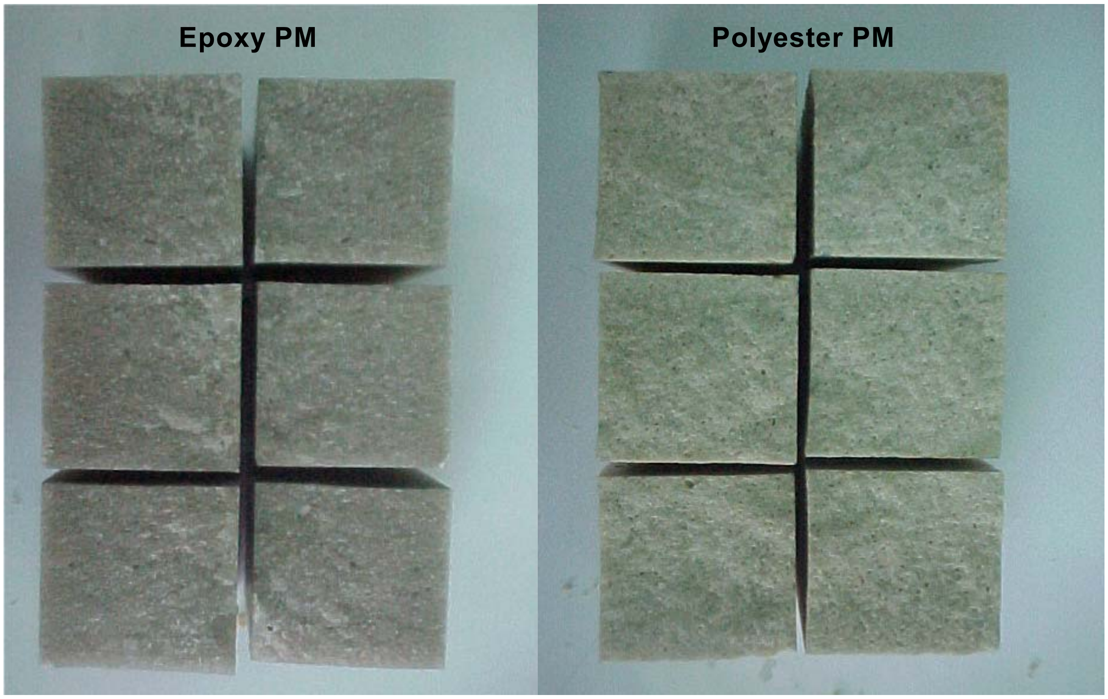

Fig. 5.17. Failure surface of PM specimens after exposure to 100 freeze-thaw wet cycles.

i) Positive thermal fatigue cycles

The influence of thermal fatigue cycles, between +20 ºC and +100ºC, on flexural strength of epoxy PM is not irrelevant. Regardless of its recovering capacities showed by last tests, the continued exposure of epoxy PM to high temperatures has a negative effect on its flexural strength. After 50 thermal fatigue cycles, a percentage drop of 14 % occurs on flexural strength, and after 100 cycles, this property falls to 75 % of its initial value.

It seems that the continuous cycling to temperatures up to 100 ºC (more than twice the epoxy resin Tg), leads somehow to partial degradation of the epoxy network. This phenomenon, not noticeable for one cycle, becomes notorious after a certain number of cycles, as degradation progresses cycle after cycle.

The described phenomenon has no significant expression in the case of unsaturated polyester mortars. In this case, the maximum cycling temperature is only 15 % higher than the polyester resin Tg, so it represents a much less severe condition to the polyester polymer network.

The flexural elasticity modulus and failure mode of both type of mortars are not affected by exposure to these thermal actions.

ii) Freeze-thaw cycles

Exposure to thermal fatigue cycles between –10 ºC and +10 ºC had no relevant influence on flexural strength of both formulations of PMs. Even for specimen’s series immersed in water, subjected to frost attack, the flexural strengths retained after 100 freeze-thaw cycles were still very high. In addition, no scaling surface was observed and no sediments appeared on water containers. This means that specimens weight change was only due to water absorption.

Frost damage is very clearly linked to water uptaking during freeze/thaw exposure or to the degree of water saturation. The obtained results may be explained by the insufficient water diffusion into PM specimens. After 100 freeze-thaw cycles, only a small amount of water up-take was observed on both types of test specimens and furthermore, as shown in Fig. 5.17, no erode rim was visible on their failure surfaces after bending tests. The low degree of water absorption and high watertightness of PM specimens, already known by the previous study (see subchapter 5.2), are most certainly the main reasons for the absence of frost damage.

This explanation is supported by Setzer research (2001). According to Setzer, the high number of freeze-thaw cycles is primarily needed to saturate the specimens artificially by a micro-ice-lens-pump, and not for the fatigue fracture process. The micro-ice-lens-pump model, described by Setzer, is based on the phenomenon that the three phases of water coexist between 0 ºC and –60 ºC with thermodynamical stability. This is only possible because a high negative pressure is generated in the unfrozen gel-water. In the cooling phase the matrix is compressed, water is squeezed out and trapped at the ice. During subsequent heating, the matrix expands and water is sucked in from external sources since the ice particles are still frozen. With every freeze-thaw cycle, the degree of saturation is increased until a critical value is reached and damage sets in. Until this point, only a relative small damage should be expected.

Water uptake during the 100 freeze-thaw cycles was not sufficiently enough to saturate the PM specimens, as indicated by weight change observed, and therefore, no noticeable damage induced by the alternate freezing and thawing actions occurred.

5.3.4 Conclusions

In this subchapter, the influence of temperature and thermal fatigue cycles on flexural behavior of binder formulations of PMs in study was briefly discussed. Based on test results, the following conclusions can be drawn:

- Flexural properties of both PM formulations are strongly affected by environment temperature. Except within a limited temperature range, flexural strength of these mortar formulations decreases drastically with raising test temperatures. The inflection points, where temperature dependency becomes notorious, are related to the heat distortional temperatures of the resins used rather than the glass transition temperatures, in accordance with the conclusions of the investigation work carried out by Oshima and co-workers (2001).

- Epoxy mortars are more sensitive to temperature than polyester mortars. The ‘HDT of epoxy mortars’ is lower than corresponding ‘HDT of polyester mortars’. After such critical points, decrease of flexural strength of epoxy-based mortars occurs at a higher rate. For temperatures lower than +10 ºC, flexural behavior of epoxy mortars improves with further decreases in temperature.
- Exposure to constant or changing temperatures (thermal fatigue cycles) has no significant influence on flexural properties of both formulations of PM, as long as specimens are taken back to their initial environmental conditions. However, recovering capacity of epoxy mortars is gradually reduced by repeated exposure to high temperatures.
- One hundred freeze-thaw cycles, between –10 ºC and +10 ºC, produce very little damage on both epoxy and polyester PMs, possibly due to a reduced degree of water absorption.

These experimental results show the relevance of material properties assessment with temperature. In particular, with epoxy PM formulation, it can be concluded that the use of such material is restricted to lower temperature environments in order to benefit from its total potential in strength. In the case of higher temperatures care should be taken in both formulations as properties may drop significantly.

5.4 Weathering Durability

5.4.1 Introduction

Most materials are subjected to weathering.

Chemical and physical processes as a result of exposure to the elements degrade the earth's crust. The rate of deterioration depends on the nature of the material: for the hardest rocks, the time scale extends to millions of years whereas for some organic polymers, major changes can be induced by exposures of a few days (Davis and Sims 1983).

Polymer composites, in many of their applications, are often exposed to the outdoor environment. Thus, there is a natural concern regarding the weatherability of these materials, partly because composites are relatively recent materials and, in part, because if the useful lifetime of these materials can be predicted their maintenance and replacement can be planned.

5.4.1.1 Agents of the weather

Sunlight, temperature, moisture, wind, dust and pollution, are among the main variables or components of the weather that cause degradation (Greathouse and Wessel 1954).

i) Sunlight:

The sun is the major cause of most climatic phenomena found on earth. Heat, atmosphere moisture, air movement and winds are primarily related to the sun.

For most polymeric materials degraded outdoors the main cause of loss of properties is the photo-oxidative attack, *i.e.* the combined action of oxygen and sunlight on their chemical structure.

In an attempt to quantify sunlight as a deterioration agent, three main approaches have been proposed based on measurement of the following aspects: sunshine duration, total solar radiation and ultraviolet radiation. In going from the former to the later, the information becomes more specific, however, the availability of such data also decreases in the same sequence. Whereas there are thousands of places where sunshine hours are computed, sites where continuous measurement of solar ultraviolet radiation is made are numbered in the tens (Davis and Sims 1983).

Efforts have been made to relate resistance to photo degradation of polymers to the number of sunshine hours they can withstand before loosing their useful properties. The main limitation arises from the fact that the measurement devices of sunshine duration, such as Campbell-Stokes and Martin-Marvin sunshine recorders, do not make the differentiation neither between early morning and mid-day sunshine hour, nor between sunshine in the tropics and sunshine in a temperate zone (Coulson 1975).

The search for a quantitative and reliable relationship between sunshine hours and global solar radiation has been the subject of considerable interest since it is recognized as a precious mean of complementing the limited amount of available solar radiation data (Collingbourne 1976). However, this scope is not as simple as the basic dependence of global radiation on latitude and on time (day hour and day year), or more accurately on sun elevation, is significantly affected by the general weather conditions, in particular the degree of cloud cover.

Approximately 6% of the total solar radiation reaching the earth’s surface is ultraviolet radiation, with wavelengths between 290 nm and 400 nm. Radiation below 290 nm is effectively eliminated by stratospheric ozone. Since most polymers have bond dissociation energies on the order of 290 nm to 400 nm wavelengths, they are greatly affected by exposure to this portion of solar spectrum (Chin et al. 2001).

The intensity of global ultraviolet radiation depends on, among other things, the altitude of the sun and therefore, like total solar radiation, it is subject to diurnal and seasonal changes. As the ultraviolet portion of the solar spectrum is attenuated more than any other region of the spectrum by passage through the atmosphere, these daily and seasonal changes are more pronounced. Further, all wavelengths within the ultraviolet region are not equally affected: as the wavelength is reduced the scattering becomes increasingly important. The relative intensities of different wavelengths can vary within wide limits. The effect of cloud cover, fog and fluctuations in the thickness of the ozone layer, which also presents diurnal and seasonal changes, increase the range of possible ultraviolet radiation intensities (Koller 1965).

For long-term outdoor exposure, ultraviolet radiation data is more meaningful, therefore, several programs have been developed to estimate ultraviolet radiation doses on a worldwide basis (Schulze and Gräfe 1969).

Coblentz (1952) has established an empirical relationship between radiation of wavelength up to 315 nm and total solar radiation for each month of the year at Washington , and various researchers have made use of these ratios to estimate ultraviolet radiation doses (McCullough 1970). However, it should be pointed out that estimates should only be attempted for sites that have sun zenith angles similar to those of Washington.

Although medical community have in the past concentrated interest in the shortest wavelengths, which are responsible for skin cancer and erythema, many natural and synthetic polymeric materials are affected by wavelengths outside the 'erythema' region (λ<310 nm), for instance, polyphenylene oxide is degraded by wavelengths up to about 400 nm. As a result of this property, this material has been used to give a continuous measure of the total solar ultraviolet radiation region at 24 sites throughout the world. (Davis et al. 1976). The total annual doses of ultraviolet radiation correlates quite well with site altitudes. Although clear sky reference sites tended to have higher annual doses than sites which had higher preponderance of cloud, it was observed that the correlation of annual ultraviolet radiation with latitude was much more obvious than that observed for total solar radiation. Estimates can be made for other sites with similar latitudes, but care should be taken as the variable distance to the sea (continental or maritime location), also has considerable influence on total solar ultraviolet radiation.

ii) Temperature:

Extreme temperatures can have an adverse effect on the performance of polymeric materials: low environment temperatures may reduce the flexibility of a normal rubbery material and the opposite may well soften the stiffest thermoset resin.

Air temperature is primarily determined by the amount of solar radiation received. In general, temperatures decrease with latitude towards Polar Regions. Until 1983, the lowest temperature ever recorded was –88ºC at Vostock in the Antarctic, and the highest temperature, 58ºC, was observed at El Fasher, in Libya, 13º 38' north of the equator (Davis and Sims 1983). These extremes, whilst they demonstrate the possible range of temperatures that could be encountered, are not realistic values for the purpose of considering the deterioration of the materials. Within this scope, it is more usual to consider the mean maximum and the mean minimum values over some interval of time, normally a month. The oceans and large landmasses modify temperature dependency on latitude. Maritime sites tend to be cooler in summer and warmer in winter than continental sites of similar latitudes. The high heat capacity of water and its high heat of evaporation and condensation have the effect of reducing the range of temperatures over oceans.

Diurnal range of temperatures, also affected by the continentally, is also an important contributing factor in weathering, as significant mechanical stresses can be induced by large temperature variations in composite systems containing materials with widely different coefficients of thermal expansion.

In summary, temperature is strongly related to latitude but factors such as altitude, local topography, cloud cover and continentally can modify this relationship significantly. However, nowadays there is a large amount of available data and one can estimate with reasonable reliability the prevailing temperature for most areas of the globe (Gates 1965; Greathouse and Wessel 1954).

iii) Moisture:

Moisture, whether in the form of dew, frost, rain or snow, also plays a major part in the weathering processes. The importance of water lies in the combination of its unique physical properties with its chemical reactivity, and it is for this reason that moisture is such an important factor in the deterioration of organic materials.

The chemical attack of water on polymer bonds and on the interface between matrix and reinforcement of polymeric composites, the physical damages caused by freeze-thaw cycles on permeable materials, the leaching of additives from plastics and rubbers, the dimensional changes caused by the systematic alternation between dry and wet periods, and the biological attack favored by long periods of wetness surface, are some of the deleterious effects of exposure to rain, snow and atmospheric moisture (Davis and Sims 1983).

Whatever the form that moisture takes, it is strongly dependent on environment temperature. There is a wide variation in the relative humidity and in the amount of rainfall recorded throughout the globe. In general, precipitation variations are larger within the tropics.

As the same way as for ambient temperature, there is a large amount of available data relatively to precipitation levels and relative humidity of almost areas of the globe (Gates 1965).

iv) Pollutants:

Pollutants, which can cause the deterioration of polymers, include inert particle's matter, biologically active materials and reactive gases (Davis and Sims 1983). Whatever the nature of the pollutant, air movement is generally the prime mean of transport.

The wind is the usual transporting agent of solid particles. Air is never without dust or smoke in suspension. The fires or volcanic eruptions furnish some of the particles carried in the air, but even more are proceeding from the erosion of earth's crust by the wind itself. The range of diameters of sand particles and dust extends from about 0.1 to 2000 μm. In general, depending upon wind velocity, the air mass in movement carrying sand is restricted to the air layer within the first meter above the ground. Therefore, most abrasion damage caused by sand grains is at or near ground level. In contrast, dust particles can remain suspended in the air indefinitely, and can settle on surfaces at any height.

High environment temperature, relative humidity below 30% and the drying action of the wind invariably aggravate the dust problems, although the correlations are not known quantitatively. A coating of dust can have a number of effects on the stability of a material. Some dusts, due to their chemical composition, can initiate or catalyze chemical attack on a material, particularly when moist. A layer of dust can also act as a trap for biologically active materials and favours hydrolytic processes, as it maintains a higher humidity level by water entrapment than would otherwise exist in equilibrium. On the other hand, dust may also have a protective effect on material. It can absorb a significant amount of solar radiation and thus have the double effect of decreasing the temperature attained by the specimen and of decreasing the extent of photo degradation (Davis and Sims 1983).

Concerning reactive gases, the most commonly found in the atmosphere are sulphur compounds, ammonia, oxides of nitrogen, aliphatic and aromatic hydrocarbons, carbon monoxide and carbon dioxide (Stern 1978). These volatile pollutants are generally associated with man's industrial and domestic activities. However, many of those are also emitted by natural sources, such as volcanic eruptions and forest fires. Sulphur dioxide is the only major pollutant that arises mainly from man-made sources.

Colour, transparency, and surface resistance of polymeric materials can be significantly altered by chemical and physical modification of the surface, and for that reason all reactive pollutants constitute a threat to the service life of these materials in the natural environment (Jellinek 1978).

Due to a synergistic effect, the combined action of aforementioned weather agents has a higher deterioration effect than the sum of the eventual damages caused by each one of them if they could act one at a time.

Atmospheric pollutants, such as sulfur oxides, hydrocarbons, dust and soot particles, may cause degradation, but in combination with solar radiation and other weather factors, they can be responsible for severe damage. Soot is acidified by interaction with moisture and other particles. In the presence of sulfur dioxide and oxygen, ultra-violet (UV) radiation causes cross-linking of polymer and is responsible for the rapid loss of color in pigment coatings (Fried 2003; Mills 1993). Micro cracks that develop on a UV irradiated surface provide pathways for rapid ingress of moisture and chemical agents. Moisture, especially in the form of dew, can also remove soluble products of photo-oxidation reactions from a UV irradiated surface, and thereby, expose fresh surfaces susceptible to further degradation by UV radiation (Fried 2003; Sinmazçelik 2006; Springer 1984).

Polymer composites' weathering is, as this way, a complicated process with ill-defined interactions among the variables (Pickett and Gardner 2005), and hardly assessed by accelerated weathering devices or by relative 'short-term' exposures to natural environments.

5.4.1.2 Weathering test methods for polymeric materials.

- Natural 'versus' accelerated and/or artificial weathering tests-

For new materials, the background data on weathering performance is generally not known. While it is preferable to have factual information on the actual long-term performance outdoors of a material, reliable prediction of durability is recognized as being a necessary substitute in most cases for the confident outdoor application of polymeric materials. Within this scope, three complementary approaches have been applied:

- Natural outdoor exposure trials;
- Accelerated outdoor exposure trials;
- Laboratory artificial weathering.

Organizing weathering test methods in this manner, a trade off exists between acceleration and confidence. In going from the former method to the later, the speed of obtaining test results increases, but the confidence or reliability of such data, (*e.g.*, the types and rates of degradation are in fact those that can be observed in the end use environment?), also decreases in the same order (Atlas 2005).

i) Natural outdoor exposure trials

Of the three approaches, that of outdoor exposure trials has the longest history.

Natural outdoor exposure testing of polymeric materials began, in the U.S.A., in the early 20th century, when painted or coated samples were exposed at sites in North Dakota (Pickett and Gardner 2005). Investigators later found that the subtropical and tropical climates would cause their paints or coatings to fail much sooner, and thus allow faster turn around of the data. The high levels of temperature, humidity and solar radiation found in such regions have proved being more aggressive to materials than those of temperate zones. As the levels of individual critical weathering variables increase, the probability of interactions between these variables also increases. Interactions can accelerate deterioration rates beyond what is expected by increased levels of critical weathering factors alone (Davis and Sims 1983).

Thus, tropical and other severe exposure trials were considered as a means of obtaining advanced information on the resistance of a material to temperate conditions.

Several commercial exposure sites were then created, and the subtropical area of South Florida, near Miami, became one of the main standard environments for outdoor weathering in the U.S.A.. Over the years, many other commercial sites have appeared all over the world, namely in Arizona and Jacksonville, desert and acid rain sites at USA, in south of France, Holland and Australia. Nowadays, many other worldwide exposure sites are regularly used; however, South Florida exposure remains as the benchmark for weathering of most materials (Atlas 2005; Pickett and Gardner 2005).

Exposure trials in the aforementioned reference environments represent the first step in accelerating degradation from traditional end use conditions. Beyond the optimization of location, the use of unbacked racks or special backs for the test specimens, as well as the criterious choice of their exposure angles, are also methods that have been widely used to slightly increase the critical weathering factors, and thus, to accelerate degradation mechanisms in a natural field exposure (Atlas 2005).

Methods of acceleration and increasing critical weathering variables beyond those discussed so far, may present considerable risks for correlating testing results back to full system end use exposures. ASTM G90 standard (2005) clearly states ‘No accelerated exposure test methods can be specified as a total simulation of natural field exposure’ .

ii) Accelerated outdoor exposure trials

Alternative approaches to natural weathering test methods involve the magnification of the conditions of outdoor exposure, either by means of sun-concentrating and following devices or by exposures under mechanical stresses.

Sun-concentrating devices, such as EMMA (Equatorial Mount with Mirrors for Acceleration) and EMMAQUA (EMMA + water spray), have been extensively used since 1960, mainly to evaluate surface coatings with regard to their color retention (Atlas 2005; Ellinger 1979). These weathering devices employ several highly reflective mirrors and a sun-tracking system to concentrate sunlight onto test specimens. Because of their natural light source, such equipments require clear sky conditions for their efficient use. Approximately, a nine and a three-fold increase in, respectively, total and ultra-violet radiation are achieved in going from natural to EMMA and EMMAQUA exposure. Whilst EMMA is designed to simulate arid conditions, the EMMAQUA, on which specimens are automatically sprayed with water at regular times, is claimed to correspond to wet climates. Definitive evaluation of these weathering instruments that intensify solar radiation has not yet been established, however, they are widely used with quite successful by many manufacturers who wish to assess rapidly the durability of their products outdoors (Davis and Sims 1983).

Exposure under stress constitutes another method to accelerate the major deterioration processes in the weathering of polymer composites, and can result in a more realistic evaluation of these materials since they are often subject to some type of mechanical stress in their practical applications. Stress facilitates the rupture of polymer chains as it causes a distortion of the bond angles and an increase in inter-atomic distances (Casale and Porter 1978). Surface breackdown, crack initiation, delamination and water ingression are some of the deterioration mechanisms that could be induced and accelerated by exposure under stress. Although there is no clear evidence as yet of stress affecting directly the rate or nature of chemical processes, other than increasing the surface area available for reaction, it is a proven way of accelerating important physical processes in the weathering/aging of certain polymer systems (Davis and Sims 1983; Hu and Sun 2000).

iii) Laboratory artificial weathering

It has been argued that natural exposure is wasteful in that ‘idle time’ is high.

Artificial weathering tests are aimed at reducing this apparent waste by increasing the combined ultraviolet radiation, temperature and water effects while keeping them properly balanced.

Nowadays, there are a considerable multiplicity and variety of artificial weathering devices for the testing of polymer materials. Most of them attempt to reproduce the sunlight-induced degradation processes by an artificial light source (carbon-arc, xenon-arc, metal halide or fluorescent tube lamps). The xenon-arc source, when properly filtered, more closely simulates full spectrum solar radiation than any other artificial light source, and its superiority in this context is a major reason for its growing use in the testing of a wide range of materials (Atlas 2005).

Corrosion testing cabinets has also been widely used to simulate the highly corrosive environment of maritime sites. These weathering devices reproduce the salt-fog cycling conditions and can switch automatically from salt fogging to dry-off state.

Over the years, as the result of continuous development, highly sophisticated weathering chambers are now available (Atlas 2005; Brunner et al. 2005; Klemann 2005). As well as the production of a constant radiation output, the temperature and humidity within these ‘weatherometers’ may also be controlled. Other features that can be incorporated into these systems include rain, dew and atmospheric pollutants.

Concerning the reliability of artificial weathering tests, some questions arise immediately: Is it possible to predict the outdoor lifetime of a material with basis on artificial weathering test results? How confident and feasible is that prevision? This issue, the value of artificial weathering tests, is a subject that has been debated for at least the last 60 years (Atlas 2005; Davis and Sims 1983).

For the addicts, the use of artificial weathering tests is a practical means of tackling methodically the subject of polymer durability. In addition to the ability to manipulate and accelerate weathering conditions on demand, they also argue that the control offered by the laboratory test, as opposed to the variability found outdoors, is a fundamental benefit as it offers the possibility of relating performance to environment more confidently. Further, each of the weather factors can be manipulated independently. Thus, research can be conducted into the specific response of the materials to various weather factors, experiments that would be impossible to conduct outdoors.

For the detractors of artificial weathering, the basic concept of trying to accelerate natural weathering is flawed. They claim that since the variability in the conditions found in nature and their interactions on the material is a major reason for the complexity of the weather process, then the conditions chosen for an artificial test will produce data results peculiar to those conditions. The critics also claim that the user of artificial weathering tests is faced with a problematic choice: either to employ the severest conditions (which presumes a deep knowledge of the degradation process, usually not yet known), or to simulate as closely as possible the environment found outdoors. The later solution invariably leads to the setting up of an environment indoors that is commonly found outdoors, and consequently, the specific advantage of speed that is claimed for the artificial tests is not profited.

The advantages and disadvantages of artificial ‘versus’ natural weathering were thoroughly discussed on research work of Davis and Sims (1983) regarding the weatherability of polymers, and it seems that the former approach is neither as perfect as its disciples claim nor so useless as its detractors state . Many of the drawbacks of the artificial weathering approach, such as the use of unrealistic extreme conditions, can be avoided and useful information concerning the likely performance of a material outdoors can be achieved by settling for realistic conditions and hence modest acceleration factors. On the other hand, the variable conditions found outdoors cannot be matched in the weathering chambers, and therefore, with more or less degree, discrepancies between artificial and natural performances will always occur.

With regard to durability study of polymeric materials, nevertheless the advantages eventually brought by the use of artificial weathering tests, this technique will not replace the natural exposure. It is a complementary method the value of which largely depends on how intelligently it is applied (Davis and Sims 1983). Accurate predictions of durability will depend on valid accelerated tests, which should be designed to simulate as closely as possible the worst-case in-service conditions. The guiding should be "*simulate, then accelerate*".

5.4.1.3 Weatherability studies of PC materials

Although the effects of natural weathering and ageing on polymer materials have extensively been studied in the literature (Alves et al. 2005; Brunner et al. 2005; Davis and Sims 1983; Hu and Sun 2000; Sinmazçelik 2006; Wypych 2003), there are extremely limited studies on weatherability of polymer concrete and mortar composites.

Olivares and co-workers (2005) analyzed the degradation process of mechanical properties of polyester PMs induced by exposure to natural environment at Seville, Spain. Four different formulations were tested for flexural and compressive strength after being exposed to natural weathering during 3, 6, 12 and 36 months. Degradation process was variable according to the pair of specimen's characteristics obtained when combining dry/wet aggregate type and orthophtalic/isophtalic polyester resin type. Decay of mechanical properties after the exposure revealed a non-linear evolution with a tendency towards the stabilization. The most stable pair was the one tried out with orthophtalic resin and dry aggregates (OD). For this formulation, after three years exposure period, 20% and 18% average losses were obtained respectively in compression and in flexure. The pair formed by isophtalic resin and dry aggregates showed the worst weathering performance, with average losses of 53% in compression and 25% in flexure after the same exposure period.

Ohama et al. (1997) studied the weatherability of polymer-modified mortars (PMM) after ten-year outdoor exposure in Koryama and Sapporo, Japan. PMMs using eight types of polymer dispersions and two types of redispersible polymer powders were prepared with various polymer-cement ratios, and tested for compressive and flexural strengths, appearance change, carbonation and chloride ion penetration after ten-year exposure to natural weathering. It was concluded that in general, depending upon polymer type and polymer-cement ratio, relative mechanical strengths of PMMs were smaller than those of unmodified mortars. However, mechanical strengths of PMMs remained higher than those of unmodified mortars, regardless of exposure site. From the points of view of surface conditions, resistance to carbonation and chloride ion penetration, PMMs also showed a superior weatherability. Except for few cases in study, it was also found that retained properties of Sapporo-exposed PMMs were somewhat superior to those of Koryama-exposed ones. Although the larger number of freeze-thaw cycles of Sapporo site, considered as one of the main deterioration factors for cement mortars and concrete materials, the higher average temperature and longer sunshine duration of Koryama region revealed being more aggressive to PMM stability.

Griffiths and Ball (2000) conducted a study in order to investigate the resistance of glass-fibre reinforced polyester PC to ultraviolet radiation exposure. Standard specimens were exposed to artificial UV radiation of wavelength 300-400 nm for periods ranging 0 to 8 weeks; - unfortunately, intensity radiation of artificial light source is not given in the reference paper-. Exposure tests were repeated for verification of the results, as the random alignment of the chopped fibre reinforcement generally leads to considerable variations in material mechanical properties. Degradation process was assessed by the decay in flexural strength. Obtained results showed that moderate to severe strength losses are possible in polyester PC after exposure to UV radiation. Flexural strength loss after eight weeks amounted to approximately 24%.

Reis and Ferreira (2005) studied the effects of marine exposure on fracture properties of plain and glass/carbon fibre reinforced epoxy PMs. The stress intensity factor and the energy of fracture were measured after two different exposure periods, Spring-Summer and Fall-Winter. The Spring-Summer exposure revealed being more grievous to epoxy PMs, in terms of degradation of fracture properties, than the same exposure time in Fall-

Winter period. For both exposure periods, glass fibre reinforced epoxy PMs showed the best weathering performance, especially stress intensity factor concerning, while PMs reinforced with carbon fibres presented the worst behavior, even relatively to plain epoxy PMs. The worst performance of carbon-fibre reinforced PMs was attributed to the higher sensitivity of carbon fibres to solar radiation.

5.4.1.4 Research objective

Like the aforementioned research works, with the aim to contribute for reducing the information gap regarding weatherability of polymer mortar and concrete materials, natural and artificial weathering tests were conducted on both epoxy and polyester PM formulations in study. Experimental results are here reported and discussed.

5.4.2 Experimental Program

In order to assess weathering durability of polymer mortar formulations, two kinds of experimental programs were carried out.

In the first one, specimens of both formulations were exposed to natural environment during one year nearby the city of Aveiro, a maritime site in the middle of Portugal.

In the second experimental program the effects of artificial weathering, by means of a solar box and a salt fog chamber devices, were considered. Test specimens were exposed for periods of 500 hours up to 10000 hours.

Flexural strength retained after exposure to the defined environments was the key parameter for the assessment of weatherability of PM formulations.

5.4.2.1 Outdoors weathering program

The natural weathering experiment was performed in Ilhavo, a little village nearby the Atlantic Ocean, very close to city of Aveiro (Lat. 40º38’N, Long. 8º39’W), Portugal.

Test specimens, with standard dimensions (16×40×40 mm^3) for flexural strength evaluation, after the usual curing treatment, were exposed to the defined outdoor environment with one-week age. They were placed on the roof floor of a private building, well away from the shielding effects of trees or other buildings, situated 100 meters far from the sea. All test specimens were exposed at an angle of 0º facing the equator. Earlier studies on weathering trials have been shown that, over the year, horizontal exposure, as opposed to 45º exposure, increases the UV radiation dose by more than 10%, for both temperate and tropical sites (Davis and Sims 1983).

Both types of PM specimens were exposed to natural environment for one year, between 17/03/02 and 16/03/03. Three different withdrawal periods were considered: Spring/Summer and Fall/Winter periods, and the entire year.

Table 5.6 presents the local weather conditions, temperature, humidity, precipitation, total solar radiation and wind, during the exposure periods. In Figs. 5.19 to 5.21, the variation of some of these climatic parameters over the entire test periods is also plotted. The meteorological tower of Aveiro University, shown in Fig. 5.18, provided the weather observation data. Additionally, in the absence of ultraviolet radiation data, the empirical relationships established by Coblentz (In: McCullough 1970) were used to estimate ultraviolet radiation doses over the entire year. Obtained previsions and respective ultraviolet to total solar radiation ratios used are presented, respectively, in Fig. 5.22 and Table 5.7.

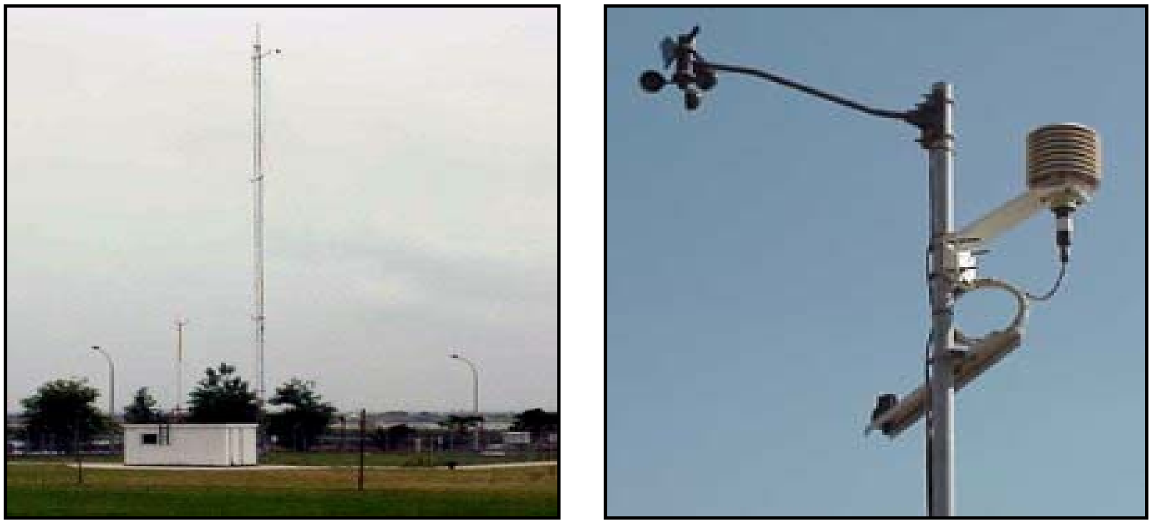

Fig. 5.18. Meteorological tower sited at Aveiro Univesity that provided hourly weathering observation data (left). Detail of measuring equipment (right).

Table 5.6. Annual weather observation data at outdoor exposure site (Meteorological Tower – Aveiro).

Observation Item [a]	Av. Temp. (ºC)	Max.Temp. | Av. Max. Temp. (ºC)	Min.Temp. | Av. Min. Temp. (ºC)	Av. Relative Humidity (%)	Precipitation (mm/month)	Av. Speed Wind (m/s)	Av. Sunshine Radiation (W/m^2)	Total Sunshine Radiation (MJ/m^2)
Mars / 02 [b]	13.2	24.4 | 18.1	6.6 | 9.2	83.67	33.0	1.70	254.15	288.20
April / 02	12.2	24.1 | 15.1	5.2 | 8.3	82.12	105.8	4.19	198.74	514.42
May / 02	13.1	23.0 | 15.8	6.8 | 10.5	85.54	106.2	4.08	-	-
June / 02	14.8	24.9 | 17.6	8.4 | 12.4	90.81	78.2	4.47	-	-
July / 02	16.0	30.4 | 19.4	10.8 | 13.3	88.51	39.4	4.71	317.56	856.26
Aug. / 02	16.3	29.0 | 19.8	10.6 | 13.5	90.30	0.4	3.54	294.70	788.28
Sept. / 02 [c]	16.6	31.5 | 20.3	10.3 | 13.7	87.94	62.0	1.05	192.92	266.69
Spr./Summer	14.6	26.6 | 17.8	8.4 | 11.6	87.18	62.9 ∑ = 425	3.73	258.63	> 2713.85
Sept / 02 [d]	17.8	26.0 | 21.6	13.4 | 15.3	84.04	102.0	2.77	163.16	197.36
Octob. / 02	16.0	24.7 | 19.7	7.4 | 13.3	87.73	111.0	2.91	128.48	344.12
Nov. / 02	11.8	18.9 | 14.4	2.0 | 9.3	91.18	300.8	3.24	74.94	172.13
Dec. / 02	11.2	17.5 | 13.7	2.6 | 8.7	89.23	237.6	0.45	65.30	173.96
Jan. / 03	9.3	16.7 | 12.7	0.6 | 6.1	74.50	425.4	2.11	80.56	215.78
Febr. / 03	9.9	17.0 | 13.1	1.5 | 7.3	81.03	233.2	1.74	106.05	256.56
Mars / 03 [e]	12.9	22.8 | 17.5	5.3 | 9.3	79.58	1174.2	1.13	171.98	237.76
Fall/Winter	12.2	19.9 | 15.5	3.9 | 9.5	84.25	324.4 ∑ = 2584	2.07	104.38	1597.67
Annual	13.4	23.2 | 16.6	6.2 | 10.6	85.72	193.6 ∑ = 3009	2.90	181.50	> 4311.52

a) All average values were obtained with basis on hourly observation data;
b) 17/03/02 to 31/03/02; c) 01/09/02 to 16/09/02;
d) 17/09/02 to 30/09/02; e) 01/03/03 to 16/03/03

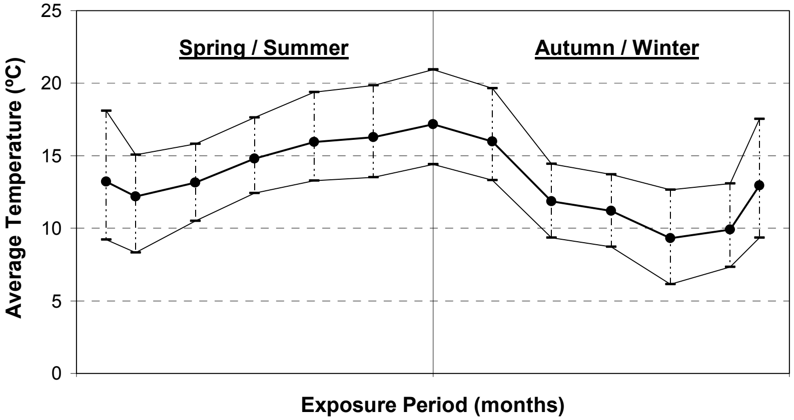

Fig. 5.19. Monthly average temperature during the exposure periods (medium, maximum and minimum average values).

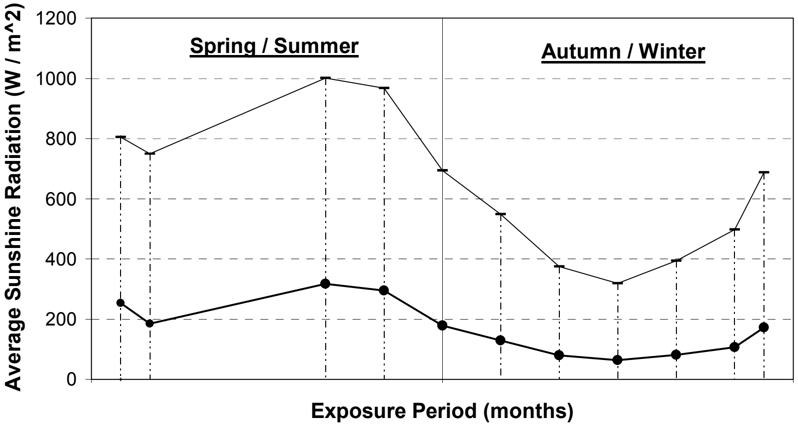

Fig. 5.21. Monthly average sunshine radiation (medium and maximum average values).

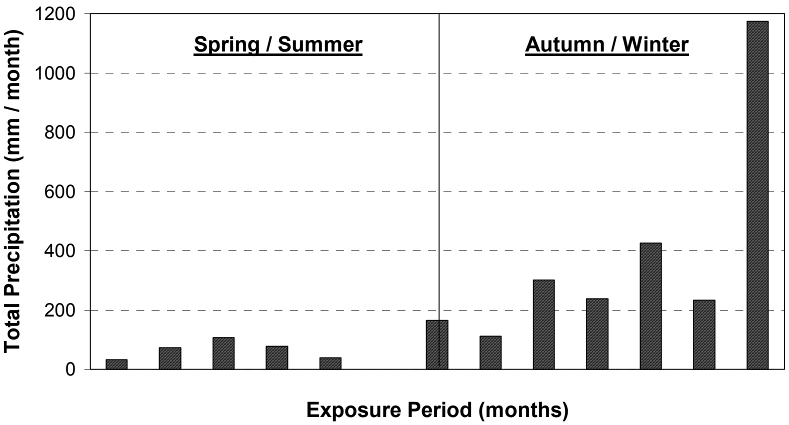

Fig. 5.20. Accumulated precipitation of each month during the exposure periods.

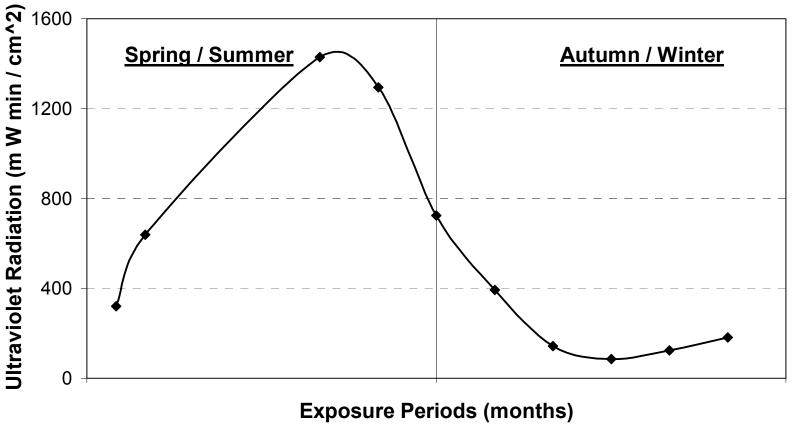

Fig. 5.22. Estimated ultraviolet radiation doses of each month during the exposure periods. Estimations were made with basis on empirical relationships established by Coblentz (see Table 5.7).

Table 5.7. Average monthly ratios of UV radiation < 315 nm [mWmin/cm^2] to total solar radiation [g cal/cm^2] at Washington (Lat. 38º 54'N) (Coblentz 1952; McCullough 1970).

	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
UV/TS	0.024	0.03	0.041	0.052	0.062	0.068	0.070	0.069	0.065	0.048	0.031	0.020

After each withdrawal interval test specimens were collected, weighted and tested for flexural strength after one day at room temperature, according RILEM PCM-8 specification (1995c).

In order to distinguish between ageing and weathering, control specimens that have been stored in the dark under normal laboratory conditions, were also withdrawn for evaluation at the beginning of the test and at each withdrawal.

The natural weathering program is summarized in Table 5.8.

Table 5.8. Summary of natural weathering program.

Type of test specimens Batches	Exposure site	Nº of test specimens	Exposure period
9 Epoxy PM 9 Polyester PM	Outdoors (Maritime site)	3 (Ref.)	0 days
		3	6 months (Spr./Sum.)
		3	12 months (Spr./Sum./Fall/Wint.)
6 Epoxy PM 6 Polyester PM	Outdoors (Maritime site)	3 (Ref.)	0 days
		3	6 months (Fall/Wint.)
9 Epoxy PM 9 Polyester PM	Indoors (Laboratory)	3 (Ref.)	0 days
		3	6 months
		3	12 months

5.4.2.2 Artificial weathering program

This part of the experimental program was carried out at Civil Department of Faculty of Sciences and Technology, New University of Lisbon. Environmental conditioning for artificial weathering took place in a salt fog chamber and in an arc-xenon solar box. Both equipments are illustrated in Fig. 5.23.

Salt fog spray artificial weathering was imposed through cycles of 16 hours of salt fog (50g/l of NaCl), at a fixed relative humidity of 98%, followed by 8 hours drying at 35ºC.

Test specimens of both formulations (160 x 40 x 40 mm) were tested for flexural strength after being exposed during 1000, 1350, 3000, 5000 and 10000 hours to salt-fog environment, which correspond, respectively, to 42, 56, 125, 208 and 418 salt-fog cycles.

Fig. 5.23. Salt fog chamber (left) and arc xenon solar box (right) artificial weathering devices.

Artificial solar radiation was imposed through filtered arc xenon rays emitted by a bulb that created an average irradiance of 550 W/m^2, with a spectral power distribution of 300-800 nm bandwidth range. This narrow band includes both high-energy ultraviolet light, considered important for photo degradation, and visible light that may have an independent or synergistic effect on materials photo degradation. The choice of 300 nm as the minimum radiation wavelength was influenced by the fact that UV radiation of shorter wavelength is mostly absorbed by the ozone layer in the atmosphere.

Test specimens of both formulations were evaluated, relatively to discoloration (qualitatively) and flexural strength, after being exposed to arc xenon rays during 500, 1000, 2000 and 3000 hours. The incidence of the rays was mostly over one lateral 160×40 mm^2 face, without rotation of the specimens, simulating the usual condition of a member subjected to solar rays solely over a part of its external surface.

The artificial weathering program is summarized in Table 5.9.

Table 5.9. Summary of artificial weathering program.

Type of test specimens Batches	Artificial Environment	Nº of test specimens	Exposure period (hours)
18 Epoxy PM 18 Polyester PM	Salt fog spray: ▪ 16 h- Salt fog: 50g/l NaCl ▪ 8h – Drying: 35ºC	3 -Ref.	0
		3	1000
		3	1350
		3	3000
		3	5000
		3	10000
10 Epoxy PM 10 Polyester PM	Arc xenon rays: ▪ Intensity: 550 W/m^2 ▪ Bandwidth: 300-800nm	2 -Ref.	0
		2	500
		2	1000
		2	2000
		2	3000

5.4.3 Test Results and Discussion

5.4.3.1 Outdoors weathering program

i) Test results

Test results, in terms of relative flexural strength and mass change of PM specimens that have been exposed to outdoors environment during Spring/Summer, Fall/Winter and one year periods, are presented in Table 5.10. Jointly, relative flexural strengths of control specimens that have been stored in the dark under normal laboratory conditions, subjected only to ageing effect, are also presented.

In order to assess weathering and ageing effects on flexural stiffness of PM formulations, some representative load-deflection curves are plotted in Figs. 5.24.

As shown in Fig. 5.25, excepting a slight color change of exposed surfaces, no visible cracks or other exterior signals of deterioration were found on both types of test specimens that have been subjected to outdoors weathering environment.

Table 5.10. Relative flexural strengths and mass changes of PM specimens submitted to natural weathering (outdoors) and ageing (indoors).-Average values and correspondent standard deviations-.

Exp. Site	Exp.Period	Relative Flex. Str. (%) | St.Dev.(%)		Mass Change (%)	
		Epoxy PM	Polyester PM	Epoxy PM	Polyester PM
Outdoors	Spr./ Sum.	92.0 | 2.0	86.1 | 5.2	0.009	0.025
	Fall/Wint.	98.6 | 1.0	94.4 | 3.2	0.020	0.177
	12 months	90.4 | 6.6	83.9 | 3.9	0.022	0.204
Indoors	6 months	98.6 | 2.2	102.7 | 3.2	-	-
	12 months	97.5 | 5.2	104.6 | 5.3	-	-

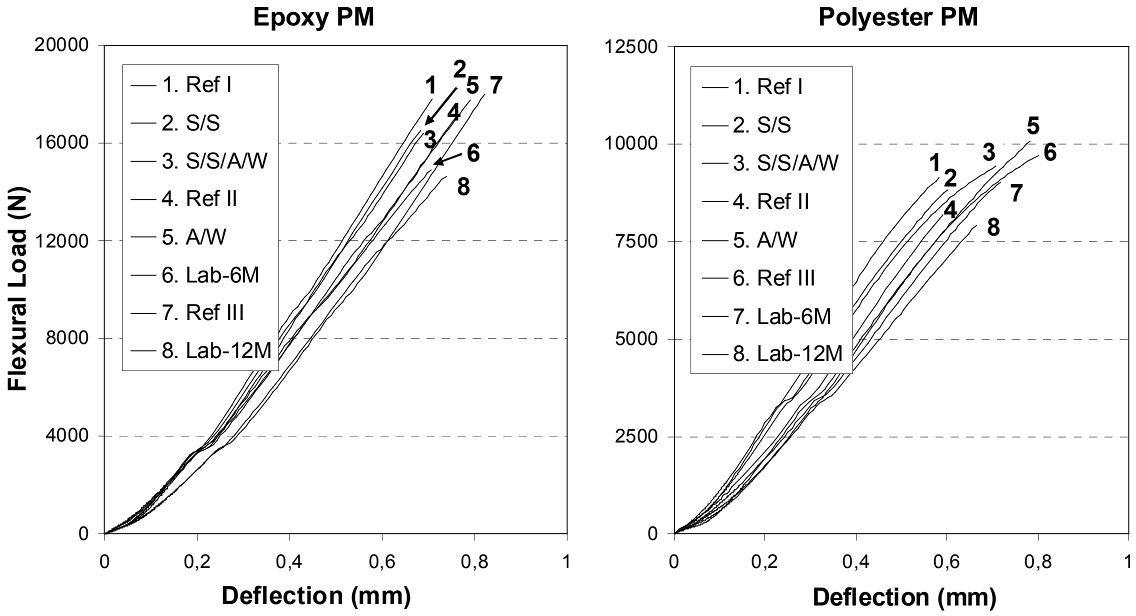

Fig. 5.24. Some representative load-deflection curves obtained from flexural tests performed on epoxy and polyester PM specimens, after being submitted to outdoors weathering and ageing test programs:

- Ref I, Ref II and Ref III: Reference test specimens relative, respectively, to Spring/Summer and 1 year outdoor exposures, Fall/Winter exposure, and indoors laboratory exposure;
- S/S: Test specimens exposed to Spring/Summer outdoor exposure;
- A/W: Test specimens exposed to Fall/Winter outdoor exposure;
- S/S/A/W: Test specimens exposed to 1 year outdoor exposure;
- Lab-6M and Lab-12M: Test specimens submitted to ageing under normal laboratory conditions during, respectively, 6 and 12 months).

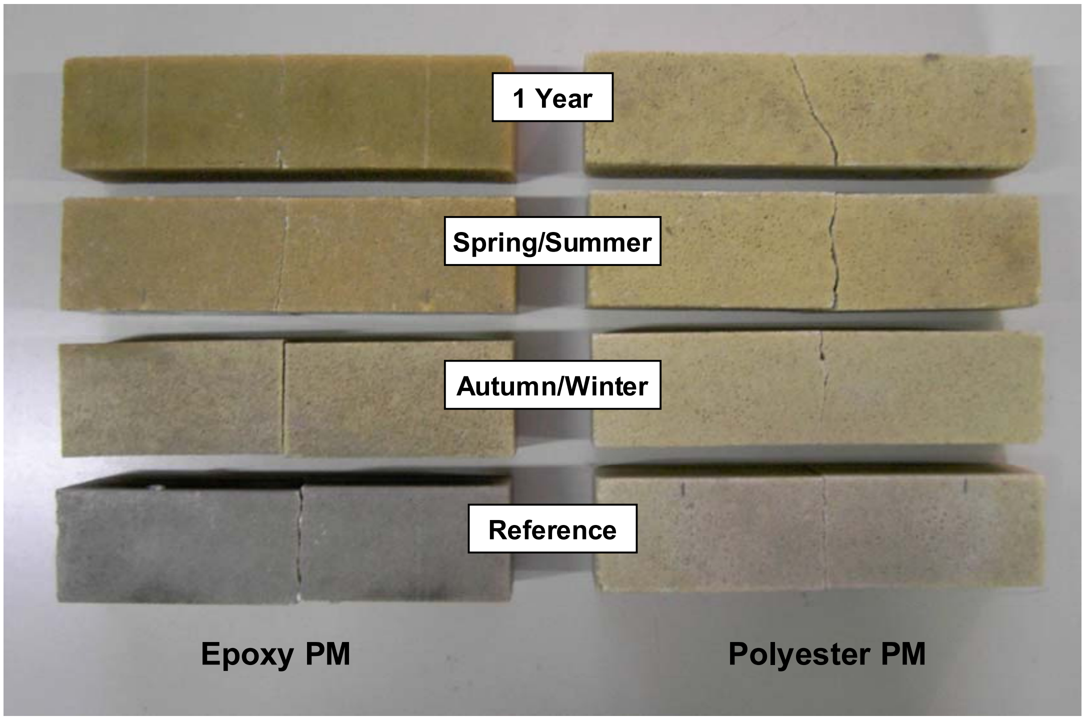

Fig. 5.25. Surface change color of epoxy and polyester PM specimens that have been exposed to natural weathering.

ii) Analysis of results

With exception of control polyester specimens that were submitted to natural ageing, all specimens suffered some kind of degradation due to weathering and/or ageing.

Epoxy based mortars present generally a better weathering performance than polyester based ones, with higher relative flexural strengths and lower scattering of results. After one-year exposure to maritime environment, an average loss of 9.6% in flexural strength was obtained for epoxy PM specimens, against an average decrease of 16.1% for polyester based mortars. These results are consistent with the consensual knowledge within the polymer degradation community, where it is usually considered that epoxy composites are in general more weather resistant than polyester composites (Davis and Sims 1983).

For both formulations, degradation rates occurred during one-year of outdoor exposure were quite similar to the sum of degradation rates corresponding to Spring/Summer and Fall/Winter exposure periods. Sums of degradation rates of 9.4% and 19.5% were obtained, respectively, for epoxy and polyester PM formulations.

The variation of load bearing capacities induced by weathering/ageing processes did not reflect on material flexural stiffness, neither for epoxy PM specimens nor for polyester based ones, as it can be seen through load-deflection curves plotted in Fig. 5.24.

Spring/Summer outdoor exposure revealed being more prone to PM specimens than Fall/Winter exposure, regardless the resin type of mortar formulations. Similar results have been found by Reis and Ferreira (2005) in their research work (see page V-50). This study, regarding the effects of marine exposure on fracture properties of epoxy polymer mortars, has a particular interest within the scope of present investigation work. Exposure site and withdrawal exposure periods were the same, and the basic formulation of epoxy PMs was precisely that one developed in this study. This is not a coincidence, as it seems, because there was a collaboration ship between the mentioned authors and the present one, as belonging to the same research team. Although the different assessing means of degradation process induced by natural weathering, (*e.g.* flexural properties *'versus'* fracture properties), obtained results on both experiments are in agreement, which is a good indicator of the reproducibility of results.

Attending to weathering observation data in Table 5.6, particularly to temperature and humidity weathering factors, there are no considerable differences between Spring/Summer and Fall/Winter periods that could explain the differentiated degradation rates. Further, taking into account the higher levels of rainfall corresponding to Fall/Winter period, reflected on higher water uptakes presented by the specimens collected at the end of that period, small differences on degradation rates would be expected. The single weathering variable that might explain the observed differentiated behavior is sunshine radiation, which assumes considerable higher values for Spring/Summer period.

As already referred, the radiation of the sun, particularly the ultraviolet (UV) portion is mainly responsible for limiting the lifetime of polymeric materials exposed to the environment. Breakage of polymer bonds and consequent oxidation process are the main degradation mechanisms involved. The sun radiation, like other light sources, is described by the wavelengths emitted and their intensities, *i.e.*, by its spectral power distribution. Both the absorption of light (a necessary first step in the interaction of light with materials), and bond breakage (a critical primary effect of the absorbed radiation), are wavelength dependent. Generally, short wavelengths are absorbed by materials to a greater extent than longer wavelengths. In addition, the shorter the wavelength, the larger the energy of the photon associated with that wavelength and the greater the propensity to break the higher energy chemical bonds. The number of photons associated to each wavelength determines the intensity of light of that wavelength. Thus, the greater the intensity light, the larger the amount of incident photons absorbed by the material and, generally, the gravest the photo-oxidative attack.

On the other hand, the temperature of materials exposed to solar radiation can have a significant influence on the effect of that absorbed radiation. The destructive effects of light are usually accelerated at elevated temperatures, mainly by increasing the rate of secondary reactions. At high temperatures, molecules have a greater mobility. Therefore, the rate of oxygen diffusion increases and free radicals fragments formed from the primary photochemical processes are more readily separated. As a result, the chance of recombination is reduced and secondary reactions are promoted. A general rule for the effect of temperature on reaction rates is hat the latter doubles for each 10ºC increase in temperature (Atlas 2005).

Thus, considerable higher intensities of sunlight radiation, specially in the UV region, in combination with quite higher levels of temperature, seem to be the major reasons for the higher degradation rates occurred on Spring/Summer exposure period.

Over the time, somehow, polyester based mortars that have been stored in the dark under normal laboratory conditions underwent some kind of post-cure process, which led to increasing flexural strengths after six and twelve month ageing. Conversely, epoxy based mortars showed some sensitivity to degradation processes due to ageing effect. After six and twelve-month ageing, slight decreases on flexural strength occurred.

It must be noted that above considerations must be taken with caution, as flexural strength variations were quite small on both cases and within the range of values expected for specimens proceeding of the same batch (see Table 4.7). Further, both the small amount of test specimens and the relative short ageing periods do not allow stating the existence of clear trends concerning polymer mortar's behavior with ageing.

Discounting the ageing or timing effect, which had different outcomes for each formulation, strength decreases due to the single effect of weather become higher for polyester PMs and, conversely, lower for epoxy PMs. In graphs of Fig. 5.26, the separated effect of weathering versus the combined effect of ageing/weathering with exposure time are plotted.

Additive mechanism of effects is also highlighted in Fig. 5.26: the sum of the two 'vectors' corresponding to flexural strength decreases of PM specimens submitted to both shorter exposure periods is practically similar to that one corresponding to flexural strength decay of PM specimens subjected to outdoor exposure during all entire year.

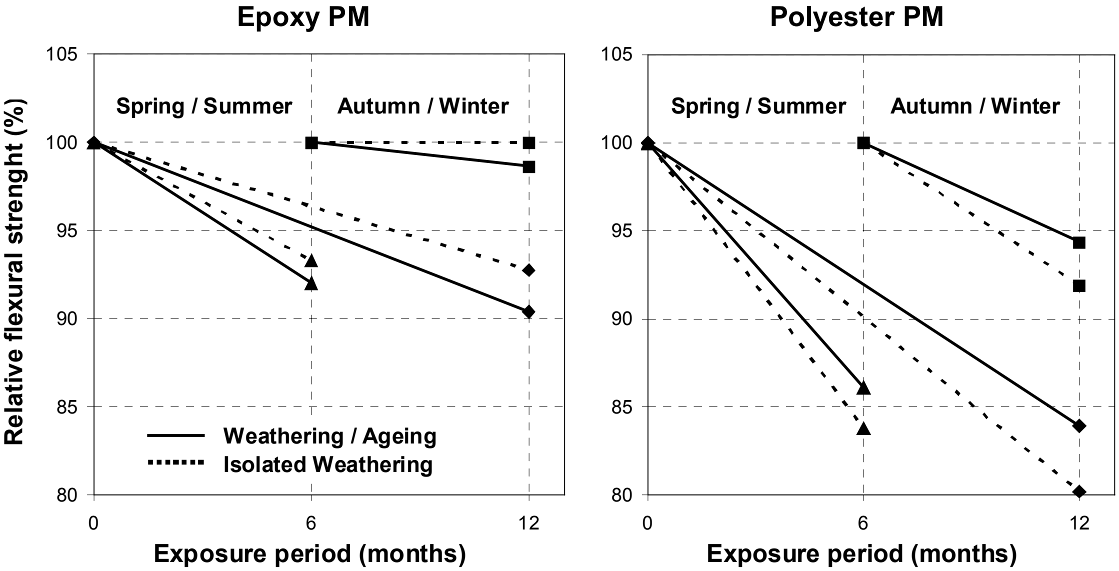

Fig. 5.26. Relative flexural strengths of epoxy and polyester PM specimens, as function of exposure time. Isolated effects of outdoors weathering 'versus' the combined effects of weathering/aging processes.

5.4.3.2 Artificial weathering program

i) Test results

Residual flexural strengths of PM specimens that have been subjected to artificial weathering in the salt fog chamber and solar box devices, for the different exposure periods, are presented in Table 5.11.

Appearance changes induced by imposed environments on epoxy PMs are illustrated in Fig. 5.27.

Table 5.11. Relative flexural strengths of PM specimens submitted to artificial weathering tests. – Average values and correspondent standard deviations-.

Artificial Environment	Exposure Period (hours)	Relative Flex. Strength (%) | St.Dev.(%)	
		Epoxy PM	Polyester PM
Salt Fog Chamber	1000	91.7 | 9.9	94.0 | 8.0
	1350	86.5 | 6.5	87.2 | 11.1
	3000	79.1 | 4.1	85.3 | 3.1
	5000	64.8 | 1.3	64.2 | 11.4
	10000	52.2 | 3.7	62.0 | 3.1
Arc-Xenon Solar Box	500	102.0 | 3.2	98.9 | -
	1000	105.1 | 1.5	96.2 | -
	2000	105.9 | 5.7	102.2 | -
	3000	110.7 | 1.3	104.9 | -

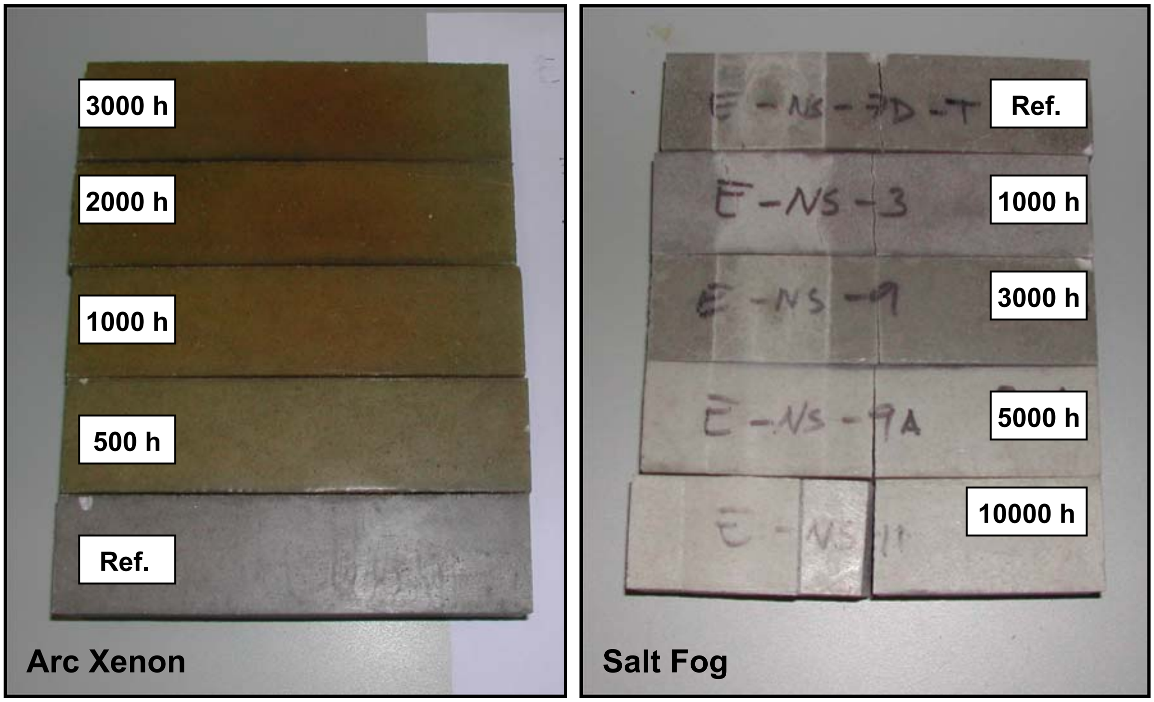

Fig.5.27. Yellowing and discoloration processes suffered by epoxy PM specimens submitted, respectively, to artificial solar radiation (in the left) and salt fog spray cycles (in the right).

A strong staining was observed on exposed surfaces of both polyester and epoxy PM specimens that have been subjected to artificial solar radiation. As shown in Fig. 5.27, the browning process was so much remarkable as longer was the exposure period. Slight whitening was also observed on the exterior surfaces of PM specimens submitted to salt fog environment, as it can be seen in the same figure, but discoloration process with exposure time was not so outstanding. Whatever both the environment that caused the color change and the exposure time, the observed phenomenon had a superficial character affecting only the exposed surfaces of the specimens, as it was verified by observation of failure surfaces posterior to bending tests.

ii) Analysis of results

Both types of PM specimens were severely affected by exposure to salt fog spray artificial weathering, specially epoxy based ones. After 10000 hours of exposure, corresponding to 478 salt fog cycles, flexural strength decays of 48% and 38% were recorded, respectively, for epoxy and polyester based mortars. Strength decrease rates showed a non-linear evolution with a tendency towards the stabilization, as shown in Fig. 5.28.

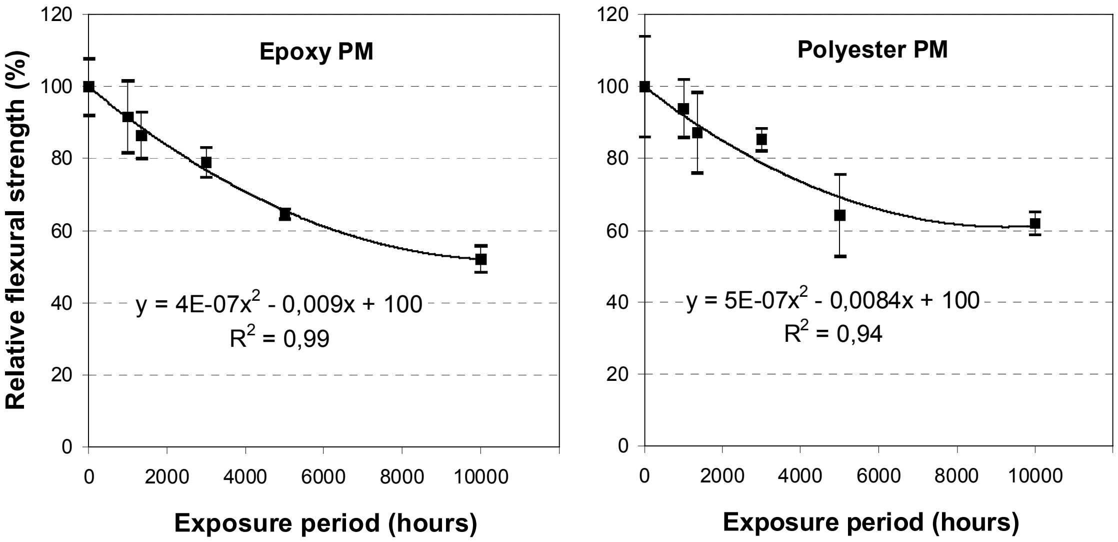

Fig. 5.28. Relative flexural strengths of epoxy and polyester PM formulations, submitted to salt-fog spray artificial weathering, as function of exposure period.

Whereas epoxy PM specimens experienced a progressive and steadily resistance loss until half of the total exposure period, and later on seemed to tend to stabilization; polyester based specimens clearly showed two different stabilization periods: between 1350 and 3000 hours and after 5000 hours of exposure.

Obtained results were completely unexpected regarding the excellent resistance showed by epoxy based mortars to saline solutions (see subchapter 5.2). After 84 immersion days (2016 hours) in 10% sodium chloride solution, this material retained 102% of its original flexural strength. It seems that the cycling process from salt fogging to dry-off conditions causes more severe damages on epoxy polymer matrix than the continuous diffusion process of salted water into mortar mass. An explanation can be advanced with basis on fatigue processes. Mechanical cyclic loading can be induced in many polymeric materials that are sensitive to expansion and contraction by moisture cycling: absorbed water results in compressive stresses on the outside and tensile stresses in the bulk; subsequent drying periods create bulk compressive and surface tensile stress gradients. Eventual microcraks induced by this fatigue process weak the overall resistance of the material, leading to early failures under higher mechanical stresses.

Conversely to what that occurred in salt fog artificial weathering tests, no mechanical degradation effects were observed on PM specimens that have been exposed to arc-xenon artificial light source. Instead, in general for both formulations, progressive increases on flexural strength were found. After 3000 hours of exposure to artificial solar radiation, increases of 11% and 5% on average flexural strengths were obtained, respectively, for epoxy and polyester PM specimens. For epoxy-based mortars, flexural strength increase with exposure time was almost linear, while for polyester based ones, this trend was only noticed after the two first exposition periods, in which some small decreases on resistance occurred.

Lack of agreement between the solar spectrum and that of the artificial light source is likely the main reason for the poor correlation between the two modes of exposure. Although the higher average irradiance associated to artificial exposure (550 W/m^2) comparing to natural one (182 W/m^2), high daily intensity peaks are found in the later, specially during Spring/Summer period, which not occur in the artificial exposure (see Fig. 5.19). Further, mismatch in the infrared region (λ> 800 nm) can cause the surface temperatures of natural and artificially exposed specimens to be quite different, and thus the synergetic effect due to combination of UV radiation and heat has rather different magnitudes in the two situations. On the other hand, the daily fatigue due to night's condensation and day's solar drying that occur in a natural exposure, interacts with photo degradation processes causing mechanisms significantly different from those that can be encountered in an arc-xenon solar box without any correspondent simulation devices (*e.g.*, dark cycles and water spray at lower temperatures). Another feature that might explain the absence of any sign of degradation, apart the browning process, is the 'solarization' mechanism. As arc xenon lamps and filters age, the quartz envelope of the burner and the filters themselves undergo a UV deterioration process, which decreases the optical transmission, specially the shorter wavelengths.

Thus, although the discrepancies found in the infrared radiation, in the light intensity and in the other mentioned environment conditions, could cause the degradation processes of natural and artificially exposed specimens to be quite different, it seems that it was differences in the ultraviolet radiation that were most likely to cause the observed differentiated behavior.

5.4.3.3 Correlation between natural and artificial weathering test results

Before drawing any considerations concerning the possible pattern that might exist between degradation processes that occurred on the different weathering tests performed, natural and artificial ones, some concepts must be clarified. These are 'correlation' and 'acceleration factor'. The usefulness of artificial weathering tests may be characterized by these two parameters.

Correlation is the degree to which data obtained in the artificial weathering test agrees with data obtained outdoors. This term has also been used with reference to the type of degradation produced on both types of tests.

Acceleration is a measure of how rapidly the test can be conducted using an accelerated weathering device compared with outdoor testing. Only if agreement exists with outdoor results is it valid to estimate the acceleration of laboratory test. The acceleration factor is the time to failure (or change in property) under natural exposure, divided by the time to failure under the accelerated test condition, both evaluated by the same technique. It can vary over a wide range of values from 1 to 100 or larger. However, for accelerated test conditions that correlate with outdoor exposure, the factors are commonly between 2 and 10 (Atlas 2005). Generally, the greater the acceleration the poorer the correlation.

Acceleration factors are material specific and vary with formulation. They also depend on the accelerated test method and, obviously, on environmental conditions of outdoor exposure. Therefore, for a variety of materials and formulations, it is not possible to establish a single acceleration factor for extrapolating test results in order to predict lifetimes under natural weathering conditions.

As already has been pointed out, no correlation was observed between data obtained in arc-xenon artificial weathering tests and test results of natural weathering program, and therefore, it is not possible to estimate correspondent acceleration factors.

Relatively to salt-fog artificial weathering test results, it is also premature to state that a good agreement exists with outdoor results. The first two exposure periods to natural weathering cannot be considered for correlation purposes, as their results were strongly affected by the time of year that those periods began. It is believed, in agreement with the folk wisdom in the polymer degradation community, that the time of year that an exposure begins is important at first but no longer makes a difference after one-two years (Pickett and Gardner 2005).

Thus, there is only one single data (one-year outdoor exposure results) that could be used for correlation effects, which is not quite enough. Assuming, however, that there is a reasonable connection between salt-fog artificial weathering test results and data obtained with one-year outdoor exposures, an attempt was made in order to estimate correspondent acceleration factors.

These parameters were calculated by dividing the number of hours of one year, by the number of hours under salt-fog cycling that would be required to achieve equivalent flexural strength decreases. For this purpose, the regression curves plotted in Fig 5.28 were applied. Acceleration factors of 7.80 and 3.97 were obtained, respectively, for epoxy and polyester PM formulations.

What are the mean and the relevance of these factors?

It can only be stated that flexural strength decrease of epoxy and polyester PM formulations, induced by one-year exposure to natural weathering (at maritime sites with similar latitudes than Aveiro), corresponds, respectively, to 46 and 92 days of salt fog spray artificial weathering (with the same set-points used in this experimental program). No reliable extrapolations can be done beyond these ones.

If posterior flexural test results of PM specimens withdrawn at longer outdoor exposure periods (more than one year) also agree with the data obtained on artificial weathering tests, and thus following the same trend, then previsions regarding outdoors lifetime of PM formulations might be done. Presuming the veracity of this hypothesis, flexural strength behavior of PM formulations with exposure time, in a natural outdoor environment similar to Aveiro, could be modeled according the following equation:

$$Y = (A / a_f^2)\, x^2 + (B / a_f)\, x + 100 \quad \text{with } x \le -(B/2A)\, a_f \tag{5.5}$$

where Y is the retained flexural strength, in percentage; *x* is the exposure time in hours; a_f is the acceleration factor, and A and B are the polynomial factors of the regression curve correspondent to material flexural strength behavior under salt fog accelerated weathering test.

According this model, predicted flexural strength behaviors of PM formulations with exposure time are plotted in Fig. 5.29.

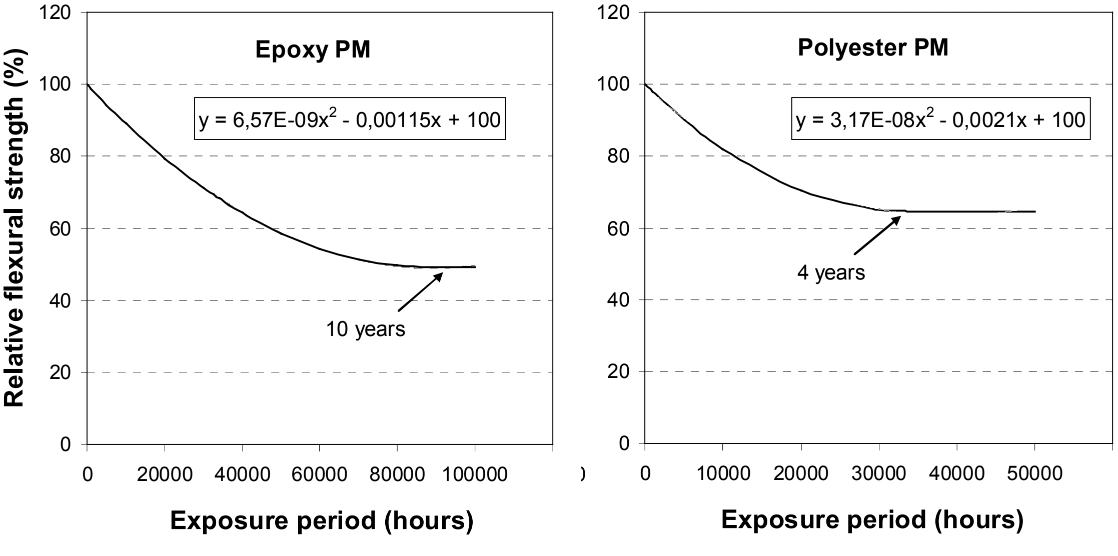

Fig. 5.29. Predicted flexural strength behaviors of epoxy and polyester PMs under long-term exposure to natural environment (similar to Aveiro site).

It must be remarked that the presented model was developed assuming that equal or very similar acceleration factors would be obtained for outdoor exposures longer than one year, which is just a mere assumption.

One important feature that may affect the acceleration factors is the time scale of the experiments. Most of the comprehensive assessments of various types of weathering tests in the literature do not include correlation data, which makes difficult any comparison with the present results. However, the few published results show that the acceleration factors tend to increase with the time scale of the experiments (Bauer 2000; Crump 1996; Klemann 2005). For all test materials studied by Klemann (2005), which include different classes of polymers, higher acceleration factors were found for two years than for one-year outdoor data. It is believed that these parameters may rise even further in longer tests, until they may eventually approach a stable long-term value.

Thus, the relationship between natural and artificial exposure is not necessarily best expressed in terms of a constant factor (Howard and Gilroy 1969). Ideally, acceleration factor should be determined not as a constant parameter but as a function of time scale.

Hence, the prediction model here presented, with basis on a short-term value of the acceleration factor, only gives a rough indication of the relationship between natural and artificial weathering. However, it has the benefit of running by the safety side, representing the worst scenario that could be encountered in a real situation of long-term outdoor exposure.

5.4.4 Conclusions

In order to assess weatherability of epoxy and polyester PMs, natural and artificial accelerated weathering tests were conducted on specimens of both formulations. Based on test results the following conclusions may be drawn:

- PM formulations are sensitive to degradation effects of natural weathering. One-year outdoor exposure to natural maritime environment, similar to that one of Aveiro region, has a moderate deleterious effect on mechanical flexural strength of both types of PMs. Epoxy based mortars revealed being in general more weather resistant than polyester based ones (- after one-year exposure, average flexural strength losses of 9.6% and 16.1 % were found, respectively, for epoxy and polyester PM specimens-).

- Spring/Summer outdoor exposure is more prone to PM specimens than equivalent exposure time in Fall/Winter period. Flexural strength decays in the former period were between two up to five times greater than those that occurred in the later one. Higher intensities of sunlight radiation, especially in the UV region, combined with quite higher levels of temperature, seem to be the major reasons for the superior degradation rates that occur on Spring/Summer period.
- Different outcomes were found for the effect of ageing on mechanical strength of PM formulations. Whereas for epoxy-based mortars, slight decreases on flexural strength were observed after six and twelve months ageing, polyester based ones underwent some kind of post cure process that led to increasing flexural strengths after the same ageing periods. Nonetheless, no clear statements can be done regarding the role of polymer aging on weathering mechanisms of epoxy and polyester PMs, as strength variations of control specimens were quite small on both cases.
- Beyond yellowing and staining processes, relative short-term exposures to arc-xenon artificial light source (up to 3000 hours), with the set-up points used in the present experimental program, has no noticeable deleterious effects on both types of PM formulations. Instead, slight increases on mechanical flexural strength were in fact observed. Lack of agreement between the solar spectrum and that of the artificial light source, especially in the infrared and UV region, appear to be the main reason for the differentiated behavior of natural and artificially exposed specimens.
- Both types of PMs are severely affected by exposure to salt-fog spray artificial weathering, specially epoxy based ones. After 10000 hours of exposure, epoxy and polyester PM flexural strengths dropped to 52% and 62% of their original values. The strength decrease rates presented a non-linear evolution with a tendency to stabilization. Mechanical cyclic loading induced by moisture cycling,

leading to fatigue processes, is likely the major cause responsible for the strong degradation rates occurred during salt-fog artificial exposure.

- Regarding the correlation between salt-fog artificial weathering test results and data obtained with natural exposure, with basis on one-year time-scale, it can be stated that the former tests accelerate 7.80 and 3.97 times the natural weathering degradation processes that occur, respectively, on epoxy and polyester PM formulations. Obtained acceleration factors can only be applied relatively to maritime sites, with similar latitudes as Aveiro, and to salt-fog artificial environments with the same set points used in this study.
- Previsions regarding the long-term behavior of PM formulations with outdoor exposure time can be attempted, but only with a merely indicative value. Within the uncertainty of the data, maximum flexural strength decreases of 50% and 35% will be expected, respectively for epoxy and polyester PMs. It is estimated that predicted residual flexural strengths, which constitute the long-term stable values, will be attained, respectively, after 10 and 4 years of outdoor exposure.

It must be pointed out that prediction models based on short-term values of acceleration factors only give rough indications about the relationship between natural and artificial weathering, representing, eventually, the worst scenario that could be encountered in a real situation of long-term outdoor exposure.

Since major deleterious effects of weathering are confined to superior layers of the material, another point that should be realized is the fact that damage magnitude becomes size piece dependent. The larger the element, the minor the importance of the damage. It is not reasonable to expect that a larger element of PM material would loss the same load bearing capacity as a standard prismatic specimen.

Nevertheless, estimated residual flexural strengths of PM formulations after long-term outdoor exposure are, even so, still competitive with those presented by ordinary cement concrete materials (not exposed to weathering processes).

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VI. FIRE PERFORMANCE OF PM FORMULATIONS

6.1 Fire Reaction

6.1.1 Introduction

An important cause of physical damaging is fire. The behavior under fire is a feature of paramount impact concerning building materials, both from the point of view of structural security as well as the security of the occupants in the building.

Composite materials made from organic matrices, depending upon matrix type and matrix content, are generally combustible. In most cases, polymers initiate or propagate fires because, being organic compounds, they decompose into volatile products when exposed to heat. The present spread of synthetic polymers has thus greatly increased the ‘fire risk’ and the ‘fire hazard’ that are respectively the probability of fire occurrence and its consequence either on humans or on structures.

Polymer concretes (PC) and mortars (PM), as organic composite materials, are not free from fire risks. Despite of their high mineral aggregate content, common resins used as binders are highly flammables, which weaken the overall behavior under fire of this kind of composite materials. Unsaturated polyesters and epoxy resins generally require flame-retardants to meet fire protection standards. In particular, flammability of epoxy resins is greater than comparable thermosetting resins since they have a reduced tendency to carbonize. After removal of the ignition source they continue to burn on their own (Horold 1999).

Therefore, in many fields, the use of polymers is restricted by their flammability, irrespective of the advantages their use may bring.

Fire performance is thus one of the main drawbacks that restrict the most the use of PCs and PMs in construction (Browne et al. 1975).

6.1.2 Fire Test Standards

The 1988 edition of fire tests compilation by the American Society for Testing and Materials (ASTM), alone, lists more than 70 tests, and ASTM is only one of the many international organizations publishing fire test standards (ASTM 1988). Thus, in the nineties it was estimated that the number of fire tests in use throughout the world was at least in the hundreds (Troitzsch 1990).

It is typical to divide the fire test standards into two broad categories: reaction-to-fire, or flammability, and fire endurance, or fire resistance.

At this point, a comment must be done concerning the distinct means of fire reaction and fire resistance. Fire resistance applies mainly to a building element, (with structural, bearing carrying or partition role), while fire reaction applies rather to a building material. Fire resistance of a building element can be defined as its capacity to perform its function under a fire situation, and it can be interpreted as the period of time under fire during which the building element continues to perform its function satisfactorily. Fire resistant tests are performed on barriers to fire and structural or load-bearing elements, such as walls, floors, ceilings, doors, windows and related items.

Reaction-to-fire of a material, by contrast, can be defined as its potential contribution to a fire. The fire reaction is determined by the material flammability and it can be characterized by the same parameters as this last one: ignitability, flame spread, heat release, and emission of smoke and toxic gases. Fire reaction tests are typically performed on combustibles materials or products. The scope of the present study is restricted to this kind of fire tests.

A larger number of different standards and test procedures exist for assessing the reaction to fire performance of construction products, and in almost of the cases, there is no consensus or equivalence between them. Just for itemizing some of them:

- The ASTM method for fire test response E 1354-04 (2004), provides means for the determination of the ignitability, heat release rates, mass loss rates, effective heat of combustion, and visible smoke development of materials and products. The heat release rate is determined with basis on oxygen consumption principle. This principle is based on the fact that the heat of combustion of organic materials per unit of oxygen consumed is approximately the same. The heat release rate is one of the most important parameters used to characterize the fire reaction (Babrauskas and Peacock 1992). It provides an indication of the size of the fire, the rate of fire growth, and as a consequence, the release rate of smoke and toxic gases, the fire rating, the type of suppression actions that are likely to be effective, and other attributes that define the fire hazard.
- Other ASTM method for fire test response, E 662-03 (2003), covers the determination of the specific optical density of smoke generated by solid materials. Measurement is made of the attenuation of a light beam by smoke accumulating within a closed chamber (chamber box) due to non-flaming pyrolytic decomposition and flaming combustion.
- The '*Gross Calorific Potential test*' (GCP) determines the potential maximum total heat release by a product when complete combustion occurs, regardless of its end use (EN ISO 1716 2002).
- The '*Oven-test for non-combustibility*' allows the identification of products that will not contribute significantly to a fire, also in spite of their intended use (EN ISO 1182 2002).
- The '*Single Burning Item test'* (SBI) evaluates the potential contribution of a material to the development of a fire in terms of heat release, smoke yield and burning droplets. The reference scenario for the SBI test, as the name suggests, is a fire originating from a single burning item in the corner of a room and growing within that room to flashover. The amount of heat and smoke developed is

measured while particle projection and flaming droplets are just observed (EN 13823 2002).

- The '*Ignitability test*' assesses the ignitability of a product in a vertical orientation when exposed to a small flame on the surface and, when appropriate, on the edge too (EN ISO 11925-2 2002).
- The French norms NF X10-702 (1994) and NF X70-100 (Part 1, 2001; Part 2, 2001) provide means for determining the opacity and the toxicity of smoke and gases released by a material under fire, which are the required parameters to calculate the 'smoke index'. This indicator allows the classification of the materials into classes rated from F0 (materials that do not release neither smoke nor toxic gases) up to F5 (materials that strongly release smoke and toxic gases), according NF F16-101 (1988).

Another classification system of grading building materials according to their fire reaction, forming the denominated 'second generation' of group of fire tests, is based on radiant panels or in the epirradiator test. Ignition times, spread flame and variation of the thermal balance are the parameters controlled in these types of tests. There are three different main versions for these standards usually known by ´The Three Sisters': the French, the British and the German ones.

- The 'German sister', regulated by DIN 4102-1 (1998) norm, establishes three types of fire tests: in the electric furnace, in the combustion chamber (Brandschacht) and in the little burner. Materials are classified as non-combustibles (Class A) or combustibles (Class B). Non-combustibles materials are subdivided into two categories: A1 and A2, according they observe, respectively, all the non-combustibility requirements, surpassing the tests of the electric furnace, combustion chamber, opacity of smoke, toxicity, thermal power and heat release rate, or only the later five.

  Combustible materials, on their turn, are subdivided into three subclasses according to their flammability: hardly (B1), medially (B2) or easily flammables (B3). These classifications are determined as function of obtained results of both combustion chamber and little burner tests.

- The British branch, specified in BS 476 (Part 4, 1970; Part 7, 1997), establishes the non-combustibility and spread flame tests as basis for fire reaction classification. Materials are classified as non-combustibles if they suppress the required criteria for the non-combustibility test, being categorized as class 0. Combustible materials are divided into four classes rated from 1 to 4, according to obtained results of spread flame test.
- The French stream, over-headed by French Norm NF P92-507 (2004), incorporates the Portuguese directive and Spanish standard, and they have no requirements for smoke or toxicity of gases produced by combustion of building materials. Materials are classified according to their combustibility and flammability into five classes rated from M0 to M4.

  A ‘M0’ class indicates that the material is not combustible. The criterion depends on the maximum heat of combustion released by the material, determined by the Gross Calorific Potential test (GPC). A ‘M1’ material is combustible, but not flammable, *i.e.*, the combustion ceases when the external heating source is interrupted. Materials ‘M2’, ‘M3’ and ‘M4’ are respectively, moderately, medium or highly flammable. For rigid materials, these classifications are determined by the ‘classification index’ value, which is calculated with basis on specific parameters obtained from the radiation or epirradiator test results.

The variation and differences between all these procedures meant that transition and comparison of performance of a material when assessed by different methods became very difficult. For instance, the same material with the same thickness, ordinary plywood, has been classified according to its reaction-to-fire as a M4 in France, as a B2/B3 in Germany, and indexed as a material 3 in the United Kingdom. The non-equivalence between the different classification systems led to a lack of consensus between certified products of different countries.

Some years ago, a researcher had tried to make a compilation of all the standards and procedures in order to simplify this task (Troitzsch 1990). His book was particularly useful, at the time, in simplifying the difficult and often confusing area of international and national regulations of fire test procedures.

Recently, a new system has been developed, which was negotiated with the national fire regulators of the EU by the European Commission. As the concept and procedures for the evaluation of reaction to fire of varying products differed from one country to another, a harmonized approach was developed by CEN (European Committee for Standardization) following a mandate from the European Commission. Today, this has resulted in new testing methods and classifications of fire reaction and fire performance for building materials– the Euroclasses.

6.1.3 Fire Reaction: Euroclassification

The European classification system, detailed in EN 13501-1 (2002), is in use since February 1st, 2002. After this date, all national classifications for construction products are still recognized on the national markets for a period of 3 to 5 years. The exact length of this transitional period has not yet been fixed. At the end of the period, only European classification will be valid, at both national and European level.

The European classification consists of seven Euroclasses: A1, A2, B, C, D, E and F.

- Classes A1 and A2 cover products that contain only traces or minor quantities of flammable elements and are, therefore, considered to be virtually or completely non-combustible.
- Classes B, C, D, and E cover the combustible products. They characterize the most dangerous products as far as their performance in fire conditions is concerned.
- Classe F relates to products about which no data concerning their fire performance is available or those products that failed the ignitability test that normally regulates access to classification E.

With exception of Euroclasses A1, E and F, two additional classifications, relating to smoke intensity and generation of burning particles or droplets supplement the main Euroclasses. These additional classifications are subdivided into three levels of severity:

- For smoke intensity: levels s1, s2 and s3 (corresponding to low, average, and high quantity and speed of emission, respectively).

- For burning particles or droplets: levels d0, d1 and d2 (corresponding, respectively, to no burning particles or droplets, no burning particles or droplets with a burning time of more than 10 seconds, and not classifiable into the last two levels).

The Euro classifications are based in a set of supporting tests. Test methods were established to simulate the three levels of thermal activity that correspond to the different stages in the development of a fire, *e.g.*: a direct attack by a small flame; additionally thermal activity due to the heat of burning object; and a fully-developed fire in the chamber. To respond to these three levels, four testing methods were selected and harmonized to define the reaction to fire of construction materials:

- The Gross Calorific Potential test (EN ISO 1716 2002);
- The Oven-test for non-combustibility (EN ISO 1182 2002);
- The Single Burning Item test -SBI (EN 13823 2002);
- The Ignitability test (EN ISO 11925-2 2002).

The criteria for classification as defined in the norm EN 13501-1 (2002) is summarized in Table 6.1. When the experimental work of this thesis concerning fire reaction of PM formulations was under development, European classification system and related standards were still in the final harmonization, thus, all the experimental work was conducted according to French normalization.

Table 6.1. Euro classification criteria for fire reaction.

Classes	Levels		Classification according to EN 13501-1
A1	-	-	The fire classification of a product is expressed as per the following example: A2 – s3, d0 (*i.e.*: a product only moderately combustible, with significant smoke emission, but without burning particles or droplets)
A2 B C D	s1	d0	
		d1	
		d2	
	s2	d0	
		d1	
		d2	
	s3	d0	
		d1	
		d2	
E	-	d2	
F	-	-	

As Euro-classification try to reflect the safety concept developed in each country, it is possible to foresee the fire performance of materials from former classifications, (British, German and French ones), to European classification taking only into account the fire contribution of each class. It must be remarked that no official decision have been achieved by any states regarding this issue, and the work is still in progress. This approach is presented in Table 6.2.

Table 6.2. Conversion trial from the German, British and French fire classification to European classification in terms of flame spread contribution (SpecialChem 2005).

Contribution to fire	No contibution	Quasi no-contibution	Very limited	Limited	Medium	High
European	A1	A2	B	C	D	E
French	M0	M0	M1	M2	M3	M4
German	A1	A2	B1	B2	B2	B3
British	0	0	0-1	1	3	4

6.1.4 Flame and Fire Retardant Additives

The fire safety of composite materials can be significantly enhanced by increased ignition resistance, reduced flame spread rates, reduced heat release rates, and reduced amounts of toxic and smoke products, preferably simultaneously (Kashiwagi et al. 1997).

The most common approach to improve fire safety performance is the use of flame retardant chemicals. The role of these modifiers is to slow down polymer combustion and degradation (fire extinction), to reduce smoke emission, and to avoid dripping.

There are two basic types of flame retardant chemicals: reactive flame retardants, which are usually introduced during the polymerization stage and copolymerized, together with other monomers; and additive flame retardants, which are introduced during a subsequent compounding stage.

Reactive flame-retardants are chemically linked to the resin matrix, so that mechanical and chemical properties are not usually affected. The main drawback lies on the higher cost associated to the flame retardancy process itself.

Additive flame-retardants are more frequently used and are very numerous, depending on the precise conditions in which the additive is expected to operate (and the desired cost level). However, the addition of a flame retardant additive into a polymer generally leads to a reduction of its mechanical properties and particularly, of impact resistance. The main challenge during the selection of a flame retardant additive system is to minimize the loss of properties at optimized cost, taking into account other performances such as mechanical resistance, UV stability, heat resistance and processability.

To understand the role of flame retardant additives on fire retardancy of polymer composites, the mechanism of fire action must be previously understood.

Fire is the result of three ingredients: heat, fuel and oxygen. Heat produces flammable gases from the pyrolysis[1] of polymer. Then, an adequate ratio between these gases and oxygen leads to ignition of the polymer. The combustion leads to a production of heat that is spread out and fed back. This heat feedback increases even more the pyrolysis of polymer and keeps the combustion going.

To limit the establishment of this combustion circle, one (or more) ingredient must to be removed. Several techniques are available in order to break down this combustion circle. Depending on the type of polymer, flame-retardants interfere into one or several stages of the combustion process: heating, decomposition, ignition, flame spread and smoke process (Hernangil et al. 2000).

6.1.4.1 Mechanism of action of flame-retardants additives

Flame-retardants can act chemically and/or physically in the condensed (solid) phase and/or in the gas phase. However, both of them occur during a complex process with many simultaneous reactions.

The main mechanisms of action of flame-retardants can be grouped into the following processes: (i) production of a protective layer, (ii) consummation of high-reactive free radicals, and (iii) release of water. All processes lead to the elimination or reduction of flammable gases.

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[1] The part of the irreversible chemical decomposition caused exclusively by a rise in temperature.

i) Production of a protective layer

Flame-retardants can cause a layer of carbon (charring) on the polymer's surface. It constitutes a two-way barrier, both for the hindering of the passage of the combustible gases and molten polymer to the flame, as well as the shielding of the polymer from the heat of the flame. Some polymers, such as phenolic resins, have a natural capacity to char, thus reducing the formation of volatiles and so they extinguish if the ignition source is removed. The high nitrogen content of urea and melamine resins also acts as an inherent flame retardant.

Intumescence's processes can also form a protective barrier. Flame retardant intumescent materials form, by heat action, foamed cellular charred layers on the surface, which protects the underlying material from the action of the heat flux or the flame. The mechanism is based on the charred layer acting as a physical barrier, which slows down heat and mass transfer between gas and condensed phase (Bourbigot et al. 1998). Generally, intumescent formulations contain three active ingredients: an acid source, a carbonization compound, and a blowing agent. First, the acid source breaks down to yield a mineral acid, then, it takes a part in the dehydration of the carbonization compound to yield the carbon char, and finally, the blowing agent decomposes leading to the release of gaseous products. These latter, cause the char to swell providing the insulating material.

Another type of shield, a vitreous type, can be produced by certain flame-retardants. Their pyrolysis leads to thermally stable compounds, which form a protective vitreous barrier with low thermal conductivity. Heat transfer from the heat source to the material is reduced, which decreases the degradation rate of the polymer and the 'fuel flow' that feeds the flame.

ii) Consummation of high-reactive free radicals:

Certain flame-retardants or their degradation products, stop the radical mechanism of the combustion process that takes place in the gaseous phase. The high-reactive radicals HO^{-} and H^{-} can react in the gas phase with other radicals resulted from flame retardant degradation, creating less reactive radicals that decrease the kinetics of the combustion. The exothermic processes, which occur in the flame, are thus stopped, the system cools down, and the supply of flammable gases is reduced and eventually, completely suppressed.

iii) Release of water:

Some flame retardant additives, when subject to high temperatures, decompose leading to an endothermic release of water. The endothermic decomposition acts as a 'heat pump' that cools the substrate and decreases the pyrolysis of the polymer. The release of water dilutes the amount of fuel. Both essentially fight against ignition.

6.1.4.2 Families of Flame Retardants:

Currently used flame retardants (FR) in polymers can be classified into the following main families:

- Halogenated additives and antimony trioxide;
- Phosphate-based materials (not halogenated).
- Metal Hydroxides
- Melanine based;
- Zinc Borate

i) Halogenated based FRs and Antimony Trioxide:

Halogenated compounds, such as chlorinated and brominated based materials, are usually introduced to increase the total halogen concentration. The mode of action is based on radical trap mechanism. Fire retarding action takes place in the gas phase by the interception of highly reactive free radicals (OH^-, H^-) by halogenated organic compounds (Br^-, Cl^-). Antimony trioxide ($Sb_2\,O_3$) is often used as a synergist together with the halogen containing flame-retardants.

Halogenated additives in resins show a remarkable efficiency as flame-retardants and do not seriously impact the mechanical, thermal, ultraviolet thermo stability or electric properties of the polymers (SpecialChem 2003). Although halogenated flame retardants are highly effective for reducing the heat release rate of common polymers, public perception of the environmental impact of recycling and incineration of certain halogenated products has become an issue in Europe (Nelson 1994). There are increasing concerns over environmental and toxicological impacts of the decomposition products formed when the blended polymer is disposed off or burned. Furthermore, halogenated flame-retardants also generate a great quantity of smoke and toxic fumes, which are unacceptable for many applications in public areas (Hillado 1998).

ii) Phosphate based FRs :

Phosphate derivatives are well known as flame-retardants for a long time and already used for wood, paper and cotton fibers. Nowadays, in the fire protection of plastics, phosphates and their derivatives are getting more and more importance (SpecialChem 2003). Non-halogenated phosphorous-based flame retardants influence the reaction taking place in the condensed phase, generally, by an intumescent process. Their efficiency depends on the chemical structure of the polymer, being particularly successful in materials with high oxygen content like polyesters, polyurethanes, epoxies or cellulose (Horold 1999). In non-halogenated phosphate compounds, we meet insoluble ammonium phosphates, water-soluble inorganic phosphates, polyphosphates and red phosphorous.

One of the most establish products, because of its versatility is ammonium polyphosphate (APP). Ammonium polyphosphate or APP based systems can be used in thermoplastics, rubbers and thermosets such as polyurethane, unsaturated polyester, epoxy and phenolic resins. APP is a non-toxic inorganic material, environmentally friendly and it does not generate additional quantities of smoke due to the unique mechanism of intumescence. Compared to other halogen free systems, requiring higher loadings, FR materials containing APP exhibit good process ability, good mechanical properties retention and excellent electrical properties. The addition of synergetic products like pentaerythritol derivatives, carbohydrates and foaming agents will significantly improve the flame retardant performance of APP. In thermosets, APP can be used in combination with aluminum trihydroxide (ATH), which allows a significant reduction of the total FR filler (SpecialChem 2003). The main drawback appears to be the increase amount of carbon monoxide generated during the combustion (by five to ten times).

iii) Metal Hydroxide based FRs :

Metal hydroxide is among the most used flame-retardants. This is due to its low cost when compared to halogen systems and phosphorous-based flame-retardants. Inorganic hydroxides are easily handled and relatively non-toxic, producing combustion products with low opacity, low toxicity and minimal corrosivity.

Metal hydroxides contribute to several flame-retardant actions. The main mechanism is based on the endothermic release of water at higher temperatures. Additionally, after degradation, a ceramic-based-protective layer is created, improving the insulating property and revealing a smoke suppressant effect.

Aluminum trihydroxide (ATH), also known by hydrated alumina, is the most widely used flame retardant additive in volume terms. It is suitable for elastomers, thermosetting resins and thermoplastics processed below 200ºC. As well as flame retarding and smoke suppressing, it is an economical filler/extender. Further, ATH is very easy to recycle, do not has impact on color, presents excellent weatherability, and as inert, it rarely interferes with the polymer or with other additives (SpecialChem 2000).

Attending to the above benefits, ATH is often used in building and construction products. Most of unsaturated polyester resins applications, such as laminated countertops and wall covering, sheet and bulk moulding compounds, are fire-protected with ATH. Epoxy and phenolic resins often use ATH in electrical/electronic and construction applications like lavatories, bathroom panels, decorative surrounds and wall panels. Pultruded products also use ATH as flame retardant for producing profiles for construction applications. However, as very high loadings of ATH (40%-70%) are required for effective levels of fire retardancy, processability and mechanical properties of final product are compromised, restricting the application field of this kind of flame retardants.

Magnesium hydroxide (MH) is a more thermally stable inorganic flame retardant and can be used in many elastomers and resins processed at higher temperatures (above 300ºC). Like ATH, MH requires high loading levels, usually between 50% and 70%. As its price is higher than ATH, MH application is practically restricted to materials that are processed to temperatures above 200ºC.

iv) Melamine based FRs :

Melamine based FRs represent a small but fast growing segment in the flame retardant market. In this family of non-halogenated flame-retardants, three chemical groups can be distinguished: pure melamine, melamine derivatives (salts with organic or inorganic acids), and melamine homologues such as melam, melem and melon. The latter finding only in experimental use at this stage.

Melamine based FRs show excellent fire retardancy properties and versatility in use, due to their ability to interfere with the combustion process in all stages and in many different ways. In the initial stage, melamine can retard ignition by causing a heat sink through endothermic processes of decomposition and sublimation. Melamine can also show considerable contribution to the formation of a char layer in the intumescent process. In combination with phosphorous, due to a synergistic effect, melamine can further increase char stability through formation of nitrogen-phosphorous substances. Last but not least melamine can act as blowing or swelling agent, enhancing the heat barrier functionality of the char layer.

The growing interest for melamine-based flame-retardants is furthermore driven by particular advantages that these products offer over existing flame-retardants, namely: cost effective, low smoke density and toxicity, low corrosion, safe handling and environmental friendliness. Currently, main areas of application are flexible polyurethane foams, intumescent coatings, polyamides and thermoplastic polyurethanes (SpecialChem 2003).

v) Zinc Borate based FRs :

Zinc borate is a boron-based fire retardant normally used jointly with other flame-retardant systems (APP, MH or red phosphorous). It functions mainly in the condensed phase, promoting the formation of a vitreous layer, which can be enhanced by the finer particle size. Zinc borate can be used in PVC, elastomers polyamides and epoxy resins and it is thermally stable up to 290ºC. Grades are also suitable for use in translucent polyester resin systems, to improve fire performance, while retaining clarity (SpecialChem 2000).

6.1.4.3 New flame-retardants: Silicon based FRs and Nanocomposites:

Silicon-based FRs constitute a new family of flame and fire retardants. Silicon-based materials are potential flame-retardants as they produce protective surface coatings during a fire, caused by a low rate of heat release. Almost forms of silicon-based materials have been investigated as flame-retardants: silicones, silicas, organosilanes, silicates and nanoclays (Beyer 2002; Gilman et al. 1999; Gilman et al. 1997; Kashiwagi and Gilman 2000; Lichtenhan and Gilman 1997).

The most common flame-retardant based on silicon is in the form of polyorganosiloxane, in particular polydimethylsiloxane. Low levels of this silicon compound in certain organic polymer systems, as low as 1 to 3 %, reduce the heat release rate by 30 to 50 % (Kashiwagi and Gilman 2000).

Inorganic silicon additives such as silica have been used as filler instead of as flame retardant, but under certain cases, the addition of silica affects the thermal stability and the flammability properties of materials. Talc, a silicate compound, can also introduce the same features. Levchik and co-workers (1994) reported the effect of talc on the flammability properties of polyamide flame retarded with APP. Fire-reaction classification improved from ‘Non-classified’, for the talc-free formulation, to the best classification (V-0), for an APP/talc ratio of 2:1.

A ‘giant’ world has been opened with the recent advances on the new class of polymer systems: the nanocomposites. Gilman et al. (1997) reported on the promising flammability properties of polymer layered silicate nanocomposites. Polymer clay nanocomposites are hybrid organic polymer-inorganic materials that consist of alternating, nanometer-thick layers of polymer and mica-type silicate. In the last years, several groups have developed the most recent methods of preparing polymer clay nanocomposites (Giannelis 1996; Hasegawa et al. 2005; Kojima et al. 1993; Usuki et al. 1997). In general, these methods achieve molecular-level incorporation of the layered silicate (*e.g.* montmorillonite) into the polymer by the addition of a modified silicate.

Polymer clay nanocomposites have unique properties when compared to conventional filled polymers: modified layered silicates as fillers are dispersed at a nanometer-level within a polymer matrix and new extraordinary properties are observed.

The main improvements are in mechanical properties such as tension, compression, bending and fracture; barrier properties such as permeability and solvent resistance; optical properties and ionic conductivity (SpecialChem 2002). For example, the mechanical properties of a nylon-6 layered-silicate nanocomposite, with only a silicate mass of 5%, show excellent improvement over those for the pure nylon: 40% higher tensile strength, 68% greater tensile modulus, 60% higher flexural strength, and 126% increase flexural modulus (Gilman et al. 1997).

Other interesting properties exhibited by polymer layered silicate nanocomposites include their increased thermal stability, and ability to promote flame retardancy at very low filling levels (2-10 wt.%). The formation of a thermal insulating and low permeability char caused by polymer degradation during a fire is responsible for these improved properties. For illustration, in the above reported research work, the peak heat release rate of the nylon-6 clay-nanocomposite was reduced by 63%, containing only a clay content of 5%.

Nanoclays are thus the basis for improved flame-retardants systems for polymer composites. Not only are very efficient in fire retardancy, but they do not have the usual shortcomings associated with other flame retardant additives. Their properties are not degraded by the additive (clay), they are greatly improved instead. Furthermore, the system does not increase the carbon monoxide or soot produced during the combustion, as many commercial fire retardants do.

6.1.5 Research Objective

The present study aims to analyze and classify fire reaction of both PMs formulations. For this purpose two types of tests were carried on: the cone calorimeter test and the radiation or epirradiador test. Jointly, both tests allow the determination of the main parameters to classify fire reaction of combustible materials: time to ignition, heat and smoke release rate, and flame spread (Wittbecker 2004).

The cone calorimeter test provides means for determining the ignitability, heat and visible smoke release rates. As stated earlier, heat release rate constitutes the single most important variable in fire hazard. It gives an indication of the size of the fire and the rate of fire growth, and as a result, the fire rating. Smoke and toxic gases emission also constitute important indexes of fire hazard. Density and opacity of fumes are parameters to take into account because of disorientation suffered by the victims. On the other hand, emission of toxic gases, such as carbon dioxide and carbon monoxide are also important factors as both are responsible for displacing the oxygen from the air, and the latter, in addition, is highly toxic due to an even greater affinity with hemoglobin than oxygen.

The epirradiador test allows the determination of the ignition times, spread flame and variation of the thermal balance, which are parameters required to classify the materials according their reaction to fire. By means of this classification, intended use and application of polymer mortars, as building materials, will be conditioned according to the present regulations.

In the second phase of this experimental program, an attempt was made in order to improve fire behavior of epoxy PM formulation. For this purpose, three additional series of epoxy PM specimens, modified with two different types of flame-retardants systems, were manufactured and tested for fire reaction. Obtained results were compared with those obtained for plain PMs.

Both type of fire tests were carried on in the ‘Laboratório de Fumo e Fogo’, which is a certified Fire Laboratory at INEGI. The cooperation and knowledge of Dr. João Rodrigues, who is in charge of this laboratory, was essential for the accomplishment of the present research work.

6.2 Heat and Smoke Release Rates

6.2.1 General

In the last years, developments in fire research and understanding of fire dynamics have highlighted the importance of heat release rate as the primary fire hazard indicator (Babrauskas and Peacock 1992; Sorathia and Ohlemiller 1997).

The rate of heat release constitutes the main characteristic determining the size, growth, and suppression requirements of a fire environment. Determination of the quantity of heat evolved per unit time allows an estimation of the potential hazard posed by a product: if the heat release rate is small, fire spread can be controlled, but if it is large, this is no longer possible as flashover is quickly reached (Wittbecker 2004).

As an indicator of the size of the fire and the rate of fire growth, heat release rate provides as a result, the fire rating, the type of suppression action that are likely to be effective, and other features that define the fire hazard. Fire hazard under a given set of circumstances of fuel load, geometric configurations, and ventilation conditions can be expressed, as this way, in terms of heat release rate, and the fire hazard analysis should include the relevant fire response parameters.

Smoke and toxic gases emission also constitute important indexes of fire hazard. They occur alongside the fire development as the rate of flame spread and heat released increases. Together with radiant heat and lack of oxygen, they represent the severest hazard concerning escape and rescue.

Thus, heat and visible smoke release rates have been the most widely used parameters for the assessment of a fire hazard or a fire risk, as they take into account all the factors that are pertinent for the evaluation of the fire hazard or fire risk of a particular end use.

In this subchapter, heat release rate properties of epoxy and polyester PM formulations in study are analyzed. For this purpose, heat release rate, effective heat of combustion, time to ignition, total heat released, mass loss rate, mean of monoxide and dioxide of carbon yield and mean specific extinction area for smoke, were measured and/or determined.

6.2.2 Experimental Program

6.2.2.1 Test apparatus, measured parameters and their significance.

Heat release rates of PM formulations, were determined by means of the cone calorimeter test performed according to ASTM standard E 1354 (2004). This test method measures the response of a small sample of material exposed to controlled levels of radiant heating and is used to determine not only the heat release rates, but also the ignitability, mass loss rates, effective heat of combustion, and visible smoke development.

The heat release rate, understood as the heat evolved from the specimen per unit of time, is determined with basis on oxygen consumption principle. This states that there is a constant relationship between the mass of oxygen consumed from the air and the amount of heat released during the material degradation. Approximately, 13.1 x 10^3 KJ of heat are released per 1 kg of oxygen consumed (Huggett 1980).

The effective heat of combustion is determined from a concomitant measurement of specimen mass loss rate, in combination with the heat release rate. It is determined by dividing the measured heat release by the mass loss for a specified time period.

Time to ignition, or ignitability, is determined as a measurement of time from initial exposure to time of sustained flame. It is considered sustained flame the existence of flame on or over most of the specimen for periods of at least four seconds.

Smoke development is measured by obscuration of light by the combustion product stream, which can be assessed by the specific extinction area. This parameter indicates the concentration of soot particles generated by the combustion, and it can be defined as the smoke that is produced per unit mass of material being volatized. Monoxide and dioxide of carbon release can also be determined by means of infrared gas analyzers.

To measure all the above parameters, the cone calorimeter apparatus is provided with the following components: a conical shaped radiant electric heater, capable of horizontal or vertical orientation; specimen holders, different for the two orientations; an exhaust gas system with an oxygen and flow measuring monitoring; an electric spark igniter; a data collection and analysis gas system; and a load cell for measuring specimen mass loss. An overall view of the cone calorimeter apparatus and the scheme of its main components are shown Figs. 6.1 and 6.2, respectively.

Fig. 6.1. Oxygen consumption calorimeter apparatus used to perform heat release tests.

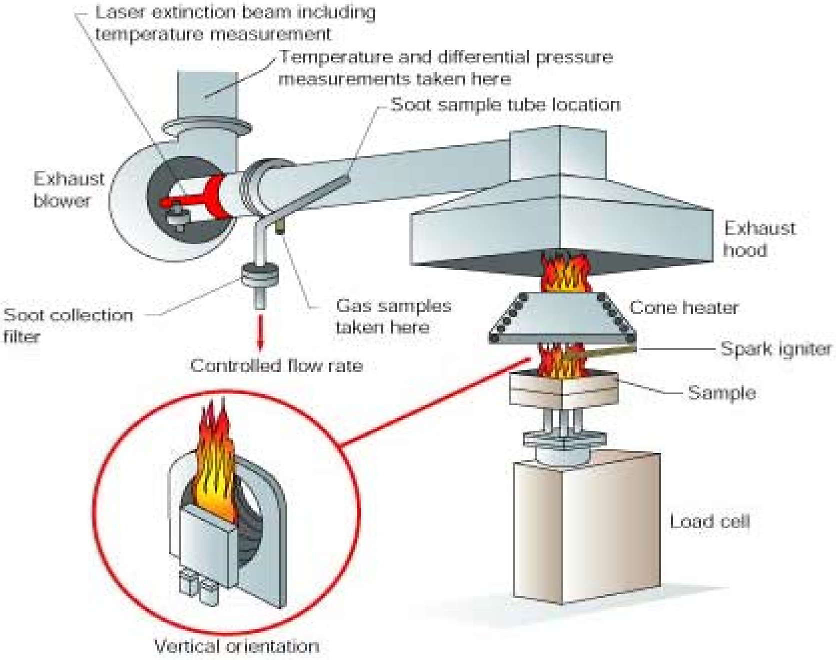

Fig. 6.2. A schematic view of the cone calorimeter showing its main components.

6.2.2.2 Test specimens and test procedure

Two specimens of each PM formulation, with 100 by 100 mm in area and 15 mm thickness, were casted. Silicon moulds were used for this purpose. The specimens, after being submitted to the usual curing treatment, were conditioned to moisture equilibrium (constant weight) at an ambient of 23ºC and a relative humidity of 50%, before being tested for heat and smoke release rate.

All the tests in the oxygen consumption calorimeter were carried out under the following conditions: horizontal orientation of the specimens, heat flux of 50.0 kW/m^2 and exhaust duct flow rate of 25 m^3/s.

The tests were performed according to the following steps. After calibration procedure of test apparatus, as specified in the norm, each test specimen, which weight was previously recorded, was held in the appropriate holder and the data collection and spark igniter were then turned on. When a sustained flaming appeared the spark was turned off, and the correspondent ignition time was recorded. After this point, the tests and the collection data did go on until one of the following situations has occurred: 2 minutes have passed after any flaming or signs of combustion have ceased; the average mass loss over a 1 minute period has dropped below 150 g/m^2, or until 60 minutes have elapsed.

In Fig. 6.3, some of different test steps are illustrated.

6.2.3 Test Results and Discussion

6.2.3.1 Experimental results

Performed tests on cone calorimeter apparatus allowed determining the values for the following parameters: heat release rate; carbon monoxide and carbon dioxide release rates; time to ignition; mass loss; effective heat of combustion; and specific extinction area.

Obtained results for these parameters (mean and peak values, when applied) are shown in Tables 6.3 for polyester and epoxy PM specimens. Figures 6.4 and 6.5 represent the variation of the main parameters as function of time. Shown results represent the average values of two specimens tested for each composition.

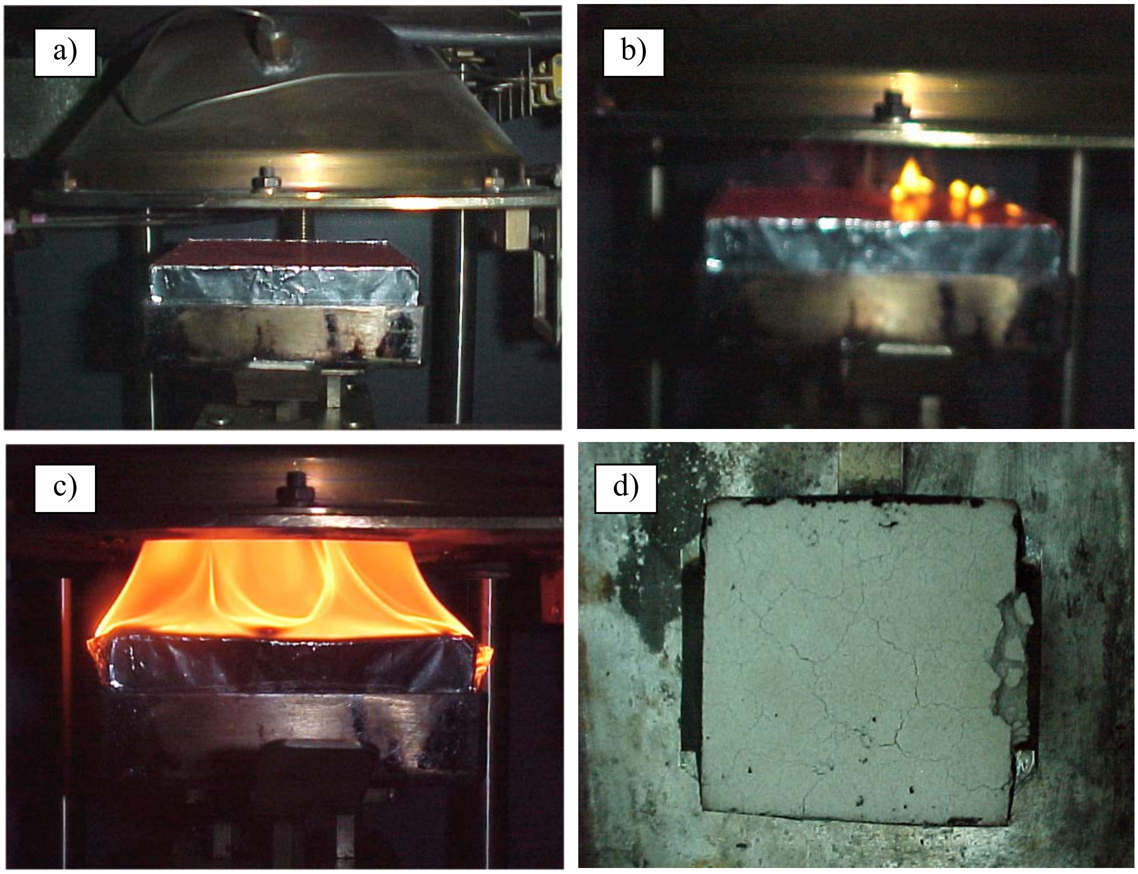

Fig. 6.3. Some sequential images taken off during the cone calorimeter test: a) Placement of test specimen on apparatus holder; b) Beginning of combustion reaction when a sustainable flame appeared; c) Maximum reaction intensity; d) Specimen appearance at the end of the test.

Table 6.3. Experimental results obtained from cone calorimeter tests performed on polyester and epoxy PM specimens.

Parameters		Polyester PM		Epoxy PM	
		Peak	Mean	Peak	Mean
Heat release rate	[kW/m^2]	210.2	134.6	325.2	158.5
Effective heat of combustion	[MJ/m^2]	29.6	20.6	34.2	24.5
Specific extinction area	[m^2/kg]	1146.5	1003.8	1170.7	965.0
Carbon monoxide	[kg/kg]	0.6606	0.0502	0.9640	0.0700
Carbon dioxide	[kg/kg]	2.66	1.75	3.20	1.81
Total heat evolved	[kJ]	1149.1		1280.4	
Time to ignition	[s]	84		82	
Mass loss	[%]	19.1		18.8	

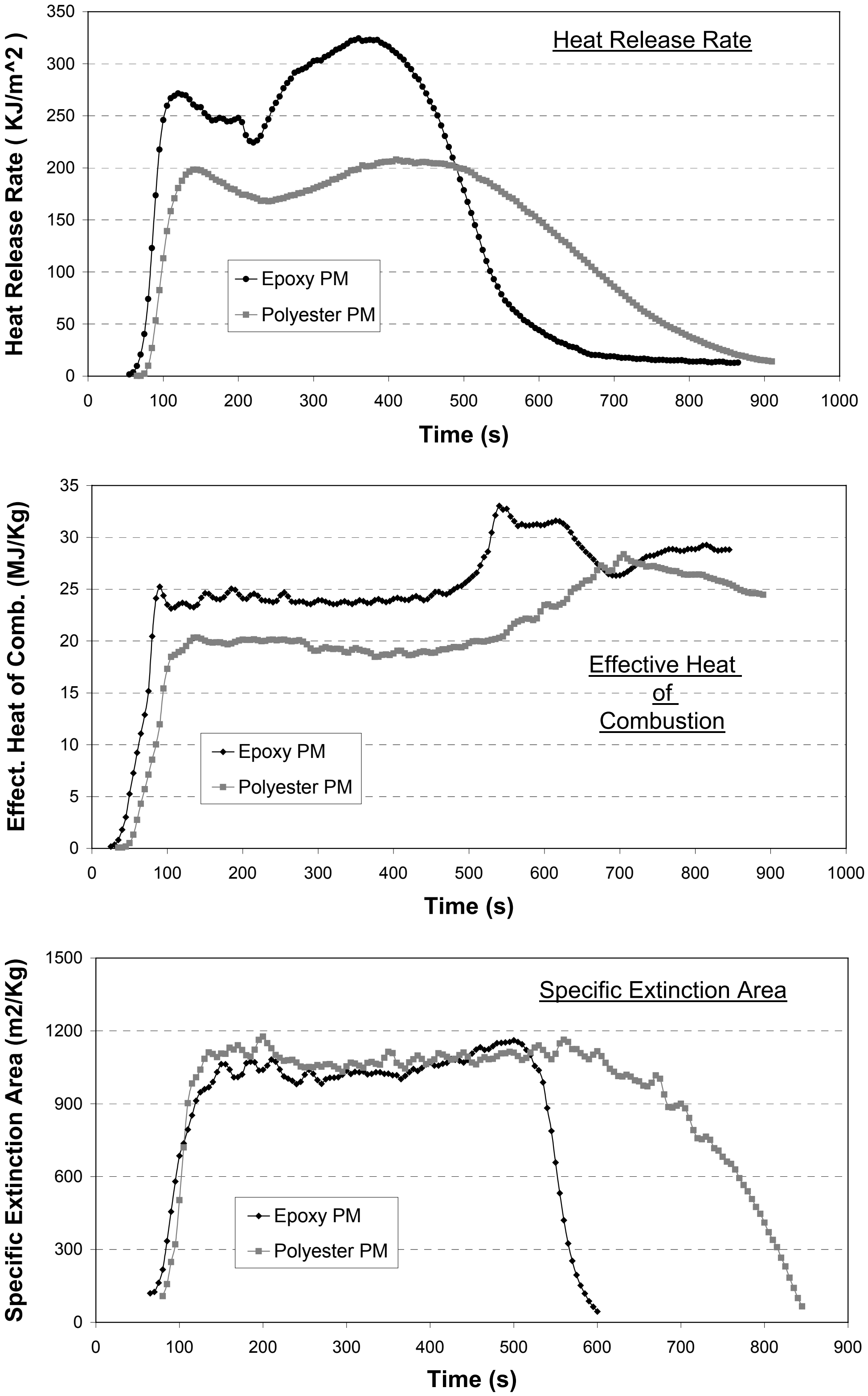

Fig. 6.4. Heat release rate, effective heat of combustion and specific extinction area as function of time, for both epoxy and polyester PM formulations.

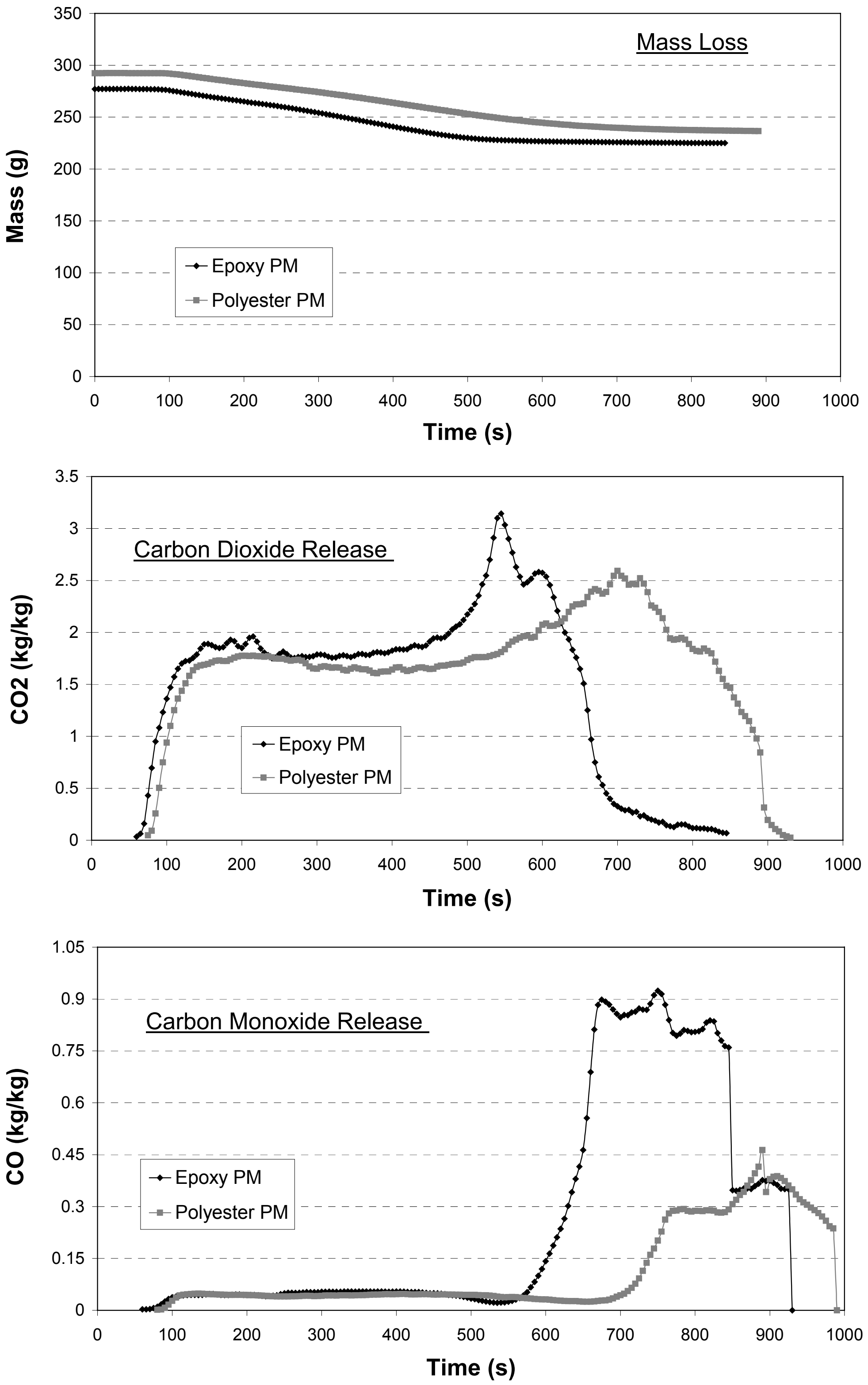

Fig. 6.5. Mass loss, carbon dioxide and carbon monoxide release as function of time, for both epoxy and polyester PM formulations.

6.2.3.2 Analysis of results and discussion

The comparative analysis of obtained results, from cone calorimeter tests performed on epoxy and polyester PM formulations, shows that epoxy PM specimens present in general, a worse behavior under fire conditions.

The mean heat release rate of epoxy-based mortars is 18% higher than polyester based ones. The weak fire performance of epoxy specimens is more notorious taking into account the difference between the peak values obtained for this parameter for both PM formulations - peak heat release rate of epoxy mortars is 55% superior than correspondent value of polyester mortars-.

The mean effective heat of combustion and total heat evolved, as parameters related with heat release rate, also present higher values for epoxy-based mortars.

The higher flammability of epoxy-based mortars is likely due to a poor thermal stability of epoxy resin when compared to unsaturated polyester resin. The general reduced tendency of epoxy resins to char could be another feature contributing for the worst performance of epoxy PMs under fire.

For both formulations, heat release-time profiles are very similar. There is an initial delay period before the specimen releases heat, as the temperature of the material is below the pyrolisis temperature of the organic matrices. After this induction period, there is a rapid rise in the heat release rate due to combustion of volatiles near to the specimen/fire interface, until a first peak is reached. Following this first peak, heat release rate decreases slightly, during a few seconds, to rise again, until a second peak, faintly larger, is attained. After this point, heat release rate decreases progressively with time as a result of the declining resin content in the sample and, eventually, due to the formation of a surface char layer that slows the decomposition reaction rate in the underlying material.

Specimens were placed in the cone calorimeter holder with the moulding surface in the upwards position. Due to migration phenomenon, this surface usually presents higher resin content, which explains the first peak. After the superficial layer has been decomposed, the underlying material, richer in sand was exposed, leading to a slight decrease in heat release rate. The second peak is attributed to the increasing amount of heat released by molten polymer as temperature of deeper underlying material reach pyrolisis temperature of organic matrix.

In hazard fire, epoxy PMs are also most problematic due to their higher toxic gas release: this material yields more 40% of carbon monoxide than polyester PM, exhibiting a peak value of 0.964 kg/kg against the comparative value of 0.661 kg/kg correspondent to polyester PM.

Based on the mass loss data, it is estimated that both epoxy and polyester PM specimens yield about 19% of their original mass as gas products, leaving 1% as char. The matrix content of both formulations was 20%, which demonstrates that these resins undergo substantial volatilization.

With respect to the other parameters, ignitability, smoke and carbon dioxide release rates, obtained results are very similar for both PM formulations.

There is a considerable amount of information concerning heat release rates of different types of polymers and composites materials but, as far as this investigation is concerned, no relevant information was found regarding heat release properties of polymer concretes or mortars. The lack of available data hinders any comparison with analogous concrete based materials, however, some considerations can be done relating other polymer composite materials.

Sorathia et al. (1999) studied the fire performance of several glass-reinforced vinyl-ester/epoxy composites commonly used for marine applications, with and without fire retardant additives or reactives. The composites were made with a glass fiber content of 70% by weight, which allowed a rude comparison with PM formulations in study (as the percentage of non-combustible reinforcement material is almost the same). Tests performed on the cone calorimeter apparatus were made according to the same conditions as these ones. Obtained results, jointly with those of the present research, are presented in Table 6.4.

For the assessment, average heat release rate during the first 180 seconds was considered instead the peak or the mean over the entire test period. Previous researches undertaken on prediction of real-scale fire hazard from brench-scale tests showed that, due to the physics of burning, an average rather than the peak of heat release rate is needed in predicting the peak hazard. Statistical considerations led to 180 seconds as a useful length of the averaging period (Babrauskas and Peacock 1992).

Table 6.4. Heat release and smoke data for various composites materials - Heat flux of 50.0 kW/m^2 and exhaust duct flow rate of 25 m^3/s- (Sorathia et al. 1999).

Test Specimens	Ignitability (s)	Avg. HRR (180s) (kW/m^2)	Avg. SEA (m^2/kg)	Avg. CO (kg/kg)
Epoxy PM	82	234	965	0.070
Polyester PM	84	153	1004	0.050
Comp. A[1]	94	245	1086	0.047
Comp. B[2]	52	112	1524	0.119
Comp. C[3]	85	226	815	0.048
Comp. A + Ad. X[4]	74	215	1185	0.048
Comp. A + Ad. Y[5]	89	182	902	0.047
Comp. A + Ad. Z[6]	85	198	998	0.044
Comp. A + Ad. W[7]	99	167	852	0.037

[1] A- Non-brominated bisphenol A epoxy vinyl-ester resin; [2] B- Brominated bisphenol A epoxy vinyl-ester resin; [3] C- Epoxy novolac vinyl-ester resin; [4] X- Siloxane powder additive (10 phr); [5] Y- Char-enhancing additive (10 phr); [6] Z- Silicate nanocomposite (10 phr); [7]W- Aluminium trihydrate (15 phr).

As it can be seen in Table 6.4, there are no considerable differences between heat release properties of PMs and those of glass-reinforced epoxy vinyl-ester composites. Obtained values in the present study are among the range of values obtained by Sorathia and co-workers (1999). Under the point of view of fire performance, PMs are not the best composite materials, but certainly, they are not the worst. Polyester based mortar actually presents better fire performance in terms of heat release rate, than certain polymeric composites, even than those modified with fire retardant additives.

Another comparison can be done with the results of other research work undertaken on heat release properties of polymeric composite materials.

Mouritz and co-workers (2005) experimentally investigated the influence of heat release rate on fire reaction properties of polyester, vinyl ester, epoxy and phenolic matrix composites, reinforced with several combustible and non-combustible fibres. For that purpose, an oxygen consumption cone calorimeter was also used. Their study showed that smoke extinction area, yield of carbon monoxide gas and total mass loss, all increase linearly with heat release rate for composites with non-combustible fibers (peak and mean values). It was also observed that heat release rate had no significant effect on ignitability or yield of carbon dioxide gas of fiber-reinforced polymer composites.

In the present research, within the uncertainty of the data, no correlation or reliable relationships were found between the former parameters and the main indicator of fire hazard. In fact, smoke extinction area and mass loss values show a slight tendency to decline for increasing values of heat release rate. Instead, only a strong correlation was observed between carbon monoxide yield and the average of heat release rate during the first 180 seconds. Likewise, the expected high relationship between the peak and the average of heat release rate is stronger, if the average during the first 180 seconds is considered instead of the mean over the entire test period. Such relationships are represented in Fig. 6.6.

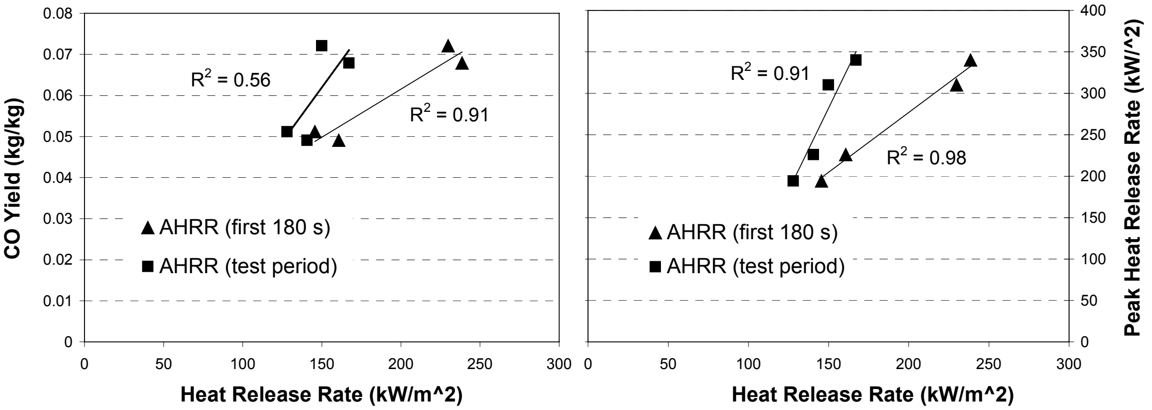

Fig. 6.6. Plot of carbon monoxide yield and peak of heat release rate against both averages of heat release rate: average during the first 180 seconds and average over the entire test period. Reported data are referred to all PM test specimens.

Despite the observed, attending to the reduced number of test specimens, no feasible considerations can be done regarding the distinct behavior of fire reaction properties of polymer mortars relatively to composites reinforced with non-combustible fibers.

6.2.4 Conclusions

Heat release rate constitute the single most important variable in a fire situation and can be considered as the driving force of the fire. In order to assess heat and smoke release rate properties of PM formulations in study, cone calorimeter tests were performed on specimens of both types of mortars. Attending to obtained results the following conclusions can put forth.

- Under a fire situation, epoxy-based mortar presents a worst behavior than polyester based one, especially in terms of heat release rate and carbon monoxide yield. Poor thermal stability and the weak tendency to char of epoxy resin seem to be the main reasons for this feature.
- Yield of carbon monoxide increases linearity with the average of heat release rate (180 s). No correlations were found between both mass loss and smoke development, and the later parameter; contrarily to what that was reported by other researchers. Reduced number of tests specimens does not allow however being preemptory in this statement.
- Heat and smoke release properties of epoxy and polyester PM are among usual values found for other polymeric composites, commonly used in the navy industry, reinforced with non-combustible materials and containing similar resin contents.

Although test results revealed that polyester PM is less-prone material than epoxy-based mortar, fire behavior of both formulations is not satisfactory for some intended uses. In those cases, in order to observe fire regulations, flame retardant additives will be needed to enhance fire behavior of these polymer mortar formulations.

6.3 Flame Spread Rate. Reaction to Fire: Classification

6.3.1 General

The classification systems often used to grading building materials according to their reaction to fire, are based either on radiant panels or in the epirradiator test. Ignitability, flame spread rate and variation of the thermal balance are the parameters controlled in these type of tests. Obtained results allow the classification of the materials into classes, according to their higher or lower contribute to the development of a fire. A material or product is allowed to be used if it complies, in terms of its classification index, with the fire safety regulatory requirements, which differ from country to country and from application to application.

The flame spread contribution constitutes the main criterion of almost all of the fire reaction classification systems developed in each country, but even so, correlation between them is hardly assessed. Despite the fact that flame spread over solid surfaces have been a research topic in combustion and fire science for more than thirty years, the observed phenomenon often differ from test to test and may not give any consist results (T'ien 2002).

Recently, in order to remove barriers to trade between the countries of European Union, a harmonized approach was developed by CEN (European Committee for Standardization) following a mandate from the European Commission. Today, this has resulted in a new and uniform classification system of reaction to fire performance of construction products, the Euroclasses. Unfortunately, when the present study was under development, national regulations taking into account the new European classification system were still in the final harmonization, therefore all the experimental work was conducted according the French normalization.

Fire radiation tests were performed in order to classify reaction to fire performance of epoxy and polyester PM in study. Additionally, three different formulations of epoxy

PMs were developed aiming to improve fire performance of this kind of mortars, which showed the weakest behavior in the first part of this study. For this purpose, two different flame retardant systems were added to original formulation. Fire reaction of modified epoxy PMs was analyzed and compared with correspondent performance of unmodified formulation.

Finally, an approach was made in order to predict fire reaction classifications of PM formulations according to the new European system, with basis on obtained results by the French classification method.

6.3.2 Experimental Program

Flammability properties of PM formulations, in terms of ignitability, flame spread and growth, were determined by means of the epirradiator test method performed according the French norm NF P 92-501 (1995). This standard is applied to building products: rigid materials, whatever their thickness, or flexible materials thicker than 5 mm.

The test method consists to submit the specimens to a constant source of radiant heat in a controlled chamber, during a certain period of time, in order to promote the ignition of yielded gases and observing the propagation of the combustion. Ignition times, flame lengths and total times of combustion are some of the measured parameters.

PM formulations were classified according to their fire reaction in accordance with the French norm NF P 92-507 (2004). This classification system is based on obtained results of fire radiation tests performed on the epirradiator apparatus. Measured parameters during the epirradiator test allow the determination of the classification index, the ‘key parameter’ to identify the combustibility class to which the specific material belongs.

6.3.2.1 Test specimens

Four specimens of epoxy and polyester PM formulations, with 300 x 400 mm in area and 10 mm in thickness were casted. Above dimensions were in accordance with those prescribed by the norm. Wood moulds were specially conceived for this purpose, as no standard steel moulds were available with the required dimensions (see Fig. 6.7 a).

Additionally, in order to assess fire behavior improvement, three extra batches of epoxy based mortar specimens modified with flame retardant additives, were also casted. The additives were previously added to the epoxy resin system prior to mixture with the sand aggregates. Two different flame retardancy systems were applied:

- Ammonium Polyphosphate (APP) based FR system (20% in weight of resin content);
- And Aluminum Trihydroxide (ATH) based FR system (40% and 80% in weight of resin content).

The APP based flame retardant system, acting as an intumescent process, was further complemented with pure melamine and pentaerythritol additives. The APP initiates the intumescent process functioning as an acid source when thermal decomposition starts. The pentaerythritol acts as a carbon supplier while the melamine works rather as a blowing agent. Through the exact interaction of these three components, the system leads to an expansion process in which a large volume high-carbon protective layer is built up that protects the substrate below from the attack of the heat.

The main mechanism of action of ATH based flame retardant system is based on the endothermic release of water at higher temperatures. The endothermic decomposition cools the substrate, reducing the pyrolysis of the polymer, and the release of water dilutes the amount of fuel, fighting against ignition. Further, together with charring products, the Al_2O_3 formed on the surface of the substrate acts as an insulating protective layer. This kind of flame retardant system, requiring very high loadings for effective levels of fire retarding, was applied with two different contents.

Characteristics and mechanisms of action of both flame retardant systems were already described and can be found in the first part of this chapter. Performance-cost ratio and compatibility with epoxy resins were the main criteria took into account for the selection of both flame-retardants systems.

All flame retardant modified epoxy PM formulations are described in Table 6.5, and the main physical/chemical characteristics of each flame retardant compound are presented in Table 6.6.

In order to assess mechanical properties degradation of modified epoxy based mortars, three prismatic specimens (100x40x40 mm) of each modified formulation were also casted for posterior flexural strength analysis.

Flexural tests were performed according the customary procedure in compliance with RILEM PCM-8 standard (1995).

All the specimens, after being submitted to the usual curing treatment, were conditioned in a climatic chamber at temperature of 23ºC (± 2) and relative humidity of 50% (± 5), during one week, prior to radiation fire tests.

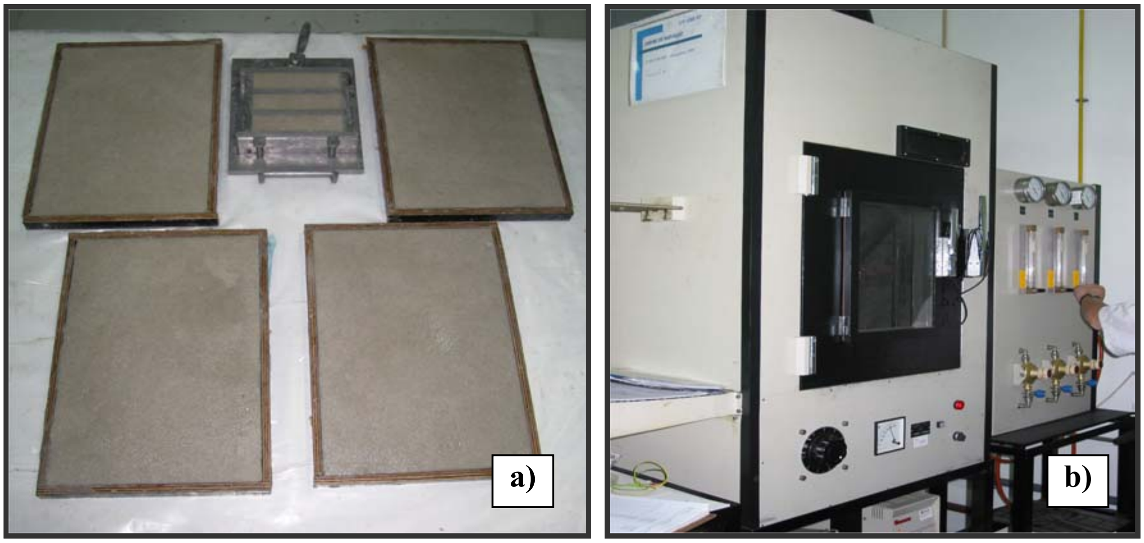

Fig. 6.7. a) Epoxy PM test specimens for fire radiation tests after casting process; b) Epirradiator test equipment used to perform fire radiation tests.

Table 6.5. Epoxy PM formulations modified with flame retardant systems (mass percentages).

Epoxy PM	Ep-APP	Ep-ATH1	Ep ATH2
Epoxy Resin (%)	19.23	18.52	17.20
Foundry Sand (%)	76.92	74.07	69.00
FR System (%)	3.85	7.41	13.80
FR Compounds	APP (60%) Melamine (20%) Pentaerythritol (20%)	ATH (100%)	ATH (100%)

Table 6.6. Physical and chemical characteristics of flame retardant compounds.

FR Compounds	Molecular Formula	Bulk density (g/cm^3)	d_{50}[a)] (μm)
ATH (Hymod® SB336CM)	Al_2O_3	1.36	15.7
APP: Crystal phase II (Budenheim® FR CROS484)	$[NH_4PO_3]_n$	0.60	18.0
Melamine: 2,4,6-Triamino-1,3,5-Triazine (Merk®)	$C_3H_6N_6$	1.57	-
Pentaerythrytol (FenChem®)	$C_5H_{12}O_4$	0.80	<10.0

a) d_{50}- Average particle size.

6.3.2.2 Epirradiator test method: Test procedure and equipment

i) Test equipment

The epirradiator test equipment, shown in Figs. 6.7 b) and 6.8, includes:

- A test chamber, commonly known as epirradiator, provided with a chimney for smoke evacuation and an extractor fan;
- A specimen frame holder, provided with a steel grate, placed at a 45º angle above to the horizontal and at a distance of 250 mm of the bottom of the test chamber;
- A radiation heating source of 500 W with a radiant surface of 100 mm diameter, placed parallel to the frame holder at 30 mm of its upper surface;
- Two gas burners: one in the lower part and the other in the upper. The burners must be movable and able to be controlled from the outside;
- A measuring device to control the difference of the temperature between incoming and outgoing gases (for calibration).

Prior to testing, test chamber must be previously calibrated and thermally balanced.

ii) Test procedure

The tests in the epirradiator apparatus were performed according to the following steps.

After calibration procedure and checking of thermal balance of test chamber, each test specimen, which weight was previously recorded, was placed in the frame holder and the chronometer was then turned on. Chamber door was closed, in less than 10 seconds, and it remained locked until the end of the test (20 minutes later).

Next, both inferior and superior inflammation devices (gas burners) were placed, as fast as possible, in position against lower and upper surfaces of the specimen.

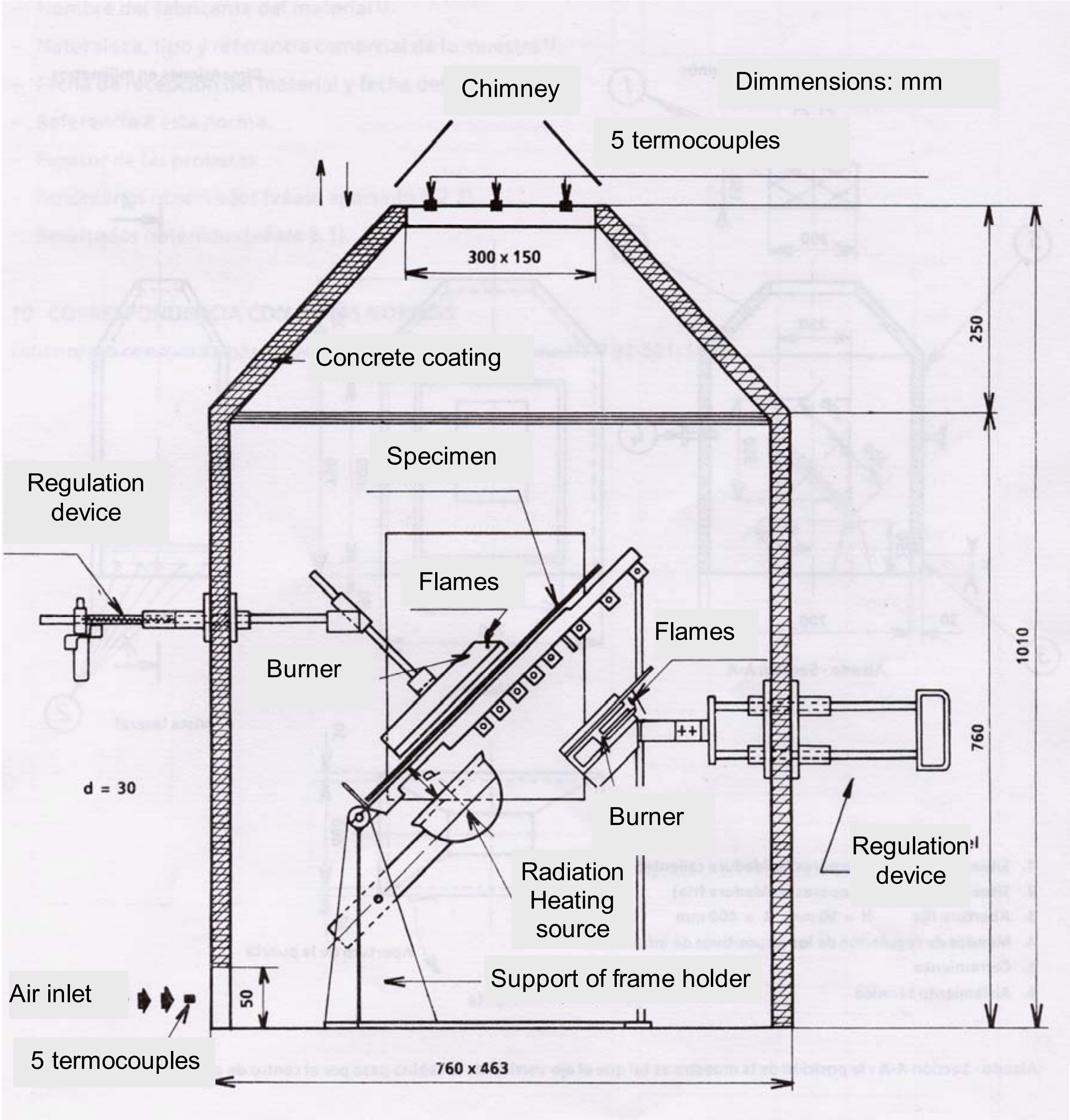

Fig. 6.8. Schematic view of epirradiator apparatus showing its main components.

As soon as an effective inflammation occurred in the material surface, correspondent inflammation device was removed and ignition time was recorded. Inflammation was considered effective if it remained for periods of at least 5 seconds.

Throughout the test, the length of flames in each surface was measured (by means of the reference points existing in the frame holder), and periodically recorded at each 30 seconds. Complementary phenomena, such as fusion or drops falling from the specimen (flaming or not) or, eventually, strong release of smoke and soot particles, were also registered. Finally, extinction times of the flames on both surfaces, if it has occurred, were also reported.

Twenty minutes gone, all the tests were considered to be over, whatever the combustion process still persisted or not, with or without flames. After the tests, specimen mass losses were determined and recorded.

Some of the above test steps were recorded and are illustrated in Fig. 6.9.

Fig. 6.9. Epirradiator test steps: a) Beginning of the test, with both gas burners already positioned against superior and inferior surfaces of test specimen; b) First effective inflammations on both faces of the specimen; c) Maximum combustion reaction, with flames reaching the maximum extent; d) Extinction of the flame on the inferior surface of the specimen; e) End of the test; f) Appearance of plain epoxy PM specimen after fire radiation test.

6.3.2.3 Reaction to fire classification

The classification of PM formulations into one of the categories M0 to M4 was determined based on epirradiator test results, according to the French norm NF P 92-507 (2004).

The classification criteria are based on the following indexes collected and/or determined during the fire radiation tests: ti, td_1, td_2, e_1, e_2, Σ h and Δ T:

- ti – Time, in seconds (ti_1 for the lower surface of the specimen and ti_2 for the upper surface), between the placement of test specimen in the frame holder and the first effective inflammation (sustained flame for periods of at least 5 seconds);
- td – Delay in seconds, until the flames exceed the upper edge of radiant surface, for the lower surface of the specimen (td_1), or the equivalent reference point 'zero', for the upper surface of the specimen (td_2);
- e – Extinction time of the flames (e_1 for the lower surface of the specimen and e_2 for the upper surface), or the time in seconds until the flames no more exceed the above reference points, whatever occurs first;
- Σ h – Sum, in centimeters, of maximum lengths of the flames on both surfaces exceeding the reference points, measured at each 30 seconds;
- Δ T – Entire period of time, in seconds, during which the effective combustion occurs. This parameter is calculated as follows:
  - If effective inflammation occurs only on one of the surfaces:

    $$\Delta T = e_1 - td_1 \quad \text{or} \quad \Delta T = e_2 - td_2 \tag{6.1}$$

  - If effective inflammation occurs on both surfaces without interruption:

    $$\Delta T = e - td \tag{6.2}$$

    with e = maximum (e_1, e_2) and td = minimum (td_1, td_2).

  - If there are several periods of effective combustion, on both surfaces, with intercalated interruptions:

    $$\Delta T = \Sigma (e_1 - td_1) + \Sigma (e_2 - td_2) \tag{6.3}$$

    Note: simultaneous inflammation on both surfaces is computed only once.

With basis on the above parameters, the index classification ‘q’ is calculated according to the following formula:

$$q = \frac{100\ \sum h}{ti\ \sqrt{\Delta T}} \tag{6.4}$$

with ti = minimum (ti_1, ti_2).

Material classification is dictated by the average of ‘q’ index determined for all test specimens. In the particular cases of test materials that do not present any inflammation, or if the flames do not exceed the superior edge of radiant surface, it is considered that index classification is null.

The material classification according to ‘q’ index value is schematized in Table 6.7, for rigid materials, whatever their thickness, or flexible materials thicker than 5 mm. The significance of each class, in terms of combustibility, as well as some representative examples of building materials belonging to those classes are presented in Table 6.8.

Table 6.7. Summary of classification of building materials according to their reaction to fire (rigid materials or flexible materials thicken than 5 mm).

Classification criteria		Flame spread rate		Heat of combustion	
q Index	Class	< 2 mm/s	> 2 mm/s	< 2.5 MJ/kg	> 2.5 MJ/kg
0	M0	-	-	M0	M1
< 2.5	M1	-	-	-	-
< 15	M2	-	-	-	-
< 50	M3	-	-	-	-
≥ 50	M4	M4	NC*	-	-

* Not classifiable.

Table 6.8. Combustibility of building materials according to fire reaction classification.

Class	Combustibility	General Examples
M0	Not combustible	Glass; iron; steel; stone; cement concrete and mortars.
M1	Combustible, not flammable	Painted paper; phenolic resins
M2	Moderately flammable	Plastic coatings; rigid PVC.
M3	Medially flammable	Non-resinous wood (thick >14mm); Resinous wood and plywood (thick >18mm).
M4	Highly flammable	Non-resinous wood (thick ≤14mm); Resinous wood and plywood (thick ≤18mm).

6.3.3 Experimental Results

6.3.3.1 Radiation fire test results

Parameters measured during epirradiator tests, for all test specimens, and correspondent index classification are presented in Tables 6.9 to 6.11. With the exception of epoxy PM specimens modified with ATH (80% of resin content), td_1 and td_2 parameters were always equal, respectively, to ti_1 and ti_2. For this reason, the former parameters are not presented for the other formulations.

Table 6.12 presents the final fire reaction classification obtained for each PM formulation, plain epoxy and polyester PM, and flame retardant modified epoxy PMs. Specific phenomena that occurred during the burning process of some particular test specimens are also illustrated in Figs. 6.10 and 6.11.

Table 6.9. Epirradiator test results and classification index of plain polyester and epoxy PM formulations.

Polyester PM	Specimen A	Specimen B	Specimen C	Specimen D
Δ m (%)	37.0	35.3	39.8	35.4
ti_1 (s)	187	184	193	211
e_1 (s)	1200	1200	1200	1200
ti_2 (s)	323	374	333	407
e_2 (s)	1200	1200	1200	1200
Σ h (cm)	2116	1893	2029	1739
Δ T (s)	1013	1016	1007	989
q ($cm.s^{-3/2}$)	35.55	32.28	33.13	26.21
Epoxy PM	**Specimen A**	**Specimen B**	**Specimen C**	**Specimen D**
Δ m (%)	34.6	34.8	33.6	31.4
ti_1 (s)	147	158	165	160
e_1 (s)	936	1176	1200	1200
ti_2 (s)	251	278	322	333
e_2 (s)	1006	1150	1171	1200
Σ h (cm)	1580	1945	1924	1802
Δ T (s)	859	1018	1035	1040
q ($cm.s^{-3/2}$)	36.67	38.58	36.24	34.92

Table 6.10. Epirradiator test results and classification index of epoxy PM formulation modified with APP flame retardant system (20% in weight of resin content).

Epoxy/APP PM	Specimen A	Specimen B	Specimen C	Specimen D
Δ m (%)				
ti_1 (s)	184	170	199	207
e_1 (s)	1123	1123	1200	1200
ti_2 (s)	301	393	560	585
e_2 (s)	1118	1143	1200	1200
Σ h (cm)	1252	1387	1522	1399
Δ T (s)	939	973	1001	993
q ($cm.s^{-3/2}$)	22.20	26.16	24.17	21.45

Table 6.11. Epirradiator test results and classification index of epoxy PM formulation modified with ATH flame retardant systems: ATH-I and ATH-II (40% and 80%, respectively, in weight of resin content).

Epoxy/ATH-I PM	Specimen A	Specimen B	Specimen C	Specimen D
Δ m (%)	5.3	4.8	7.5	5.5
ti_1 (s)	179 / 198 / 217	261	176	160
e_1 (s)	188 / 209 / 1001	1200	1200	973
ti_2 (s)	287	365	276	283
e_2 (s)	991	1200	1200	971
Σ h (cm)	1248	1524	1761	1351
Δ T (s)	804	939	1024	813
q ($cm.s^{-3/2}$)	24.59	19.06	31.27	29.61
Epoxy/ATH-II PM	**Specimen A**	**Specimen B**	**Specimen C**	**Specimen D**
Δ m (%)	2.1	2.3	2.5	2.3
ti_1 (s)	166	162	196	164
td_1	210	210	229	164
e_1 (s)	925	1037	1200	889
ti_2 (s)	271	326	328	260
td_2	271	326	328	260
e_2 (s)	787	928	1200	954
Σ h (cm)	464	521	985	840
Δ T (s)	715	827	971	790
q ($cm.s^{-3/2}$)	10.45	11.18	16.13	18.22

Table 6.12. Fire reaction classification of all PM formulations in study.

PM formulations	Classification Index*	Class	Combustibility
Polyester PM	31.8	M3	Medially flammable
Epoxy PM	36.6	M3	Medially flammable
Epoxy/APP PM	23.5 (-36%)	M3	Medially flammable
Epoxy/ATH-I PM	26.1 (-29%)	M3	Medially flammable
Epoxy/ATH-II PM	14.0 (-62%)	M2	Moderatly flammable

* Average of four specimens.

Fig. 6.10. Intumescent process occurring during fire radiation tests of epoxy PM specimens modified with APP flame retardant system.

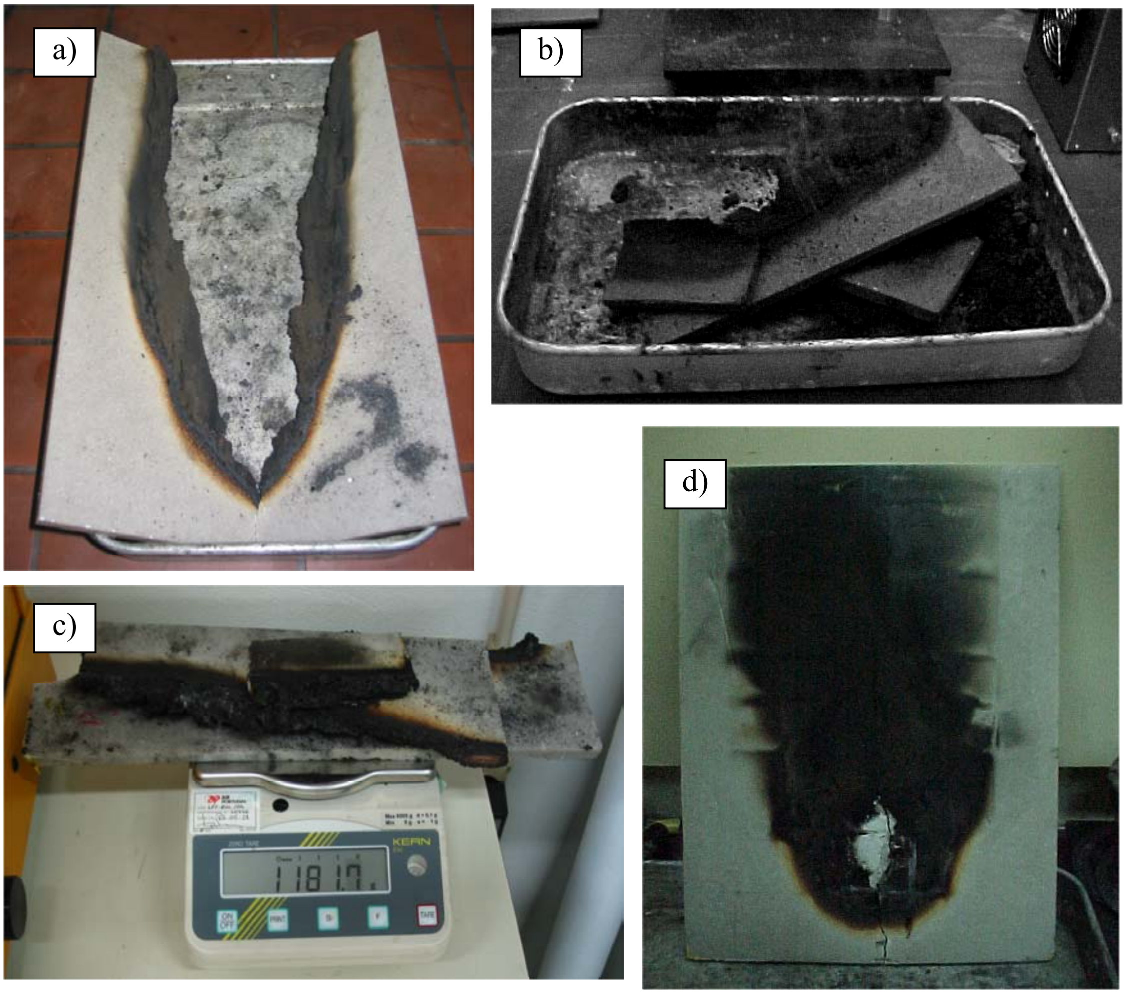

Fig. 6.11. Final appearance of PM specimens after fire radiation tests: a) Epoxy PM specimen: b) Polyester PM specimen; c) APP modified epoxy PM specimen; and d) ATH-II modified epoxy PM specimen, where is visible a white vitreous layer caused by FR system.

A very large quantity of black smoke was produced during all the tests, but no burning droplets were observed. The occurrence of burning droplets would require, additionally, the performance of other kind of fire test, the '*dripping test*', regulated by French norm NF P 92-505 (1995).

6.3.3.2 Flexural test results

Results of flexural tests performed on epoxy PM specimens, in terms of maximum load and flexural strength average values, are presented in Table 6.13.

In order to assess the influence of flame retardant additives on stiffness material, load-deflection curves are also plotted in Fig. 6.12.

Table 6.13. Flexural test results (average values) of all epoxy PM specimens (modified and not modified with flame retardant additives).

Epoxy PM formulations	Max. Load [kN]	Max. Deflection [mm]	Flex. Strength / St. Deviat. [MPa]
Epoxy PM	17.54	0.83	41.11 / 0.41
Epoxy/APP PM	17.63	0.81	41.33 / 0.71
Epoxy/ATH-I PM	17.47	0.78	40.95 / 3.96
Epoxy/ATH-II PM	15.04	0.67	35.26 / 3.44

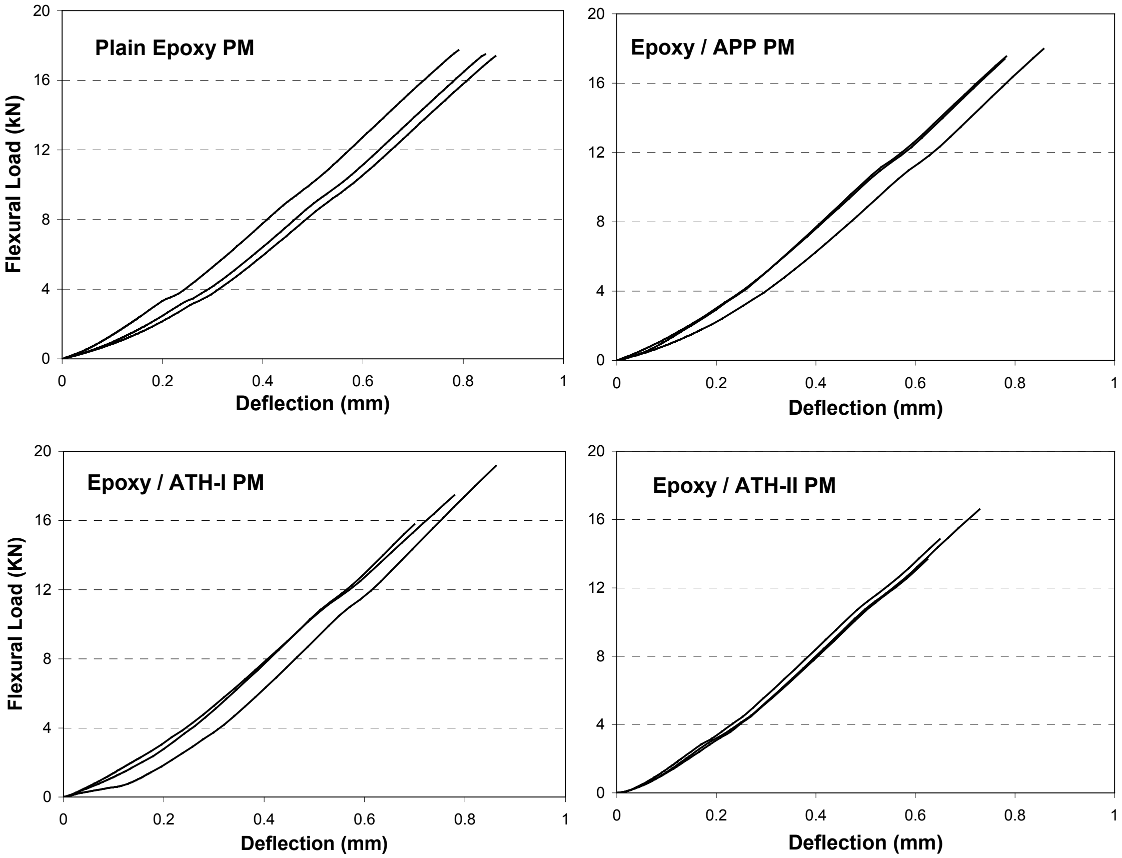

Fig. 6.12. Load-deflection curves obtained from flexural tests performed on plain epoxy PM specimens and epoxy PM specimens modified with flame retardant systems: APP, ATH-I and ATH-II.

6.3.4 Discussion of Results

6.3.4.1 Polyester and epoxy PMs

Plain polyester and epoxy PM are classified as medially flammable materials, into class M3. Likewise to what occurred during cone calorimeters tests, epoxy based mortars showed the worst performance in terms of reaction to fire. The classification index of these kind of mortars was rather near the lower limit value of M4 class (50) than the upper limit of M2 class (15), in opposition to classification index of polyester based mortars. Ignition time was also shorter for epoxy PM formulation.

The classifications obtained for PM formulations were not unexpected. According to Kaeding (1991), polymer concrete and mortars with resin contents up to 10%, generally, do not feed the combustion, but for higher contents, these materials hardly met the non-flammability requirements.

San José (1996), in his investigation work undertaken on fire behavior of polymer concretes, also obtained a fire reaction classification of M3 for epoxy and polyester PC formulations. Resin contents were 10% and 14% in weight for, respectively, epoxy and polyester formulations. Fire radiation tests and classification system were performed according to the Spanish standards UNE 23-721 (1990) and UNE 23-727 (1990), which follow the French stream. Although the lower resin contents, the obtained results were similar to those of present study.

Worst results were found by Galán et al. (2003). Their research was also focused on fire reaction of polyester PM formulations. An unsaturated orthophtalic and isophtalic polyester resins (20% in weight), jointly with a specific limestone aggregate (albero), were used to produce PM materials. Performed fire radiation tests and material classification, according the same Spanish standards, produced a M4 classification for both formulations.

6.3.4.2 Epoxy PMs modified with FR systems

The use of APP and ATH-I (40%) flame retardant systems on epoxy-based mortars reduced considerably the classification index, but not sufficiently enough to reach a suitable reduction on the combustibility class. Decreases on the classification index of

36% and 29% were achieved, respectively with the APP and ATH-I flame retardant additives, but even so, the M3 classes were maintained.

However, these flame retardant systems, with the applied contents, were effective in enhancing material fire behavior without significant losses on flexural mechanical properties. Flexural strength and stiffness of epoxy formulations were not affected by the modifications introduced by these flame retardant additives.

APP-based flame retardant system was more efficient in fire retardancy than ATH compound, especially taking into account the content levels applied of each additive system. Even so, intumescent flame retardant system did not work out as well as it was expected. The inclusion of chlorinated paraffin compound in the APP flame retardant system could be an efficient solution to improve retardancy capacity of intumescent process. The main drawback of this flame retardant system is associated to its cost, which is substantially higher than ATH compound (approximately four times higher).

The use of ATH flame retardant system, with a higher content (80% in weight of resin content), was effective in reducing the material combustibility class. However, the larger amount of this filler additive also led to a slight decrease on flexural strength of the final product. Classification index dropped 62%, which allowed classifying the material within M2 class, as a hardly flammable material. Flexural stiffness was not significantly affected, (it was actually slightly enhanced, as shown in Fig. 6.13), but a decrease of 14% on maximum load bearing capacity occurred.

Flame retardant additives are expected to be effective in improving fire performance without excessive loss of other important performance characteristics. The main question consists in defining what is acceptable in terms of properties' loss. San José (1996), in his investigation work on fire behavior improvement of PC modified with ATH flame retardant systems, established as a mark, neither increase the final cost of the product nor deteriorate its mechanical properties, both on more than 10%. As well as the present research, that goal was not achieved for the formulations in study.

Both ATH modified epoxy PM formulations show a large scatter of results, either in terms of flexural tests or in terms of fire radiation tests. Standard deviations of 3.96 and 5.50 for ATH-I formulation, and standard deviations of 3.44 and 3.80 for ATH-II formulation, were found, respectively, for the average values of flexural strength and classification index. Data scattering was probably due to an insufficient mixture of ATH filler with the resin matrix, which resulted on a non-homogenized mortar material.

The mixture procedure must be improved in order to minimize this feature. Automatic mixing technique instead of manual process could be an efficient solution for this issue.

A last remark must be done concerning mass losses during fire radiation tests. For all ATH modified epoxy PM specimens, mass variation was very low, especially for those containing the higher content of ATH additive. Mass losses were in fact lower than the correspondent organic matrix contents, which allowed sand aggregates to remain conglomerated in an whole piece (average mass variations of 5.8 % and 2.3 % were found, respectively, for ATH-I and ATH-II formulations). On the other hand, large mass losses occurred for the other formulations. However, these amounts are not meaningful and do not correspond to the effective mass loss of the specimens due to burning process. Large quantities of broken pieces of the specimens stayed behind in the test chamber, as shown in Fig. 6.9 e), and they were not computed for the final weight.

Nonetheless, the low mass losses suffered by ATH modified PM specimens were effective, as test specimens remained intact at the end of the tests, and constitute another feature that reinforce even more the suitability of this kind of flame retardant system for polymer mortars and concretes.

6.3.4.3 Restrictions to end-use

According to the present national regulations of fire safety in housing buildings, RSCIEH (D.L.64/90 1990), allowed applications of construction materials classified into M3 and M2 combustibility classes, are restricted to the following areas discriminated in Table 6.14.

According to the present regulation, epoxy and polyester PM formulations without any flame retardant additives, cannot be applied for cladding (or surface coating) of walls and ceilings in common areas of multifamily buildings, such as corridors, staircases, lifts or areas included in fire evacuation paths. But in the same regulation, no restrictions are given neither for cladding materials in other interior areas of the building, nor for linear elements such as corner brackets, joint caps, strips, banisters, or skirting boards.

If it is intended to use these materials in the mentioned restricted areas, or in even more demanding places (*e.g*. hospitals, hotels, schools, public buildings, etc) the constraints are very clear. But for the rest, PM formulations in analysis can be applied without modifications, as there are not higher requirements for coating and finishing materials. The most popular building applications of polymer mortars and concretes, such as wall panels, floor tiles, window-sills, ornamental and architectural shapes, etc., may consider the use of present formulations.

Table 6.14. Summary of regulatory requirements for materials used on constructive elements of housing buildings.

Application	Class	Article
One-family buildings:		Part II
- Cladding / coating of exterior walls;	M3	16.1
- Window frames;	M3	16.1
- Roof coverings;	M3	17.1
- Interior staircases (if provided of inferior coating of class M1);	M3	18.2
- Roof linings	M2	17.3
Multifamily buildings with less than 28 m height:		Part III
- Cladding / coating of exterior walls (if building height ≤ 9 m);	M3	37.1
- Cladding / coating of exterior walls (if building height > 9 m);	M2	37.1
- Window frames;	M3	37.2
- Roof coverings (if not accessible);	M3	38.1
- Floor coatings of CHC[1]	M3	30.5.b)
- Ceiling and wall coatings of CHC[1];	M2	30.5.b)
- Floor coating of interior staircases.	M2	32.7 a)
Multifamily buildings with more than 28 m height:		Part IV
- Window frames;	M2	67.2
- Floor coatings of CHC[1];	M2	58.5 b)
- Floor coating of interior staircases;	M2	60.7 a)
- Floor coating of fire-resistive chambers;	M2	56.3 e)

[1] Common areas with horizontal circulation (halls, corridors..)

Taking into account the new classification system, the Euroclasses, new versions of RSCIEH and related regulations are foreseen. Nevertheless, it is expected that no deep modifications will be made on their basic structures. The present fire reaction classes will be replaced by the Euroclasses, and for the conversion trial, the characteristics of each material class in terms of flame spread contribution will be preponderant.

At this moment, only an approach can be done regarding the expected Euroclassifications of PM formulations in study. According to the conversion approach presented in Table 6.2, only based on fire contribution of each class, M2 and M3 classes will correspond, respectively, to C and D Euroclasses. However, other features such as intensity of smoke and occurrence of burning droplets are also parameters that will affect the classification into the Euro-subclasses. Regarding this subject, another attempt was made in order to arrive at a comparison between the French classification and the Euroclasses, including the subclasses (Collignon 2004). This approach is presented at Table 6.15.

Table 6.15. Comparison table between the French and the European classifications (Collignon 2004).

Europe	A1	A2	A2	B	C	D	D	E	F
		s1	s1 / s2 / s3			s1 / s2 / s3	s1 / s2 / s3		
		d0	d0 / d1			d0 / d1	d0	d2	
France	M0	M0	M1		M2	M3	M4 NB*	M4	

* NB- No burning droplets.

According to this last approach, and taking into account to what that was observed during the epirradiator tests, a classification of D-s3;d0 is expected for epoxy and polyester PM formulations, (*e.g*. materials medially combustibles, with significant smoke emission, but without burning particles or droplets). Likewise, a C-s3;d0 classification is expected for epoxy PM formulation modified with ATH flame retardant system (with 80% in weight of resin content).

6.3.5 Conclusions

Fire reaction classification is the single common index used by the different fire safety regulatory systems to ascertain the possible applications of building materials. Within this scope, in the present work, fire radiations tests were conducted in order to determine flame spread rate of epoxy and polyester PM formulations, and accordingly, their reaction-to-fire classifications and allowable applications. Three additional epoxy based mortar formulations, modified with Aluminium Trihydroxide (ATH) and Ammonium Polyphosphate (APP) flame retardant systems, were also developed and tested for fire reaction.

Based on obtained results, the following conclusions can be drawn:

- Both epoxy and polyester PM formulations are classified, as medially flammable materials, into fire reaction class M3 (according French normalization). Taking into account the Portuguese regulations of fire safety in buildings, M3 materials can be applied, in general, as cladding or surface coating of exterior walls (buildings with less than 9 m height), roof coverings and floors;
- The addition of APP and ATH flame retardant systems, with the content levels of 20% and 40%, respectively, in weight of resin content, improves significantly fire behavior of epoxy-based mortars, but not enough to reach an effective reduction of combustibility class. Fire behavior enhancement, however, is achieved without loss of flexural mechanical properties;
- The use of ATH compound, with a higher content (80%) ATH-II, is effective in reducing the material combustibility class to M2 (hardly flammable material). However, the addition of this amount of filler additive also leads to a decrease of 14 % in flexural strength of the final product. As a M2 material, the application field of epoxy based mortars is considerably enlarged: ATH-II modified epoxy PM can be applied for cladding and surface coating of exterior and interior walls, ceilings and floorings, in all habitation buildings whatever their height.
- Taking into account the fire reaction Euro classification system, new national regulations concerning fire safety in building are foreseen. Merely as an indication, it is expect that plain epoxy and polyester PM and ATH-II modified epoxy PM formulations will be classified, respectively, as D-s3;d0 and C-s3;d0 materials.

Comparing with other polymer mortars with similar resin contents, PM formulations in study (unmodified ones) are quite good in terms of reaction to fire. Nonetheless, it does not seem to be advisable to use these ‘new’ materials, indoors, without improving their fire behavior, either by incorporation of flame retardant systems, or by means of fireproofing coatings further applied on the outer surface of the material.

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VII. CONCLUSIONS AND RECOMMENDATIONS

7.1 Synopsis

In this thesis work two PM formulations were developed and optimized regarding flexural strength property. For that purpose, Taguchi method and the analysis of variance were applied, respectively, for the planning of the experiments and for the analysis of the results.

Obtained optimized formulations were thoroughly characterized in terms of physical and static mechanical properties. Fresh state properties, setting shrinkage, specific gravity, air content, coefficient of thermal expansion, mechanical strength in compression, bending and tension, deformability properties and stress-strain relationships were determined and compared with the general properties of conventional concrete materials. A special emphasis was given to characteristics addressed to durability issue. Chemical resistance tests to several aggressive agents were performed, mechanical performances under different environment temperatures were investigated, resistances to thermal fatigue cycles and to freeze-thaw cycles were analysed and the weatherability, either by means of natural weathering tests or by accelerated and/or artificial weathering tests, was assessed.

Behavior under fire, as an important shortcoming associated to these materials, was also analysed and discussed. Heat release, ignition time, flame spread, smoke and toxic gases release rates were some of the parameters determined, which allowed the assessment of fire performance of PM formulations. The effect of different flame retardant systems on material's fire reaction was also investigated.

Finally, two different applications for the developed PM formulations were approached: *i)* composites structural beams made with GFRP (Glass Fibre Reinforced Plastics) profiles filled with a PM material, and *ii)* lightweight structural concretes based on PM materials modified with lightweight natural aggregates, such as cork granules and wood shavings. For both foreseen applications, the first investigation steps were performed. Models were conceived and produced, mechanical performances were analysed and the viability of their appliances was evaluated.

As the same time as the above tasks were developed, another goal aimed for this thesis work was attained: to make a state of the art review on PC materials, helping to fill the still existing gaps in certain issues addressed to these materials, and contributing for a better bridge between polymer technology and construction materials' science.

7.2 Main Conclusions

In the following sections, the main conclusions inferred from the studies carried out throughout this thesis are compiled and briefly discussed.

i) Optimization process of PM formulations:

Within the range of variables investigated in this study, the following can be concluded:

- For the same processing conditions, the most influencing factor on bending strength of PM formulations is the resin type, followed by resin content and filler content;
- Curing treatment by seven days at room temperature has the same effect on flexural strength of PMs than one day at room temperature followed by three hours at 80ºC;
- The optimal combination that leads to the most flexural resistant PM results of the mixture of foundry sand (80% by weight) with epoxy resin binder (20% by weight), without filler addition. However, the combination that leads to the best relationship between cost and flexural performance is achieved by using unsaturated polyester as binder, instead of epoxy resin system, while keeping the other material factors (binder content, filler content and sand type).

Taguchi methodology, and the analysis of variance ANOVA, can be applied with success to PC material's design. With these techniques, the experimental plan is significantly reduced and the influence of several material factors and their interactions on a certain desirable or undesirable feature can be easily assessed. Care should be taken, however, in selecting the most representative material factors, with adequate levels, and the most convenient Taguchi orthogonal array. Insensate choices may result on poor results. Special care should also be put on the number and type of interaction to study, as masked interactions, not considered in the orthogonal array, may confuse excessively the plan leading to erroneous conclusions.

ii) Physical and short term mechanical properties:

Physical and mechanical properties of both PM formulations obtained on all tests performed are summarized in Table 7.1. Some comments concerning obtained results and observed behavior during testing are depicted in what follows:

Physical properties:

- Both PM formulations present good workability, especially, epoxy based one. However mixture workability and consistency are considerably time-dependent. At room temperature, 15–20 minutes after mixing, polyester PM formulation is no more workable, whereas epoxy mortar formulation shows a considerable decrease on workability; 35-40 minutes after this point, epoxy formulation cannot also be casted. Polyester based formulation, with a shorter working life, is more sensitive to environment temperature, catalyst content and total amount of mass produced by batch.
- Final setting shrinkage (24 hours) of polyester PM formulation is up to two times higher than epoxy-based formulation and almost eighteen times higher than Portland cement concrete. However, shrinkage phenomenon occurs quickly and after 24 hours or less is negligible due to relaxation.
- Both PM formulations can be classified into the category of structural lightweight concrete materials, as their densities are lower than 1.9 kg/dm^3 and their compressive strengths are higher than 17 MPa.

Table 7.1. Summary of physical and short-term mechanical properties of PM formulations.

Physical Properties	Test Method	Sample size	**Epoxy PM** Average | St. Dev.	**Polyester PM** Average | St. Dev.
Slump Test	RILEM PC-3	2	56 mm	52 mm
Flow Test	RILEM PC-3	2	128 mm	125 mm
Working Life	RILEM PC-4	2	42 min	18 min
Setting Shrinkage	Int. Method	2	2.24 ‰	5.99 ‰
Specific Gravity	RILEM PCM-4	41	1.80 ± 0.02 kg/dm^3	1.88 ± 0.02 kg/dm^3
Air Content	RILEM PCM-4	41	15.21 ± 0.98 %	8.33 ± 1.10 %
Coef. Thermal Expansion	Int. Method	3		
[-15ºC, +23ºC]			27 μm/m.ºC	25 μm/m.ºC
[+23ºC, +60ºC]			46 μm/m.ºC	34 μm/m.ºC
Coef. Water Absorp[a]	RILEM PC-11	3	0.023 ± 0.004 %	0.070 ± 0.007 %
Mechanical Properties				
Flex. Strength (3-Point)	RILEM PCM-8	114 - 66	40.40 ± 3.18 MPa	22.10 ± 1.76 MPa
Comp. Strength (prism.)	UNE 83821	18	73.23 ± 3.15 MPa	65.03 ± 3.09 MPa
Comp. Strength (cyl.)	RILEM PC-5	9	70.16 ± 6.74 MPa	64.13 ± 1.43 MPa
Comp. Secant Elasticity Modulus	RILEM PC-8 ASTM C 469	3	12.60 ± 0.32 GPa	11.57 ± 0.17 GPa
Máx. Comp. Strain[b]	RILEM PC-8 ASTM C 469	3	10.45 ± 0.24 ‰	15.99 ± 0.35 ‰
Ultimate Comp. Strain[c]	-	3	30 ‰ to 35 ‰	25 ‰ to 30 ‰
Poisson Ratio	ASTM C 469	1	0.26	0.22
Flex. Strength (4-Point)	RILEM PC-7	3	25.82 ± 1.07 MPa	16.99 ± 0.81 MPa
Flex. Elast. Modulus	Int. Method	3	9.82 ± 0.48 GPa	9.74 ± 0.51 GPa
Máx. Tensile. Strain[b]	-	3	3.08 ± 0.08 ‰	3.74 ± 0.22 ‰
Splinting Tensile Strength	RILEM PC-6	3	17.44 ± 0.53 MPa	12.07 ± 0.37 MPa
Direct Tensile Strength[d]	-	3	18.1 to 18.7 MPa	12.2 to 12.6 MPa
Charpy Impact Strength[e]	ISO 179-1	10	1.82 ± 0.13 kJ/m^2	1.06 ± 0.11 kJ/m^2

[a] Determined with basis on water uptake of specimens immersed during 48 hours in water;

[b] Strain at peak stress;

[c] Strain at failure;

[d] Estimated with basis on splitting tensile and four-point bending strength;

[e] Charpy impact tests performed on the Department of Polymer Engineering (University of Minho) by courtesy of Dt. Paulo Nóvoa.

- Although the lower density of polyester resin, polyester based mortars present higher density than epoxy mortars. The high value of air content present on epoxy PMs, almost twice of polyester PM, is surely the responsible factor for this feature. The higher values found for slump and flow of epoxy PM formulation, in spite of the higher viscosity of its resin binder, are certainly due to this great amount of air content. Other mixture process for the resin and hardener components of epoxy resin system must be though in order to decrease accidental air entrainment into the mixture.
- Coefficients of thermal expansion of both PM formulations vary continuously within the temperature range of –15ºC to +60ºC, presenting higher coefficients at higher temperatures than at lower temperatures. The variation of thermal expansion with temperature, follow rather a polynomial law than a bilinear law. However, for practical use, when a higher precision is not required, it may be considered a bilinear law with transition points at room temperature (see Table 7.1).

The method applied to determine the coefficient of thermal expansion, (-thermal strains measured by means of self-temperature compensated strain gages, indicated for test materials without thermal expansion-), is quite precise with excellent accuracy for practical purposes, does not require any specific devices or special equipment and it is very simple to implement, which make it a good alternative to conventional methods.

Short-term compressive properties:

- Epoxy PMs present higher compressive strength than polyester based mortars. However, this difference (9% and 15% higher for, respectively, cylinder and prismatic specimens) is not as outstanding as in the case of flexural strength, which is almost two times higher. This is in accordance with the assumed premise that flexural resistance is a better parameter for the mechanical assessment of PC materials. Obtained compressive strengths of PM formulations were within the usual range of values obtained for polyester and epoxy PMs.
- Secant compressive elasticity modulus of epoxy PM specimens is slight higher than polyester based mortars. The same pattern is observed for initial tangent

elastic modulus. Both obtained values are closer to the lower limit of the common range of values found for PC materials.

- A higher stiffness is shown by epoxy PM specimens than by polyester based mortars and the determined secant elasticity modulus (at 40% of peak stress) does not reflect this large difference in stiffness of the two materials. The ascending branch of stress-strain curves of epoxy PM specimens is not only steeper, but also almost linear up to 60% of maximum stress; whereas polyester based mortars present rather a more ductile behavior, with corresponding ascending branches approximately linear only up to 40% of peak stress.

  Post-peak behavior is also very distinct for both PM formulations. Descending branch of polyester PM formulation is almost symmetric to the ascending part, but it has a limited extension as a brittle failure occurs at compressive strains around 25‰ to 30‰ (approximately at 80% of maximum capacity load). Conversely, softening branch of epoxy PM specimens is less steep than the ascending part and greatly larger than in the case of polyester based mortars. Furthermore, failure is not brittle. Instead, a progressive and steady loss of load capacity occurs as compressive strain increases.
- The two-parameter relationship purposed by Sargin, defined by Eq. (4.18), shows a good agreement with the experimental data, for both types of PM specimens, and can be applied with success to modelling compressive stress-strain behavior of PM formulations.

Short-term flexural properties:

- Average three-point flexural strength of epoxy PM formulation is rather near the upper limit of the common values found for this type of mortar (usually within the range of 15 MPa to 45 MPa, as function of binder content). Relatively to polyester PM formulation, average flexural strength is within the range of values commonly found for these types of resin-based mortars. With 95% confidence, it may be predicted that the correct estimates of the mean flexural strength, f_{fl}, are in the range of 39.7 to 41.0 MPa for epoxy PM formulation, and between 21.5 and 22.6 MPa for polyester based formulation.

- Flexural elasticity modulus of PM formulations cannot be assessed by load-deflection curves obtained from three-point bending tests performed on prismatic specimens, with a height to span ratio of 0.4. Even considering shear effect on calculation procedure, through Timoshenko simplified approach for the deflection at mid-span of a rectangular bar with allowance for shear, introduced simplifications on calculation of elasticity modulus lead to rough and large errors.
- Flexural to cylinder compressive strength ratios of 0.57 and 0.34 were found for, respectively, epoxy and polyester PM formulations. These ratios are much higher than similar parameters found for conventional cement concretes (around 0.2), mainly due to the great flexural resistance of PMs, especially of epoxy based ones.

Short-term tensile properties:

- Average direct tensile strength, estimated with basis on splitting tensile strength and modulus of rupture, results on values around 18 MPa and 12 MPa for, respectively, epoxy and polyester PM formulations. Obtained results are within the range of values commonly found for these materials.
- Flexural-tensile elasticity modulus values, directly obtained for both formulations by means of stress-strain curves (four-point bending tests), are also within the common range of values found for these materials, and are coherent with material composition.
- Like in compression, a higher stiffness is shown by epoxy PM specimens than by polyester based mortars, and the determined flexural-tensile elasticity modulus does not reflect this distinct behavior. Departure from linearity of the stress-strain relations occurs at similar stress/strength ratios for both formulations, between 45% and 50%, but after this point, the stress-strain curves of polyester based mortars bend drastically comparing with those of epoxy PMs. In spite of the higher modulus of rupture reached by epoxy mortars, a higher tensile strain is sustained by polyester based mortars until failure.
- Tensile to cylinder compressive strength ratios of 0.26 and 0.18 were found for, respectively, epoxy and polyester PM formulations. These ratios are much higher

than similar parameters found for conventional cement concretes (around 0.1). This feature is mainly due to the tighter bonding between the polymeric binders and the aggregates, since the cracking of ordinary concretes is usually initiated from the interfaces of cement paste and aggregates.

Making an overall comparison, similarities in fact exist between static mechanical behavior of PC materials and conventional cement concretes. However, significant and considerable differences also coexist. PC materials withstand much more strain during mechanical loading than ordinary concretes do, and this feature is greater the lower the loading rate. Compressive and tensile strains at peak stress four to seven times higher than the usual values observed in ordinary concretes are commonly found in PC materials. This implies that polymer based concrete is a more ductile material than portland cement concrete. This characteristic arises from the viscoelastic nature of matrix binder. Higher bond capacity of polymer binders also justify the higher flexural/tensile to compressive strength ratios found for PC materials

Thus, some of the PC material's behavior can be understood by considering the known behavior of regular concrete, and some of its behavior can be understood by examining the behavior of polymers.

ii) Durability properties:

Durability properties of PM formulations in terms of chemical resistance, thermal durability and weatherability are summarized in Table 7.2. Main conclusions obtained with durability experimental program are described in the following:

Chemical durability:

- Epoxy PM mortars are hardly affected by immersion in water, sulphuric acid and sodium chloride solutions, which is a good indicator of the excellent chemical resistance of this material to acids and salts. On the other hand, polyester based mortars are fairly affected by immersion in the same solutions, showing some sensitivity to these chemicals (reductions in the range of 16% to 31% were observed).

  Both PM formulations are markedly attacked by sodium hydroxide solution, but even so, retained flexural strength after 84 immersion days in the alkalis solution is in the same magnitude (polyester PM) or much higher (epoxy PM) than that of ordinary concretes without any degradation process.

- There is a positive correlation between water uptake and flexural strength reduction of PMs immersed in water, alkalis and acid solutions. This correlation is stronger for epoxy than for polyester PMs. Similar correlations were found in other studies undertaken chemical resistance of PC materials. Hence, it is reasonable to presume that the most likely factor causing the reduction in strength is the deterioration of the interface matrix/aggregate due to water diffusion into PM.

Thermal durability:

- Flexural properties of both PM formulations are strongly affected by environment temperature. Except within a narrow temperature range, (between 10ºC and 25ºC for epoxy mortars, and between -20ºC and 30ºC for polyester mortars), flexural strength of these mortar formulations decreases drastically with raising test temperatures, especially in the case of epoxy based mortars. Loss of loading bearing capacity with increasing temperatures is accompanied with a progressive loss of material stiffness. The inflection points, where temperature dependency becomes notorious, are related to the heat distortional temperatures of the resins used rather than the glass transition temperatures. The ‘heat distortional temperatures’ of both formulations (approximately at 25ºC and 30ºC for, respectively, epoxy and polyester PMs) are both located around 10ºC lower than the HDT of resin binders.

  For temperatures lower than +10 ºC, flexural behavior of epoxy mortars improves with further decreases in temperature, while polyester mortars present rather stable values.

- Exposure to constant or changing temperatures (thermal fatigue cycles) has no significant influence on flexural properties of both formulations of PM, as long as specimens are taken back to their initial environmental conditions. However, recovering capacity of epoxy mortars is gradually reduced by repeated exposure to high temperatures.

Both PM formulations show an excellent resistance to freeze-thaw cycles and frost attack. One hundred freeze-thaw cycles, between –10 ºC and +10 ºC, produce very little damage on both epoxy and polyester PMs, due to a reduced degree of water absorption.

With basis on obtained results, it can be concluded that the use of epoxy PMs is restricted to lower temperature environments in order to benefit from its total potential in strength. In the case of higher temperatures, care should be taken in both formulations as properties may drop significantly.

Weatherability:

- PM formulations are sensitive to degradation effects of natural weathering. One-year outdoor exposure to natural maritime environment has a moderate deleterious effect on flexural strength of both types of PMs. Epoxy based mortars are in general more weather resistant than polyester based ones.
- Spring/Summer outdoor exposure is more prone to PM specimens than equivalent exposure time in Fall/Winter period. Higher intensities of sunlight radiation, especially in the UV region, combined with quite higher levels of temperature, seem to be the major reasons for the superior degradation rates observed.
- Beyond yellowing and staining processes, relative short-term exposures to arc-xenon artificial light source (up to 3000 hours) has no noticeable deleterious effects on both types of PM formulations. Instead, slight increases on mechanical flexural strength were in fact observed. Lack of agreement between the solar spectrum and that of the artificial light source, especially in the infrared and UV region, appears to be the main reason for the differentiated behavior of natural and artificially exposed specimens.
- Both types of PMs are severely affected by exposure to salt-fog spray artificial weathering, specially epoxy based ones. The strength decrease rates presented a non-linear evolution with a tendency to stabilization. Mechanical cyclic loading induced by moisture cycling, leading to fatigue processes, is likely the major cause responsible for the strong degradation rates occurred during salt-fog artificial exposure.

Table 7.2. Summary of durability characteristics of PM formulations.

Durability property	**Epoxy PM** Relative Flex. Str. | St. Dev.	**Polyester PM** Relative Flex. Str. | St. Dev.
Chemical resistance (84 immersion days)		
• Distilled Water	98 ± 3 %	70 ± 3 %
• Sulphuric Acid (10%)	91 ± 5 %	69 ± 4 %
• Sodium Chloride (10%)	102 ± 9 %	84 ± 3 %
• Sodium Hydroxide (10%)	57 ± 2 %	33 ± 2 %
Flexural resistance under different temperatures		
• -20ºC	125 ± 6 %	99 ± 5 %
• -10ºC	117 ± 4 %	97 ± 13 %
• 0ºC	111 ± 2%	98 ± 6%
• + 10ºC	102 ± 5 %	100 ± 11 %
• +23ºC (Ref.)	100 ± 3 %	100 ± 1 %
• +30ºC	81 ± 1 %	93 ± 4 %
• +40ºC	45 ± 2 %	93 ± 2 %
• +50ºC	17 ± 1 %	75 ± 1 %
• +60ºC	8 ± 0 %	63 ± 1 %
• +80ºC	3 ± 1 %	34 ± 1 %
• +100ºC	2 ± 1 %	12 ± 1 %
Thermal fatigue resistance (100 cycles)		
• +20ºC - +100ºC	76 ± 4%	96 ± 8 %
• -10ºC +10ºC (dry cycles)	96 ± 5 %	105 ± 1 %
• -10ºC +10ºC (wet cycles)	95 ± 4 %	100 ± 3 %
Natural weathering (exposure site: Aveiro)		
• 6 months (Fall/Winter)	99 ± 1 %	94 ± 3 %
• 6 months (Spring/Summer)	92 ± 2 %	86 ± 5 %
• 12 months	90 ± 7%	84 ± 4 %
Ageing (under normal Lab conditions)		
• 6 months	99 ± 2 %	103 ± 3 %
• 12 months	98 ± 5 %	105 ± 5 %

Table 7.2 (cont.). Summary of durability characteristics of PM formulations.

Durability property	**Epoxy PM** Relative Flex. Str. | St. Dev.	**Polyester PM** Relative Flex. Str. | St. Dev.
Salt Fog resistance (16h: 50g/l NaCl ; 8h: drying 35ºC)		
• 1000 hours	92 ± 10 %	94 ± 8 %
• 1350 hours	86 ± 6 %	87 ± 11 %
• 3000 hours	79 ± 4 %	85 ± 3 %
• 5000 hours	65 ± 1 %	64 ± 11 %
• 10000 hours	52 ± 4 %	62 ± 3 %
Arc Xenon rays resistance (Int: 550W/m^2 ; Band.: 300-800 nm)		
• 500 hours	102 ± 3 %	99 %
• 1000 hours	105 ± 2 %	96 %
• 2000 hours	106 ± 6 %	102 %
• 3000 hours	111 ± 1 %	105 %

- Regarding the correlation between salt-fog artificial weathering test results and data obtained with natural exposure, with basis on one-year time-scale, it can be stated that the former tests accelerate 7.80 and 3.97 times the natural weathering degradation processes that occur, respectively, on epoxy and polyester PM formulations. Obtained acceleration factors can only be applied relatively to maritime sites, with similar latitudes as Aveiro, and to salt-fog artificial environments with the same set points used in this study.
- Previsions regarding the long-term behavior of PM formulations with outdoor exposure time can be attempted, but only with a merely indicative value. Within the uncertainty of the data, maximum flexural strength decreases of 50% and 35% will be expected, respectively for epoxy and polyester PMs. It is estimated that predicted residual flexural strengths, which constitute the long-term stable values, will be attained, respectively, after 10 and 4 years of outdoor exposure.

It must be pointed out that prediction models based on short-term values of acceleration factors only give rough indications about the relationship between natural and artificial weathering, representing, eventually, the worst scenario that could be encountered in a real situation of long-term outdoor exposure.

Since major deleterious effects of weathering are confined to superior layers of the material, another point that should be realized is the fact that damage magnitude becomes size piece dependent. The larger the element, the minor the importance of the damage. It is not reasonable to expect that a larger element of PM material would loss the same load bearing capacity as a standard prismatic specimen. Nevertheless, estimated residual flexural strengths of PM formulations after long-term outdoor exposure are, even so, still competitive with those presented by ordinary cement concrete materials (not exposed to weathering processes).

iv) Fire Performance:

Major conclusions obtained from cone calorimeter and radiation tests conducted on both PM formulations and on epoxy PMs modified with flame retardant systems are summarized in the following:

- Under a fire situation, epoxy-based mortar presents a worst behavior than polyester based one, especially in terms of heat release rate and carbon monoxide yield. Poor thermal stability and the weak tendency to char of epoxy resin seem to be the main reasons for this feature.
- Both epoxy and polyester PM formulations are classified, as medially flammable materials, into fire reaction class M3 (according French normalization). Taking into account the Portuguese regulations of fire safety in buildings, M3 materials can be applied, in general, as cladding or surface coating of exterior walls (buildings with less than 9 m height), roof coverings and floors.
- The addition of APP (Ammonium Polyphosphate) and ATH (Aluminium Trihydroxide) flame retardant systems, with the content levels of 20% and 40%, respectively, in weight of resin content, improves significantly fire behavior of epoxy-based mortars, but not enough to reach an effective reduction of combustibility class. Fire behavior enhancement, however, is achieved without loss of flexural mechanical properties.

- The use of ATH compound, with a higher content (80%) ATH-II, is effective in reducing the material combustibility class to M2 (hardly flammable material). However, the addition of this amount of filler additive also leads to a decrease of 14 % in flexural strength of the final product. As a M2 material, the application field of epoxy based mortars is considerably enlarged: ATH-II modified epoxy PM can be applied for cladding and surface coating of exterior and interior walls, ceilings and floorings, in all habitation buildings whatever their height.
- Taking into account the fire reaction Euro classification system, new national regulations concerning fire safety in building are foreseen. Merely as an indication, it is expect that plain epoxy and polyester PM and ATH-II modified epoxy PM formulations will be classified, respectively, as D-s3;d0 and C-s3;d0 materials (*i.e.*, materials medially -D- or limitedly –C- combustibles, with significant smoke emission –s3-, but without burning particles or droplets –d0-).

Comparing with other polymer mortars with similar resin contents, PM formulations in study (unmodified ones) are quite good in terms of reaction to fire. Nonetheless, and although test results revealed that polyester PM is less-prone material than epoxy-based mortar, fire behavior of both formulations is not satisfactory for some intended uses. Therefore, it does not seem to be advisable to use these ‘new’ materials, indoors, without improving their fire behavior, either by incorporation of flame retardant systems, or by means of fireproofing coatings further applied on the outer surface of the material.

7.2 Recommendations

A number of future investigations could be attributed as an extension or complement to the present work. Also some gaps were detected, demanding further analysis.
For that propose, the following complementary studies are strongly recommended:

- Analysis of the effect of an intermediate level of filling or charge, between 5% to 20%, on flexural and compressive performance of epoxy and polyester PM formulations;

- Accurate statistical analysis of compressive and tensile properties of PM formulations with basis on a more representative sample size; Additionally, determination of tensile strength through performance of direct tensile tests;
- Development and improvement of embedding process of Fibre Bragg Grating (FBG) sensors into PMs for in-time real monitoring;
- Determination of acceleration factors between natural and artificial weathering tests with basis on a longer time-scale;

As an extension of the present work the following studies are suggested:

- Investigation of long-term mechanical properties of PM formulations: flexural fatigue performance and accelerate flexural creep behavior under high temperatures;
- Development of hybrid composite structures based on the assembly of GFRP pultrusion profiles and precast PC materials;
- Analysis of thermal and acoustic characteristics of PMs modified with lightweight organic aggregates;
- Development of ultra-lightweight PMs, with densities lower than water, with basis on polyester 'polychips' and cork aggregates;
- Improvement of fire performance and thermal resistance of PMs through the use of matrix binders modified with nanoclays.

It is believed that with the progress in polymer technology and continuing research in PC materials, it will be able to develop composite materials that can benefit from the advantages that the polymer-concrete matrix offers, such as versatility, rapid cure, excellent mechanical strength and durability, and avoid the drawbacks of polymers, such as high creep and shrinkage, sensitivity to temperature, and vulnerability to fire.

This composite is not intended to replace conventional concrete, but its field of application should be where other materials would provide less than satisfactory or adequate performance.

APPENDIX A

GFRP-Polymer Concrete Hybrid Beams

i) 'Analysis of hybrid beams composed of GFRP profiles and polymer concrete'*, International Journal of Mechanical and Materials and Mechanics in Design*, Vol.1 (2004), 143-155. .... A-3

ii) 'Flexural behaviour of GFRP-polymer concrete hybrid structural systems', *6th International Symposium on FRP Reinforcement for Concrete Structures -FRPRCS-6*, July 8-11, 2003, Singapore, 695-704 .... A-17

iii) Development of composite hybrid structures based on polymer concrete – GFRP pultrusion profiles assembly system, *3rd International Conference on Composites in Construction*, July 11-13, 2005, Lyon, France A-27

International Journal of Mechanics and Materials in Design **1:** 143–155, 2004.

Analysis of hybrid beams composed of GFRP profiles and polymer concrete

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Abstract. In this paper, a numerical approach for the analysis of a new type of hybrid composite beams is presented. Such beams are composed of composite materials that resist shear and tensile stresses, and polymer concrete accommodating compression stresses.The beams offer an optimized configuration in terms of stiffness and strength, with much potential for mechanical and civil engineering structures.The current numerical model is based on a finite element formulation for layered shell-like structures. The model accounts for a polymer concrete material model, orthotropic material model, and considers the analysis of geometric and material nonlinearities. The first-order shear deformation theory is used in order to describe the shell deformation under a total Lagrangian formulation. The model is validated experimentally and a close agreement with experimental results makes this model an attractive solution method for this type of composite hybrid beams.

Key words: polymer matrix composites, polymer concrete, FRP composite materials, hybrid beam, FEA

1. Introduction

1.1. FRP–POLYMER CONCRETE HYBRID SYSTEMS

Research in polymer concrete has initiated interest amongst the scientific community in recent years (American Concrete Institute, 1986; Dikeou, 1986; Fowler 1997 and 1999; Chawalwala, 1999). Polymer concrete is made from thermoset resins and natural aggregates. This type of concrete has very high compressive strength, good chemical resistance, and relatively low elastic modulus. The good characteristics of this material did promote its industrial production, which is already established in the market, mainly in the field of precast components for the building. The use of steel or fiber reinforced plastics (FRP) allowed the application and growth of polymer concrete as structural elements.

In recent years, an innovative structural concept was developed involving a combination of FRP pultruded profiles with conventional cement concrete to produce lightweight, corrosion-free and yet inexpensive hybrid systems, see Deskovic et al. (1995), Sekijima et al. (2001) and Hall and Mottram (1998). According to this new concept, a FRP profile beam is combined with a concrete layer cast onto the top flange, which replaces the thick FRP compressive flange of traditional pultruded profiles. The method maximizes system performance using materials by combination, and can be thought of as a better way of producing structural members based on the pultrusion process. Interestingly, FRP researchers have developed a number of hybrid systems either by simply replacing steel with FRP pultruded profiles in conventional steel-concrete composite constructions or by developing new structural systems (Mirmiran, 2001).

This paper is concerned with the analysis of hybrid structures composed of GFRP profiles and polymer concrete. Exploiting the better performance of resin concrete, it is believed that hybrid systems can lead to:

(a) section reduction and reduced weight as a result of higher compressive and flexural strength of polymer concrete,
(b) use in highly corrosive environments, as a result of their enhanced chemical resistance,
(c) easier production of precast components and site applications as a result of faster curing time.

In a previous investigation (Ribeiro et al., 2001), small-scale models of four different hybrid beams were designed, manufactured and tested in four-point bending test. Flexural behaviour of such composite structures, in terms of load–deflection history, load capacity and failure mode was analyzed and compared with the flexural behaviour of its material constituents. The four hybrid beam models were designed considering a GFRP pultrusion profile that works in tension, and an epoxy polymer concrete filling, that works mainly in compression. Experimental results showed the high potential of these hybrid systems, revealing a pronounced synergetic effect associated with the assembly of polymer concrete and GFRP profiles. However, some strength problems were detected. Interface debonding provoked premature failure. Further studies were necessary in order to improve bond strength between polymer concrete and the GFRP profiles.

In this paper, we report our findings of new experiments considering GFRP-polymer concrete hybrid beams, with improved adherence between the different material components. Three new series of small-scale hybrid beam specimens were manufactured and tested in bending. A special treatment was given to GFRP profile internal surfaces to promote the adhesion to epoxy polymer concrete. A significant improvement of flexural performance of the hybrid beams is observed.

1.2. Numerical model

Early studies showed that cracking, deflection and ultimate load behaviour of FRP–reinforced concrete beams could be predicted with the same degree of accuracy as the behaviour of regular steel reinforced concrete beams and that a theoretical correlation is possible, see Nawy and Neuwert (1977), Saadmatmanesh and Ehsani (1991) and Al–Salloum et al. (1996).

The present work reports a numerical model for the analysis of concrete with arbitrary shell structures reinforced with composite materials, particularly with FRP pultruded materials. The proposed model is capable of predicting deflections and stresses in concrete and in FRP reinforcement for geometrical and material nonlinear behaviour. The model makes use of constitutive laws for concrete material, based on smeared crack concepts, and high-strength composite materials. The model is implemented in a degenerated shell element as proposed by Ahmad et al. (1970), Owen and Figueiras (1984), and more recently by Ferreira et al. (2001). In order to check the model applicability, it was applied to predict the flexural behaviour of GFRP-polymer concrete hybrid beams. A good agreement between experimental and numerical results was found. The tests were only performed in beams, but the model is generally applicable to plates or shells of arbitrary shape.

2. Finite element model: Assumptions and implementation

2.1. COMPRESSIVE BEHAVIOUR OF CONCRETE

A perfect plastic and a strain-hardening plasticity approach are used to model the compressive behaviour of the concrete examined in this study. A dual criterion for yielding and crushing in terms of stresses and strains is considered, which is complemented by a tension cut-off representation.

The yield condition for thick plates and shells accounting for transverse shear effects is formulated in terms of the first two stress invariants as

$$f(I_1, J_2) = [\beta(3J_2) + \alpha(I_1)]^{1/2} = \sigma_0, \tag{1}$$

where α and β are material parameters and σ_0 is the effective stress obtained from a uniaxial compression test. Relating this expression to results by Kupfler et al. (1969), the material parameters are

$$\alpha = 0.355\sigma_0, \qquad \beta = 1.355. \tag{2}$$

In the perfectly plastic model, σ_0 is taken as the ultimate compressive stress obtained from a uniaxial compressive test (f'c). An elastic response is assumed up to when the effective stress reaches f'c, after which a perfectly plastic response follows until the crushing surface is reached. Figure 1 illustrates the one-dimensional representation of both perfectly plastic and strain-hardening model (Kupfler et al., 1969; Owen and Figueiras, 1984; Ferreira, 1997; and Ferreira et al., 2001).

The crushing condition is a strain-controlled phenomenon. The lack of experimental information forces to assume for a direct conversion of (1) into strains. Thus,

$$\left[\beta(3J'_2) + \alpha I'_1\right]^{1/2} = \varepsilon_0^2, \tag{3}$$

where I'_1 and J'_2 are strain invariants, and ε_0 is an ultimate total strain extrapolated from uniaxial test results.

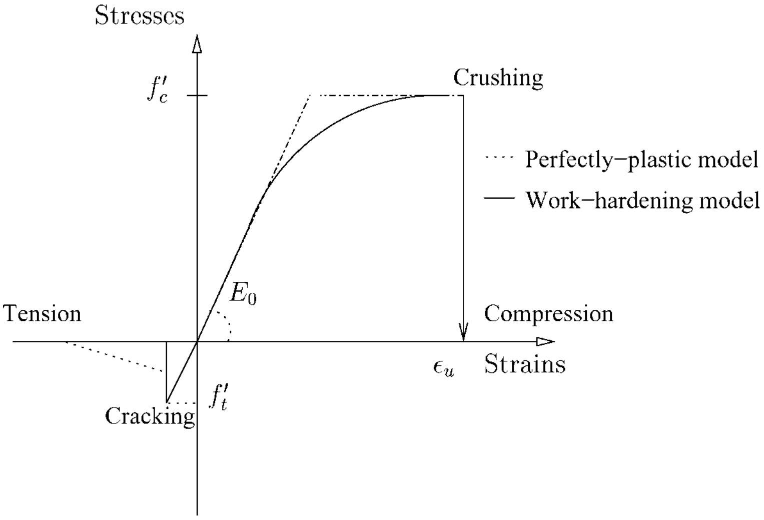

Figure 1. One-dimensional representation of the concrete constitutive model.

Crushing or compressive type of fracture is assumed to occur when the effective total strain reaches the limit value, which is usually taken as the maximum compressive strain in a uniaxial compression test. Once crushing occurred, the concrete is assumed to lose all its characteristics of stiffness at the point under consideration. Therefore, the corresponding elasticity matrix D is taken as a null matrix and the vector of total stresses is reduced to zero.

2.2. Tensile behaviour of concrete

The relative weakness of concrete in tension and the resulting cracking is a fundamental factor affecting the nonlinear behaviour of reinforced concrete plates and shells. It is assumed that when concrete is subjected to a tensile stress it behaves in a semi elastic-brittle material. Formation of cracks can be considered as in other materials a brittle process. In our model we assume for simplicity that the concrete strength in the tension-loading direction decreases to zero after such cracks have formed (Figure 2).

2.3. Smeared crack model

In our analysis, we are not interested in the tensile strength of concrete, but in the influence of the cracked concrete zones on the structural behaviour. A simplified averaging procedure for finite element representation is adopted, based on smeared cracked concrete, which assumes that cracks are distributed across a region of the finite element (Kupfler et al., 1969; Owen and Figueiras, 1984; Ferreira, 1997; Ferreira et al., 2001).

In this model, cracked concrete is supposed to remain a continuum and the material properties are then modified to account for the damage induced in the material. After the first crack has occurred, the model assumes that concrete becomes orthotropic with the material axes oriented along the directions of cracking (Figure 3).

The response of concrete under tensile stresses is assumed to be linear elastic until the fracture surface is reached. This tensile type of fracture or cracking is governed by a maximum tensile stress criterion (tension cut-off). Cracks are assumed to form in planes perpendicular to the direction of maximum tensile stress, as soon as this stress reaches the specified concrete tensile strength (f'_t). A sudden and total release of the normal stress in the affected direction, or its gradual relaxation according to a tension-stiffening diagram is adopted after cracking has occurred. The elasticity modulus and the Poisson's ratio are reduced to zero in the direction perpendicular to the cracked plane, and a reduced shear modulus is employed (Kupfler et al.,

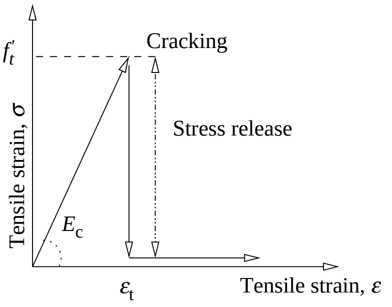

Figure 2. Linear elastic-brittle behaviour of concrete in tension.

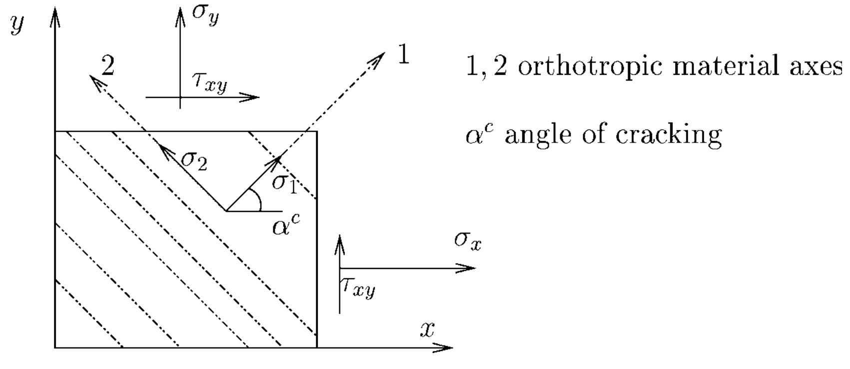

Figure 3. Smeared crack model and the corresponding material axes for concrete.

1969; Owen and Figueiras, 1984; and Ferreira, 1997; Ferreira et al., 2001;). Prior to cracking, concrete is assumed to be an isotropic material, with the following stress strain relationship:

$$\begin{Bmatrix} \sigma_x \\ \sigma_y \\ \tau_{xy} \\ \tau_{xz} \\ \tau_{yz} \end{Bmatrix} = \begin{bmatrix} \frac{E}{1-\nu^2} & \frac{\nu E}{1-\nu^2} & 0 & 0 & 0 \\ \frac{\nu E}{1-\nu^2} & \frac{E}{1-\nu^2} & 0 & 0 & 0 \\ 0 & 0 & G & 0 & 0 \\ 0 & 0 & 0 & \alpha G & 0 \\ 0 & 0 & 0 & 0 & \alpha G \end{bmatrix} \begin{Bmatrix} \varepsilon_x \\ \varepsilon_y \\ \gamma_{xy} \\ \gamma_{xz} \\ \gamma_{yz} \end{Bmatrix} \tag{4}$$

with x and y being the axes in the plane of the structure and E the elasticity modulus, ν the Poisson's ratio, G the shear modulus, $G = E/2(1+\nu)$ and α the shear correction factor, $\alpha = 5/6$. Taking 1 and 2 as the two principal stress directions in the plane of the structure (see Figure 3), the stress-strain relationship for concrete cracked in the 1-direction (crack plane normal to 1-direction) is

$$\begin{Bmatrix} \sigma_1 \\ \sigma_2 \\ \tau_{12} \\ \tau_{13} \\ \tau_{23} \end{Bmatrix} = \begin{bmatrix} 0 & 0 & 0 & 0 & 0 \\ 0 & E & 0 & 0 & 0 \\ 0 & 0 & G^c_{12} & 0 & 0 \\ 0 & 0 & 0 & G^c_{13} & 0 \\ 0 & 0 & 0 & 0 & \alpha G \end{bmatrix} \begin{Bmatrix} \varepsilon_1 \\ \varepsilon_2 \\ \gamma_{12} \\ \gamma_{13} \\ \gamma_{23} \end{Bmatrix}, \tag{5}$$

where G^c_{ij} are the reduced shear modulus of cracked concrete (Kupfler et al., 1969; Owen and Figueiras, 1984; Ferreira, 1997; Ferreira et al., 2001). When the tensile stress in the 2-direction reaches the value (f'_t), a second cracked plane perpendicular to the first one is assumed to form and the stress-strain relationship for concrete cracked in two directions becomes

$$\begin{Bmatrix} \sigma_1 \\ \sigma_2 \\ \tau_{12} \\ \tau_{13} \\ \tau_{23} \end{Bmatrix} = \begin{bmatrix} 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & \frac{G^c_{12}}{2} & 0 & 0 \\ 0 & 0 & 0 & G^c_{13} & 0 \\ 0 & 0 & 0 & 0 & G^c_{23} \end{bmatrix} \begin{Bmatrix} \varepsilon_1 \\ \varepsilon_2 \\ \gamma_{12} \\ \gamma_{13} \\ \gamma_{23} \end{Bmatrix}, \tag{6}$$

In this case, cracked concrete becomes anisotropic and these relations must be transformed to the reference axes, similarly as done with composite materials.

2.4. FINITE ELEMENT IMPLEMENTATION

The formulation presented so far was implemented in the Ahmad shell element, in the same format as in (Kupfler et al., 1969; Owen and Figueiras, 1984; Ferreira, 1997; Ferreira et al., 2001). For the sake of completeness, the basic formulation is here presented.

Two basic assumptions are employed in the Ahmad shell element. Firstly, it is assumed that 'normals' to the mid-surface remain practically straight after deformation. Secondly, the stress component normal to the shell mid-surface is constrained to be zero in the constitutive equations. When applied to plates this formulation is equivalent to that developed by Mindlin (1951) in that it accounts for transverse shear deformation effects. The element displacement field is expressed in terms of three displacements of the reference (mid) surface and two rotations of the 'normal', defined at each element node, and appropriate shape functions, see Zienkiewicz (1991) and Bathe (1982).

Ahmad degenerated a three-dimensional brick element to a curved shell element, which has nodes at the mid-surface (Ahmad et al., 1970), (see Figure 4). This element is capable of layer definition and is able to model laminates either of composite materials or reinforced concrete strengthened with composite laminates.

The coordinates **x** of a point within the element are obtained as

$$\mathbf{x} = [x, y, z]^{\mathrm{T}} = \sum_{k=1}^{n} N_k(\xi, \eta)\left[\mathbf{x}_k^{\mathrm{mid}} + h_k\zeta/2\bar{\mathbf{v}}_{3k}\right] \tag{7}$$

and the displacements by

$$\mathbf{u} = \sum_{k=1}^{n} N_k(\xi, \eta)\left[\mathbf{u}_k^{\mathrm{mid}} + h_k\zeta/2[\bar{\mathbf{v}}_{1k} - \bar{\mathbf{v}}_{2k}]\begin{bmatrix}\beta_{1k}\\ \beta_{2k}\end{bmatrix}\right], \tag{8}$$

where n is the number of nodes per element, h_k is the shell thickness at node k, i.e., the respective 'normal' length, $\mathbf{u}_k^{\mathrm{mid}}$ and $\mathbf{x}_k^{\mathrm{mid}}$ are, respectively, the displacements and the global coordinates at the mid-surface, β_{1k} and β_{2k} are the rotations about local axes, $N_k(\xi, \eta)$ are the element shape functions and ξ, η are curvilinear coordinates (see Figure 4).

The strain vector, ε', is expressed in the local coordinate system, through the derivatives of the local displacements, u', v' and w' in order to x', y' and w'. These local derivatives are obtained from the curvilinear derivatives of u, v and w as (Ahmad et al., 1970; Bathe, 1982; Owen and Figueiras, 1984; Ferreira, 1997); where θ is a matrix of transformation of coordinates.

$$\begin{bmatrix} u'_{,x'} & v'_{,x'} & w'_{,x'} \\ u'_{,y'} & v'_{,y'} & w'_{,z'} \\ u'_{,z'} & u'_{,z'} & u'_{,z'} \end{bmatrix} = \boldsymbol{\theta}^{\mathrm{T}} \begin{bmatrix} x_{,\xi} & y_{,\xi} & z_{,\xi} \\ x_{,\eta} & y_{,\eta} & z_{,\eta} \\ x_{,\zeta} & y_{,\zeta} & z_{,\zeta} \end{bmatrix}^{-1} \begin{bmatrix} u_{,\xi} & v_{,\xi} & w_{,\xi} \\ u_{,\eta} & v_{,\eta} & w_{,\eta} \\ u_{,\zeta} & v_{,\zeta} & w_{,\zeta} \end{bmatrix} \boldsymbol{\theta}. \tag{9}$$

Taking the assumption $\sigma_{z'} = 0$ into consideration, the stress vector σ' in the local coordinate system is obtained from ε'

The constitutive equations are derived for an orthotropic material with the material axes 1 and 2 parallel to the plane x–y, and rotated by some θ in relation to the axes x and y, being the material axe 3 parallel to z. Taking into account that $\sigma_z = 0$, the stresses σ at a layer of the element are related to the deformations ε by (Ahmad et al., 1970; Bathe, 1982; Ferreira, 1997; Owen and Figueiras, 1984)

$$\boldsymbol{\sigma} = \left[\sigma_x, \sigma_y, \tau_{xy}, \tau_{xz}, \tau_{yz}\right]^{\mathrm{T}} = D\boldsymbol{\varepsilon} = T'^{T}\bar{D}T'\boldsymbol{\varepsilon}, \tag{10}$$

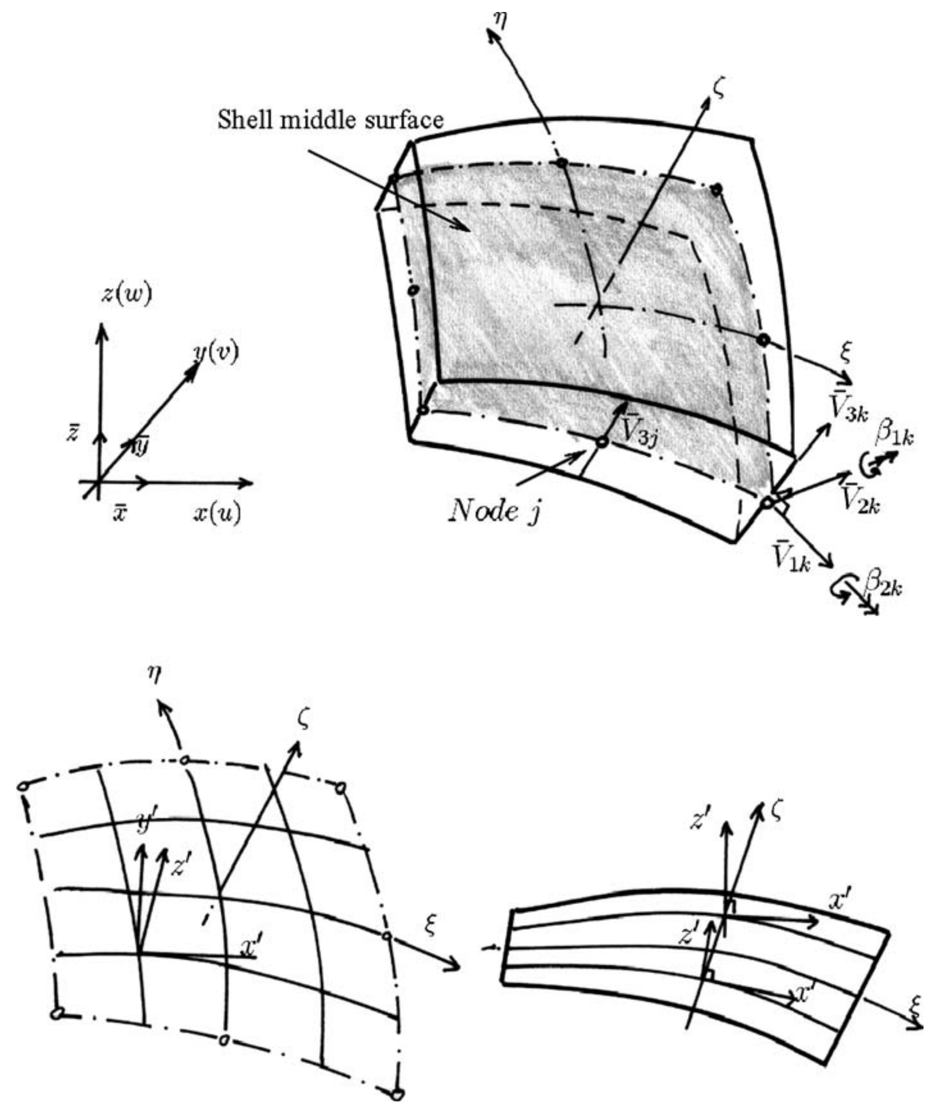

Figure 4. Degenerated shell element (after Ahmed et al. 1970).

where $\mathbf{T}'$ is the strain transformation matrix, defined as

$$\mathbf{T}' = \begin{bmatrix} \mathbf{T}_1' & \mathbf{O} \\ \mathbf{O} & \mathbf{T}_2 \end{bmatrix}, \qquad \mathbf{T}_1' = \begin{bmatrix} c^2 & s^2 & cs \\ s^2 & c^2 & -cs \\ -2cs & 2cs & c^2 - s^2 \end{bmatrix}, \quad \mathbf{T}_2 = \begin{bmatrix} c & s \\ -s & c \end{bmatrix} \tag{11}$$

in which $c = \cos\theta$ and $s = \sin\theta$.

The material elasticity matrix $\bar{\mathbf{D}}$ is defined for the material axes 1–3, having non-zero terms

$$\bar{D}_{11} = \frac{E_1}{1 - \nu_{12}\nu_{21}}, \qquad \bar{D}_{22} = \frac{E_2}{1 - \nu_{12}\nu_{21}}, \qquad \bar{D}_{33} = G_{12}, \tag{12a}$$

$$\bar{D}_{12} = \nu_{12}\bar{D}_{22}, \qquad \bar{D}_{44} = k_{13}G_{13}, \qquad \bar{D}_{55} = k_{23}G_{23}, \tag{12b}$$

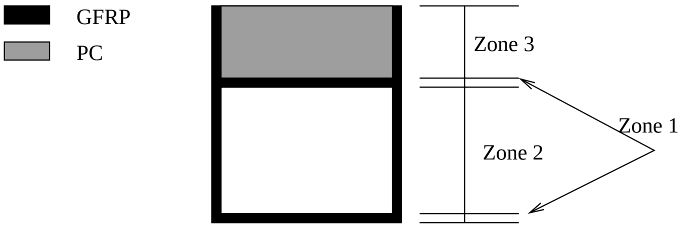

Figure 5. Layered system used for finite element model.

in which E_1 and E_2 are the Young's moduli in the 1 and 2 directions, respectively, v_{ij} is Poisson's ratio for transverse strain in the i-direction when stressed in the j-direction and G_{13} and G_{23} are the shear moduli in the 1–3 and 2–3 planes, respectively; the terms k_{13} and k_{23} are shear correction factors in the 1–3 and 2–3 planes, respectively (Ahmad et al., 1970; Bathe, 1982; Ferreira, 1997; Owen and Figueiras, 1984).

2.5. ASSUMPTIONS MADE IN NUMERIC MODEL APPLICATION

The approach used for the hybrid beams relies on a homogenization procedure of the distinct zones of their cross-sections, both for stiffness and strength. In Figure 5, these zones are identified.

In Zone 1, the equivalent material is considered to be a composite laminate only, due to the laminate construction (Ferreira et al., 2000, 2001). The equivalent material follows the law of mixtures.

In Zone 2, FRP walls are taken in account. Due to the shell formulation, an equivalent material in stiffness and strength is considered.

In Zone 3, a combination of FRP and polymer concrete occurs. In this case, it is assumed that no contribution is given by FRP walls to support compressive solicitations. Therefore, compressive strength of the assembly layer is the compressive strength of the concrete, while tensile strength and elasticity modulus follows a law of mixtures:

$$\Lambda^{\mathrm{eq}} = (\Lambda^{\mathrm{PC}} \,.\, \lambda^{\mathrm{PC}} + \Lambda^{\mathrm{FRP}} \,.\, \lambda^{\mathrm{FRP}})/\lambda^{\mathrm{TOT}}, \tag{13}$$

where $\Lambda^{\mathrm{PC}}, \Lambda^{\mathrm{FRP}}$ are the strength or stiffness, of polymer concrete and FRP material, respectively; Λ^{eq} is the equivalent strength or stiffness of the layer; $\lambda^{\mathrm{PC}}, \lambda^{\mathrm{FRP}}$are the thickness of polymer concrete and FRP material in the layer, respectively and λ^{TOT} is the total thickness of the layer.

3. Experimental work

3.1. COMPONENT MATERIALS OF HYBRID BEAMS

Low viscosity epoxy resin, and foundry sand with a very uniform and fine grain (d_{50} of 342 μm) were used for the polymer concrete mixture. Resin content, without any other chemical additive, was 20% in mass. This formulation corresponds to an optimized result from previous research (Tavares et al., 2000; Ribeiro et al., 2002; Tavares et al., 2002), and its mechanical properties

Table 1. Dimensions and mechanical properties of GFRP profiles

GFRP	Tensile strength (MPa)	Tensile elasticity Modulus (GPa)	Cross-section (mm)
Profile A	395	25.1	55 × 60 × 5
Profile B	310	25.3	30 × 40 × 4
Profile C	350	25.6	50 × 40 × 5

are already known. Although this resin content is probably higher than expected for commercial purposes, it proved to be very good in mechanical terms, and also necessary due to workability factors. Compressive strength and compressive elasticity modulus are 82 MPa and 11.5 GPa, respectively; with ultimate strain defined to be equal to 0.01. Compressive properties were obtained from uniaxial testing according to RILEM TC-113 standards.

Three types of standard U-shaped GFRP pultruded profiles were used. The pultrusion profiles consisted of continuous strand mat and roving of glass fibers, impregnated with unsaturated polyester resin and having an external veil pulled through a die. Volume content of glass fibers was 60–65%, and roving occupied the most part of it. The GFRP profiles cross section dimensions and mechanical properties, obtained from uniaxial tension tests according ISO-527/4 standard, are summarized in Table 1.

3.2. HYBRID BEAMS: DESIGN, MANUFACTURING AND TESTING

Among the four models of hybrid beams initially designed, only three models—those which showed better flexural performance in first test series—were chosen for this experimental program. Cross-sections of the three models, referred to hereinafter as HB I, HB II and HB III are illustrated in Figure 6. All the small-scale models were 600 mm length.

HB I and HB III beams have all the section full of concrete. HB II beam is lighter with only a thin layer of concrete positioned in the upper part of the profile. Cross section of concrete layer,

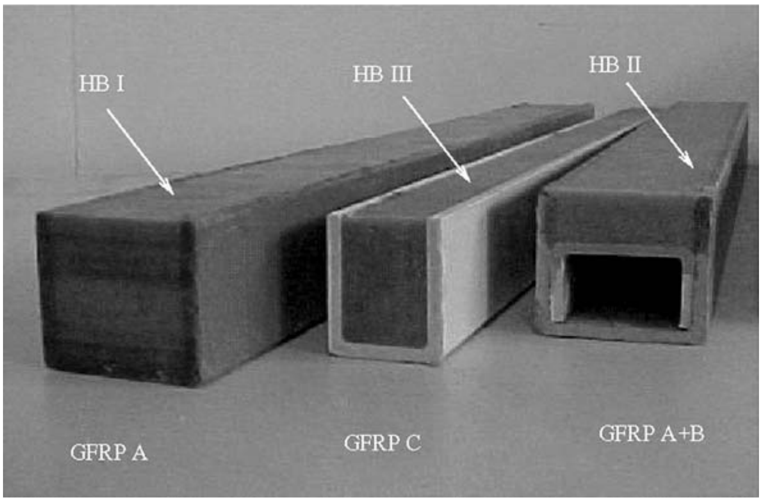

Figure 6. Small-scale models of GFRP-polymer concrete hybrid beams.

in this model, was designed in order to support only compressive stresses in the elastic range. The neutral axis was determined using a homogenization of the hybrid cross-section of the GFRP material.

In order to prevent premature failure due to interface debonding, adhesion between GFRP profiles and polymer concrete was improved through both mechanical and chemical processes. Internal surfaces of GFRP profiles were previously sandpapered and a layer of silane adhesion promoter was applied before concrete casting. In addition, in HB II specimens, profile ‘B’ was bonded to profile ‘A’ with a special epoxy adhesive. In the first specimen’s series, the resin of concrete that drained during casting process assured junction between these two profiles.

For each hybrid model, three specimens were manufactured. All specimens, before being tested, were allowed to cure for seven days at room temperature, and postcured at 80°C for 3 h.

Four-point bending tests on three specimens of each type of hybrid beams were performed. The specimens were loaded with a span of 510 mm and a constant moment zone of 100 mm. Load was gradually increased up to failure at a rate of 1mm/min under displacement control. Test procedures were identical to those applied to perform flexural tests of first series of GFRP-polymer concrete hybrid beams. Four-point bending tests were also performed to evaluate the synergetic effect of the assembly on each constituent material of each hybrid beam.

4. Validation of model

For each type of beam, the average of maximum load capacity and the related synergetic effects are summarized in Table 2. Synergetic effect was calculated by dividing the capacity load of the assembly by the sum of capacity load of each of its two elements. In order to evaluate the improvement of flexural strength reached through profiles surface treatment, experimental results obtained in first specimen’s series are also presented.

Load deflection curves, obtained from both 1st and 2nd test series of composite beams and correspondent components, are illustrated in Figure 7. Numerical results obtained by finite element modeling are also plotted.

Numerical predictions agree quite well with experimental. The accuracy of the model is very good in most of the load range examined. At this stage, the model can predict with reasonable accuracy the load–displacement curves. Near the ultimate load range, the model fails to predict accurately due to difficulty in modeling complex failure modes, such as web shear failure, buckling failure or bond failure.

Table 2. Summarized flexural tests results

Hybrid beam type	Max. capacity load (kN)		Synergetic effect (%)	
	1st series	2nd series	1st series	2nd series
HB I	38.07	46.30	233	284
HB II	26.96	43.09	203	319
HB III	32.06	32.96	258	266

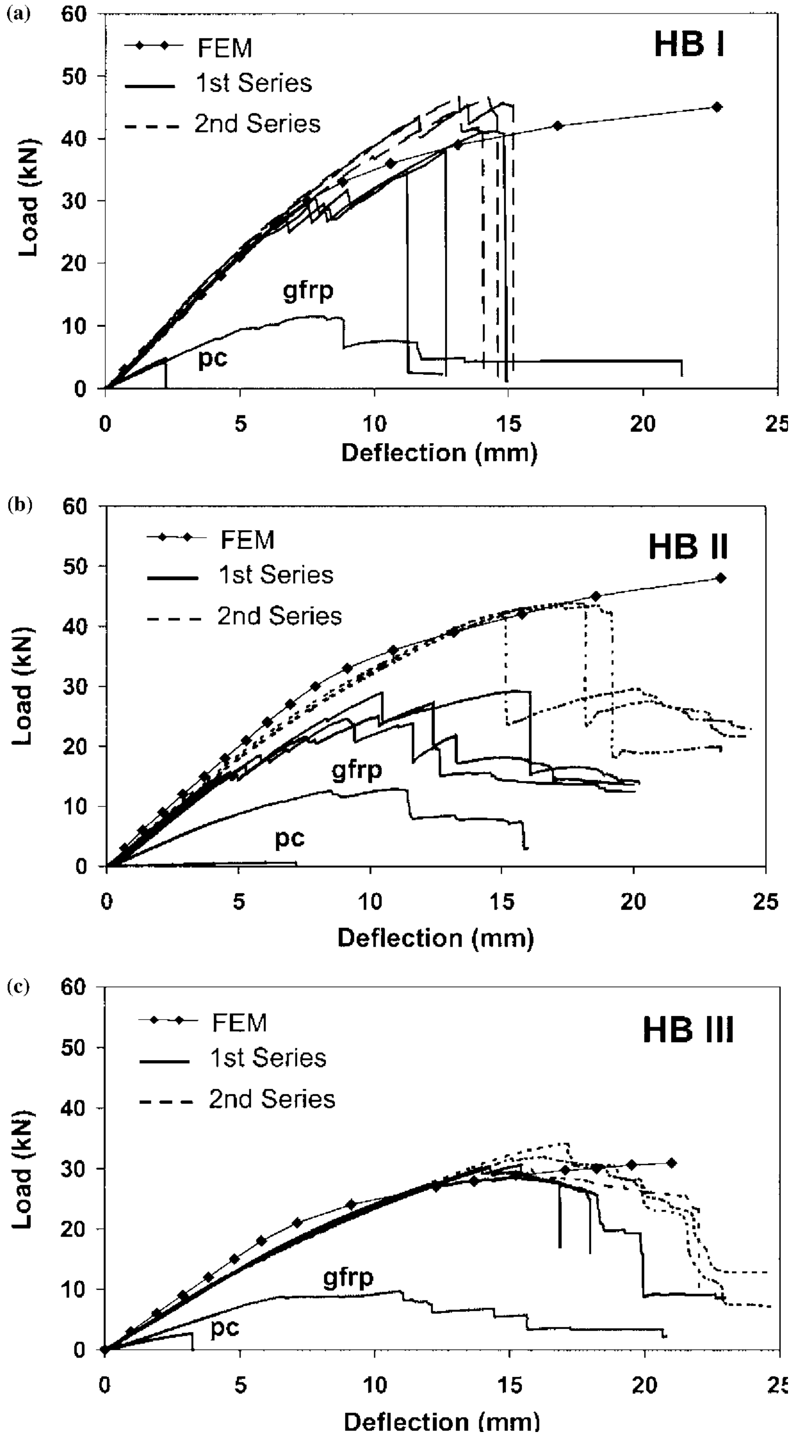

Figure 7. Numerical versus experimental load-deflections curves obtained from 1st and and test series of a) HB I, b) HB II and c) HB III hybrid beams, and correspondent components (GFRP and PC).

5. Conclusions

Hybrid rectangular beams were designed, manufactured and tested. The assembly allows for a critical combination of polymer concrete and composite pultruded materials. A better flexural performance was reached with the improved interface bonding between material components. This innovative design produces highly optimized behaviour with a pronounced synergetic effect. The highest strength to mass ratio and the highest synergetic effect associated to HB II beams, due to a more precise placement of material in stress zones, make this design model very promising for further investigations on large-scale GFRP-polymer concrete hybrid beams.

The numerical model used for flexural behaviour analysis of hybrid systems was implemented in a finite element code. The material and geometrical nonlinearity for reinforced concrete strengthened with FRP composite materials was considered. The material model for concrete was implemented using Ahmad's degenerated shell element with a layered approach to account for a laminated material organization through the shell thickness. The model predictions agree reasonably well with the experimental results.

Acknowledgements

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FLEXURAL BEHAVIOUR OF GFRP-POLYMER CONCRETE HYBRID STRUCTURAL SYSTEMS

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In this paper it is reported the development of a research work undertaken in hybrid structural systems, where GFRP pultruded profiles are assembled, in an innovative way, with a layer of polymer concrete. Several beams, with three different hybrid designs, were tested in four-point bending and the flexural behaviour of such structures was analyzed. Model designs produced a highly optimized flexural behaviour, with a pronounced synergetic effect. A new finite element model for gfrp-polymer concrete hybrid beams was also developed. Due to non-linearity of polymer concrete and the need to account for interaction aspects, a geometric and material nonlinear analysis was performed. A thick shell element was considered, incorporating a layered approach for laminated composite modeling.

INTRODUCTION

FRP-Polymer Concrete Hybrid Systems

In the last years, an innovative structural concept was developed involving the combination of FRP pultruded profiles with conventional cement concrete, to produce lightweight, corrosion-free and yet inexpensive hybrid systems [1, 2]. According to this new concept, a FRP profile beam is combined with a concrete layer, cast onto the top flange, which replaces the thick FRP compressive flange of traditional pultruded profiles. The method maximizes system performance using materials by combination, and can be thought as a better way of producing structural members based on pultrusion process. In the last decade, FRP researchers have developed a number of hybrid systems, either by simply replacing steel with FRP pultruded profiles in conventional steel-concrete composite construction, or by developing new structural systems [3].

Following these studies, this paper presents the development of a research work undertaken with hybrid structures composed by GFRP profiles and polymer concrete. Polymer concrete is a mixture of mineral aggregates and a polymer binder in which the polymeric resin replaces the

Portland cement-water binder of hydraulic concrete. This type of concrete has very high compressive strength, good chemical resistance, and relatively low elasticity modulus [4, 5]. Since the 50's, when it was initially applied to produce synthetic marble, its applications have increased tremendously, mainly in the field of precast components for building industry [6, 7]. Exploiting the better performances of resin concretes, it is believed that the potential of the hybrid systems can be improved:

(a) The higher compressive and flexural strength of polymer concrete allow a cross-section reduction and, therefore, a lightweight beam;
(b) The better chemical resistance enlarge the application field of these structural systems to highly corrosive environments;
(c) The faster curing time, early high strength and good workability of resin concrete make it suitable, either for production of precast components, either for an easier in site application.

In a previous investigation work [8], small-scale models of four different hybrid beams were designed, manufactured and tested in four-point bending test. Flexural behaviour of such composite structures, in terms of load-deflection history, load capacity and failure mode was analyzed and compared with the flexural behaviour of its material constituents. The four hybrid beams models were designed considering a GFRP pultrusion profile that works in tension, and an epoxy polymer concrete filling, that works mainly in compression. Experimental results showed the high potential of these hybrid systems, reveling a pronounced synergetic effect associated to the assembly of polymer concrete and GFRP profiles. However, some technical problems were detected. Interface debonding promoted premature failure, hindering the maximum of load bearing capacity to be reached. Further studies were necessary in order to improve bond strength between polymer concrete and GFRP profiles.

In this paper it is reported some new experiments done on GFRP-polymer concrete hybrid beams, with improved adherence between material components. Three new series of small-scale hybrid beam specimens were manufactured and tested in bending. A special treatment was given to GFRP profile internal surfaces to promote the adhesion to epoxy polymer concrete. A significant improvement on flexural performance of the hybrid beams was reached.

Numerical Modelling

Past studies showed that cracking, deflection and ultimate load behaviour of FRP-reinforced concrete beams could be predicted with the same degree of accuracy as the behaviour of regular steel reinforced concrete beams, and that a theoretical correlation is therefore possible [9]. Theriault and Benmokrane [10] proposed alternative formulas for prediction of deflection. They concluded that usual formulas for such prediction were misleading. Most of these previous studies are related to concrete beams. Very few studies of FRP reinforced plates or shells have been proposed, if any.

The present work reports a numerical model for the analysis of concrete arbitrary shell structures reinforced with composite materials, particularly with FRP pultruded materials. The proposed model is capable of predicting deflections and stresses in concrete and in FRP reinforcement, for geometrical and material non-linear behaviour. The model includes constitutive laws for concrete material, based on smeared crack concepts and is applicable for high-strength composite materials. The model is implemented in a degenerated shell element as proposed by Ahmad et al.[11], Owen and Figueiras [12], and more recently by Ferreira and Barbosa [13]. In order to check the model capacities, the model was applied to predict the flexural behaviour of GFRP-polymer concrete hybrid beams. A good agreement between experimental and numerical results was found. The tests were only performed in beams, but the model is generally applicable to plates or shells of arbitrary shape.

EXPERIMENTAL PROGRAM

Component Materials

Low viscosity epoxy resin, and foundry sand with a very uniform and fine grain (d_{50} of 342 microns) were used for the polymer concrete mixture. Resin content, without charge, was 20% in weight. This formulation corresponds to an optimized result from previous research [5, 14], and its mechanical properties are already known. Compressive strength and compression elasticity modulus are 82 MPa and 11.5 GPa, respectively; with ultimate strain defined to be equal to 0.01. Compression properties were obtained from uniaxial testing according to RILEM TC-113 standards.

Three types of standard U-shaped GFRP pultruded profiles were used. The pultrusion profiles consisted of continuous strand mat and roving of glass fibers, impregnated with unsaturated polyester resin and having an external veil pulled through a die. Volume content of glass fibers was 50% to 55%, and roving occupied the most part of it. The GFRP profiles cross-section dimensions and mechanical properties, obtained from uniaxial tension tests according ISO-527/4 standard, are summarized in Table 1.

Table 1. Dimensions and mechanical properties of GFRP profiles

GFRP	*Tensile Strength (Mpa)*	*Tensile Elasticity Modulus (GPa)*	*Cross Section (mm)*
Profile A	395	25.1	55 * 60 * 5
Profile B	310	25.3	30 * 40 * 4
Profile C	350	25.6	50 * 40 * 5

Hybrid Beams: Design and Manufacturing

Among the four models of hybrid beams initially designed, only three models, - those that showed better flexural performance in first test series-, were chosen for this experimental program. Cross-sections of the three models, hereinafter referred as HB I, HB II and HB III, are illustrated in Figure 1. All the small-scale models were 600 mm length.

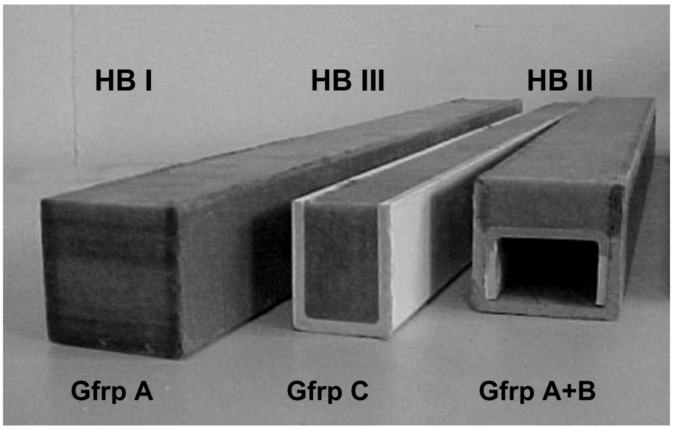

Figure 1. Small scale models of GFRP-polymer concrete hybrid beams analyzed.

HB I and HB III beams have all the section full of concrete, with the profiles behaving, simultaneously, as reinforcement and as permanent formwork. HB II type beam is lighter, with only a thin layer of concrete positioned in the upper part of the profile. Cross-section of concrete layer, in this model, was designed in order to support only compressive stresses in the elastic range. Neutral axis was determined through the homogenization of the hybrid cross-section on GFRP material.

In order to prevent premature failure due to interface debonding, adherence between GFRP profiles and polymer concrete was improved through both mechanical and chemical processes. Internal surfaces of GFRP profiles were previously sandpapered, and a layer of silane adhesion promoter was applied before concrete casting. In addition, in HB II specimens, profile 'B' was bonded to profile 'A' with a special epoxy adhesive. In the first specimen's series, the resin of concrete that drained during casting process assured junction between these two profiles.

For each hybrid model, three specimens were manufactured. All specimens, before being tested, were allowed to cure for seven days at room temperature, and post-cured at 80ºC during 3 hours.

Testing Procedure

Four-point bending tests on three specimens of each type of hybrid beams were performed. The specimens were loaded with 510 mm of span and 100 mm of constant moment zone. Load was gradually increased up to failure at the rate of 1mm/minute (displacement control mode). Test procedures were identical to those applied to perform flexural tests of first series of GFRP-polymer concrete hybrid beams. In order to evaluate the synergetic effect of the assembly, on each constituent material of each type of hybrid beam, four-point bending tests were also performed.

NUMERIC MODEL: ASSUMPTIONS AND IMPLEMENTATION

The model is based on a dual criterion for polymer concrete. Crushing and cracking of concrete is considered by modification of the material stiffness and strength. Also composite materials are modeled with a layered approach. Each material layer is considered to be orthotropic. Elasto-plasticity of the material can be used, if necessary.

The approach used for these hybrid beams relies on a homogenization procedure of the distinct zones of their cross-sections, both for stiffness and strength. In Figure 2, these zones are identified.

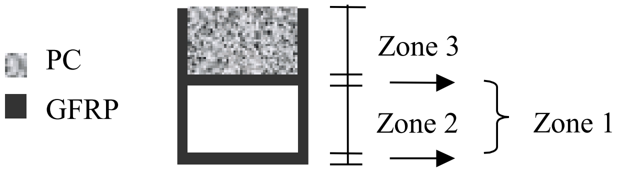

Figure 2. Layered system used for finite element approach.

In zone 1, the equivalent material is considered to be a composite laminate only. Therefore, a typical FRP material formulation is considered[13, 15].

In zone 2, FRP walls are taken in account. Due to the shell formulation, an equivalent material in stiffness and strength is considered.

In zone 3, a combination of FRP and polymer concrete occurs. In this case, it is assumed that no contribution is given by FRP walls to support compressive solicitations. Therefore, compressive strength of the assembly layer is the compressive strength of the concrete, while tensile strength and elasticity modulus follows a law of mixtures:

$$\Lambda^{eq} = (\Lambda^{PC}.\, \lambda^{PC} + \Lambda^{FRP}.\, \lambda^{FRP}) \,/\, \lambda^{TOT} \qquad (1)$$

where Λ^{PC}, Λ^{FRP} = stength or stiffness, of polymer concrete and FRP material, respectively; Λ^{eq} = equivalent strength or stiffness of the layer; λ^{PC},λ^{FRP} = thickness of polymer concrete and FRP material in the layer, respectively; λ^{TOT} = total thickness of the layer.

EXPERIMENTAL VERSUS NUMERICAL RESULTS

For each type of beam, the average of maximum load capacity and the related synergetic effects are summarized in Table 2. Synergetic effect was calculated by dividing the capacity load of the assembly by the sum of capacity load of each of its two elements. In order to evaluate the improvement of flexural strength reached through profiles surface treatment, experimental results obtained in first specimen's series are also presented.

Table 2. Summarized flexural tests results

Hybrid Beam Type	*Max. Capacity Load (kN)*		*Synergetic Effect (%)*	
	1st Series	*2nd Series*	*1st Series*	*2nd Series*
HB I	38.07	46.30	233	284
HB II	26.96	43.09	203	319
HB III	32.06	32.96	258	266

Load deflection curves, obtained from both 1st and 2nd test series of composite beams and correspondent components, are illustrated in Figure 3. Numerical results obtained by finite element modeling are also plotted.

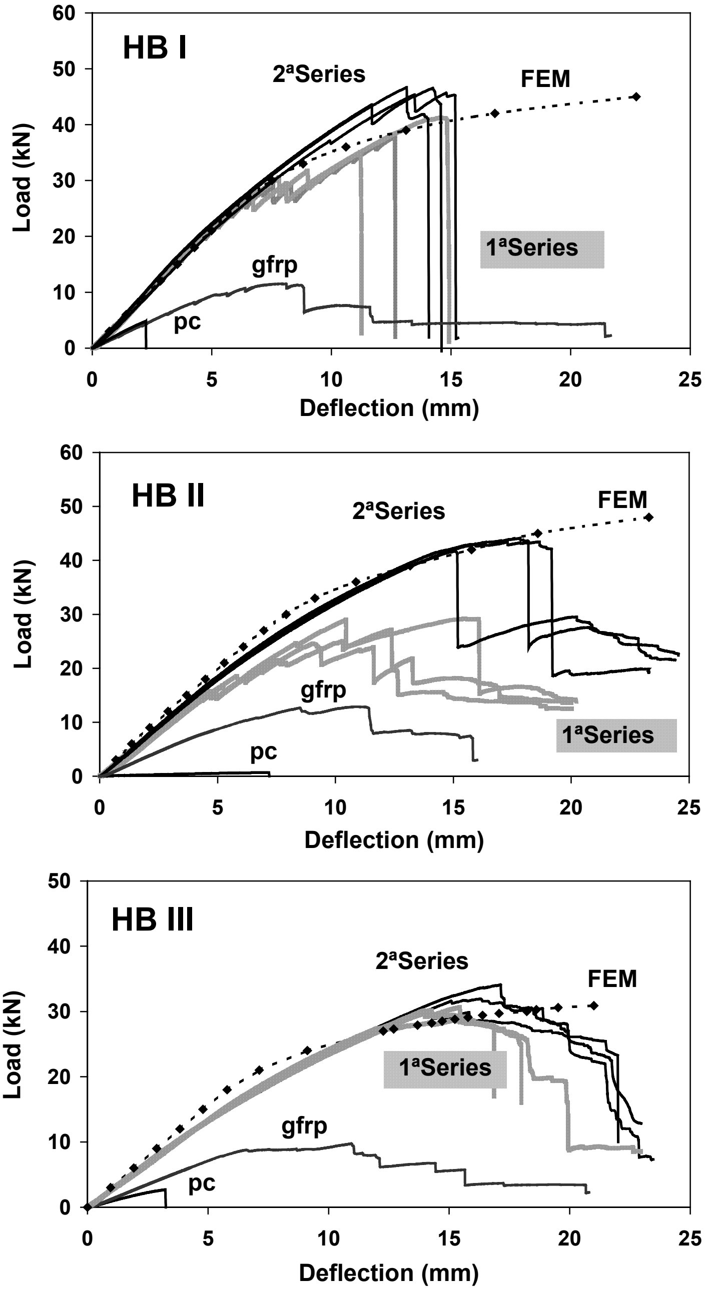

Figure 3. Numerical versus experimental load-deflections curves obtained from 1st and 2nd test series of hybrid beams, and correspondent components (GFRP and PC).

Except for HBIII type beams, a significant increase of load bearing capacity occurred for the 2nd series of hybrid beams tested. Failure modes were also distinct. HBI and HBII type beams, which failed prematurely at the first series due to interface debonding, collapsed in the second series due to GFRP webs shear fracture, as it is shown in Figure 4. For HB I type beams, an explosive rupture of concrete occurred, resulting of shear crack propagation and consequent gradual loss of cohesion between components. Collapse of HB II beams was less brittle due to slower crack propagation, thus giving some warning of eminent collapse.

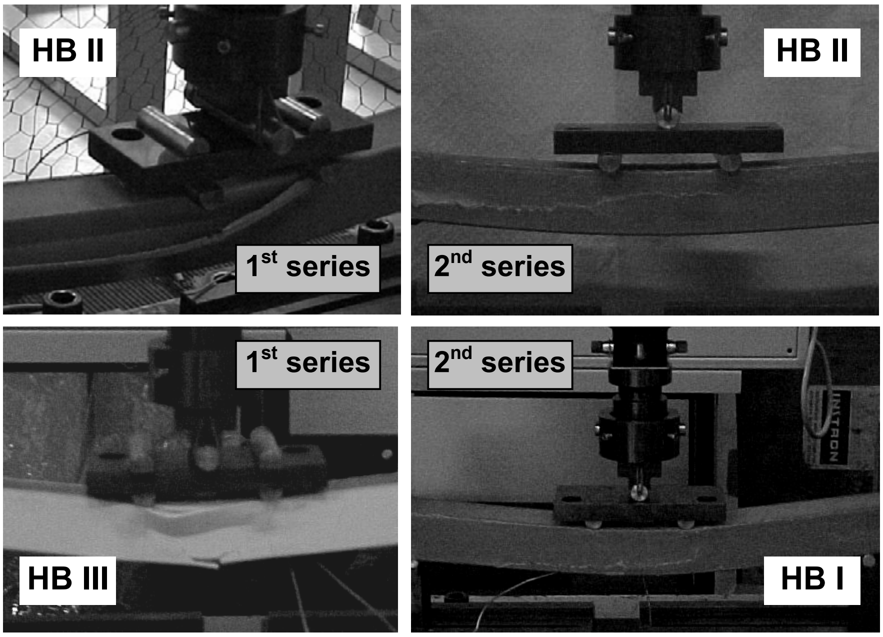

Figure 4. Typical failure modes of GFRP-polymer concrete hybrid beams: 1st and 2nd test series.

Type III beams, in the same way that occurred for the first series, failed due to tensile failure of lower surface of GFRP profile, followed by rupture of concrete. Cross-section of profile C is slightly narrower at the top, which made the slip of concrete more difficult. This fact explains why the improvement of bond, between concrete and GFRP profile on 2nd specimen series, had no significant effect on its flexural performance.

Numerical results agree quite well with experimental results, according to the modeling hypothesis. At this stage, the model can already predict with reasonable accuracy the load-displacement curves. Although predicted initial stiffness and failure loads are reasonably modeled, the model has still to be improved to account for web shear failure and other failure mechanisms.

CONCLUSIONS

Hybrid rectangular beams were designed, manufactured and tested. The assembly allows for a critical combination of polymer concrete and composite pultruded materials. A better flexural performance was reached with the improved interface bonding between material components. This innovative design produces highly optimized behaviour with a pronounced synergetic effect. The highest strength to weight ratio and the highest synergetic effect associated to HB II beams, due to a more precise placement of material in stress zones, make this design model very promising for further investigations on large scale GFRP-polymer concrete hybrid beams.

The numerical model used for flexural behaviour analysis of hybrid systems was implemented in a finite element code. The model predicts with very reasonable accuracy the load-displacement curves for all tested type beams. This model is still in progress. The results so far allow for a very interesting expectation in terms of a finite element code for the analysis of this kind of hybrid systems.

ACKNOWLEDGMENTS

The support of Fundação para a Ciência e Tecnologia under POCTI/EME/42820/2001, ‘Desenvolvimento de estruturas híbridas betão polimérico/compósitos’ is gratefully acknowledged.

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DEVELOPMENT OF COMPOSITE HYBRID STRUCTURES BASED ON POLYMER CONCRETE – GFRP PULTRUSION PROFILES ASSEMBLY SYSTEM

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ABSTRACT: In this paper, the development of a research work undertaken in hybrid structural systems, where GFRP pultruded profiles are assembled with a layer of polymer concrete (PC), is reported. PC is a material where a thermoset resin binds together natural or artificial aggregates. The main advantages of polymer or resin concrete over ordinary Portland cement concrete are higher mechanical strength, lower permeability and improved chemical resistance. The combination of PC with GFRP composite materials can profit from the best characteristics of each class of materials. Small-scale beams, with two different hybrid designs (reinforced and un-reinforced for shear), were tested on four-point bending and the flexural behaviour of such structures was analysed. Model designs were made considering an h-shape pultrusion profile that will work mainly in tension, and a u-channel profile, filled with a high strength epoxy PC, that will work in compression. Experimental results showed the high potential of this new concept, which leads to a pronounced synergistic effect due to an optimal combination of materials.

1. INTRODUCTION

One of the most effective uses of FRP is in the form of composite or hybrid construction with concrete, in which the FRP is the load-carrying partner and protective measure for concrete. The main advantage of such system lies in the optimal use of materials based on their mechanical properties and resistance to corrosive environments [1]. In the last decade, FRP researchers have developed a number of hybrid systems, either by replacing steel with FRP profiles in conventional steel-concrete composite construction, or by developing new structural systems [1-4]. Following these studies, this paper presents the development of hybrid structures composed by GFRP profiles and epoxy PC.

PC is a mixture of mineral aggregates and a polymer binder, in which the resin replaces the Portland cement-water binder of hydraulic concrete. PC has very high compressive strength, good chemical resistance and relatively low elasticity modulus [5,6]. Since the 50's, when it was initially applied to produce synthetic marble, its applications have increased tremendously, mainly in the field of precast components for building industry [7]. Exploiting the better performances of resin concretes, it is believed that the potential of the hybrid systems can be improved:

- The higher compressive and flexural strength of PC allow a cross-section reduction and, therefore, a lightweight structure;
- The better chemical resistance extends the application field of these structural systems to highly corrosive environments;
- The problem of alkalis attack of glass fibres by the concrete is avoided;
- The shorter curing time, early high strength and good workability of resin concrete make it suitable, either for precast components or for an easier in site application.

Small-scale models, with two different model designs, were manufactured and tested in bending. Model designs considered an h-shape pultrusion profile working mainly in tension, and a u-channel profile bolted onto the top flange of h-profile, filled with a high strength epoxy PC, which works in compression. The u-channel profile acts as a permanent shuttering, allowing a fast moulding. A special treatment was given to the internal surfaces of this component to promote the adhesion to epoxy PC. On one of the models, the web of h-profile was thickened strengthened on both sides with FRP laminates in order to improve shear behaviour. Flexural performance of this new kind of hybrid structures was analysed and discussed.

2. INTRODUCTION

2.1 Component Materials and Characterization

PC Mixture: Low viscosity epoxy resin (Eposil 551) and siliceous sand, with a very uniform and fine grain (d_{50} of 240 μm), were used for the PC mixture. Unfilled resin content was 20% in weight. This formulation corresponds to an optimised result from previous research [8,9], and its mechanical properties are already known. Compressive strength and compressive elasticity modulus are 82 MPa and 11.5 GPa, respectively, with ultimate strain defined to be equal to 0.01.

GFRP Pultrusion Profiles: Two types of standard GFRP pultruded profiles were used: an h-profile (150 x 75 x 8 mm) and a u-channel (150 x 40 x 6 mm). Design parameters were restricted here, as material properties and dimensions of GFRP profiles were predefined through the manufacturers availability list. The GFRP profiles consisted of continuous strand mat and roving of E-glass fibres, impregnated with unsaturated polyester resin. Volume content of glass fibres, determined by the resin burn-off method, was 68% and 51% for the h-profile and the u-channel, respectively. General mechanical properties of GFRP profiles, supplied by the manufacturer, are summarized in Table 1.

Table 1̃ Mechanical properties of GFRP profiles.

GFRP Properties	Lengthwise (MPa)	Crosswise(MPa)
Tensile Strength	250	60
Comp. Strength	240	70
In-Plane Shear Strength	25	
Interlaminar Shear Strength	75	25
Tensile Modulus	23000	8000
Comp. Modulus	10000	4000
Shear Modulus	3000	3000

In order to check some mechanical properties given by the supplier, tensile tests were performed on coupons of h-profile according ISO:527-4 norm [10]. An average tensile strength of 380 MPa was obtained, with an ultimate strain of 1.18%. Additionally, both flexural and shear stiffness of h-profile beam were determined by performing three-point bending tests for a number of different spans, in accordance with the European Standard EN 13706-2 [11]. Plotting the three-point bending test results, the effective section longitudinal elastic (E_L) and shear modulus (G_{LT}) can be computed. The following values were found: $E_L = 25.0$ GPa and $G_{LT} = 3.2$ GPa.

FRP Laminates: A balanced E-glass woven roving, with fibre orientation at ± 45º and a coarse texture of 300g/m^2, jointly with an isophtalic polyester resin matrix, were used to produce the FRP laminates. Hand lay-up and vacuum bag techniques were applied in the manufacturer process. Mechanical properties of FRP laminate, shown in Table 2, were deduced from linear equations given by the EuroComp Design Code [12]. In the absence of experimental data, these equations are usually applied to estimate stiffness and strength properties of typical E-glass WR/polyester hand lay-up systems. In order to determine accurate values for shear strength and shear modulus, posterior in-plane shear tests were performed on coupons of FRP laminate according ASTM D3518M [13].

Table 2̃ Mechanical properties of FRP laminates

Properties	Estimated values (MPa)	Experimental values (MPa)
Tensile Strength	54.6 – 111.6	-
In-plane Shear Strength	42.8	40.5
Tensile Modulus	6200 - 10200	-
Shear Modulus	3600	1900

2.2 Hybrid Beams Manufacturing

The two 1.5 m length beams (HB1 and HB2) were manufacture by stages: a) Preparation of GFRP profile surfaces; b) Application of FRP plate reinforcements on web of h-profile; c) Assembly of u-channel profiles with h-section beams; d) Casting of PC into u-channels and curing. Details of all these steps are detailed in the next paragraphs.

a) Internal surfaces of u-channel profiles were previously brushed and sandpapered in order to remove the resin surface veil, and hence, to promote adhesion to PC. In addition, a layer of silane adhesion promoter (2% Silane A174 aqueous solution) was applied before concrete casting. Web surfaces of h-profile corresponding to shear reinforced beam also received the same treatment.

b) FRP laminates for web shear reinforcement were directed moulded onto the web surfaces of h-profile using hand lay-up and vacuum bag moulding techniques. Only one of the beams was reinforced, herein designated by HB2. Both shear spans on both sides of the web were reinforced, one side at a time. The positioning and dimensions of FRP laminates are shown in Fig. 1. A rubber dam-like sealing line was initially applied around the area where the laminates were to be applied, to form a seal for the vacuum bagging process (Fig. 2a). A layer of unsaturated polyester resin was then applied with a brush, after which the first layers of woven roving were laid down, one on each shear span (Fig. 2b). The woven roving was impregnated with further resin and then rolled with a ‘split washer’ roller to consolidate the laminate and remove entrapped air (Fig. 2c and 2d). The second layers of fibre reinforcement were applied and the above steps were repeated. A porous release fabric and a bleeder/breather layer were finally applied to the lay-up, to allow the air and the excess of resin to be drawn from the laminate when the vacuum (0.2 bar) is applied. A vacuum bag material was then placed over the laminate, sealed down, and the vacuum was applied during 30 minutes (Fig. 2e). The laminate was cured at room temperature during 48 hours and then post cured at 80ºC, after concrete casting, during 5 hours. Laminates with a final thickness of 1mm were obtained.

c) The fastener connection between u-channels and h-profiles was attained through bolted mechanical joints. A methacrylate adhesive was initially applied in the joint surfaces to seal the assembled parts. Two rows of 8 mm diameters bolts, at a uniform spacing of 85 mm throughout the span, were applied. The height of the bolts inside PC was 20 mm. At loading points, spacing between bolts was reduced and, furthermore, four 3 mm thick wood stiffeners were mounted on both sides of the web. Dimensions and cross-section of hybrid beams are also illustrated in Fig. 1.

d) After the assembly of the pultruded beams, mixing and casting process PC took place. Epoxy resin was initially mixed with the hardener, poured into an automatic mixer together with the sand aggregates, which had been previously dried, and the paste was thoroughly mixed until the aggregates were fully ‘wetted’. PC was then directly cast into the u-channel profiles. Additionally, six control prismatic specimens (40 x 40 x 160 mm) were also cast. Hybrid beams and control specimens were allowed to cure at room temperature during 24 hours, before being submitted to thermal treatment in an autoclave (5 hours at 80ºC). Final weight of the hybrid beams per unit length was 152.2 N/m and 153.7 N/m, respectively for the HB1 and HB2 test specimens.

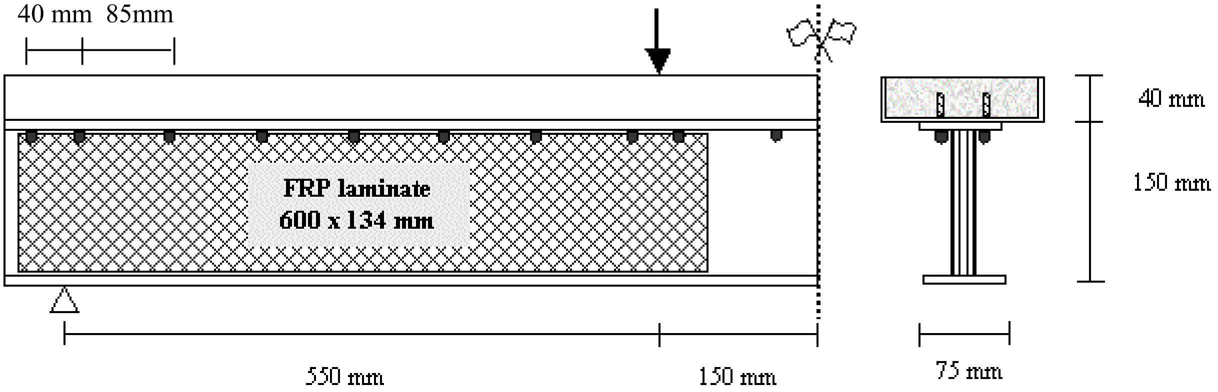

Figure 1 – Dimensions and cross-section of hybrid beams (not at scale). Positioning of FRP laminates (HB2).

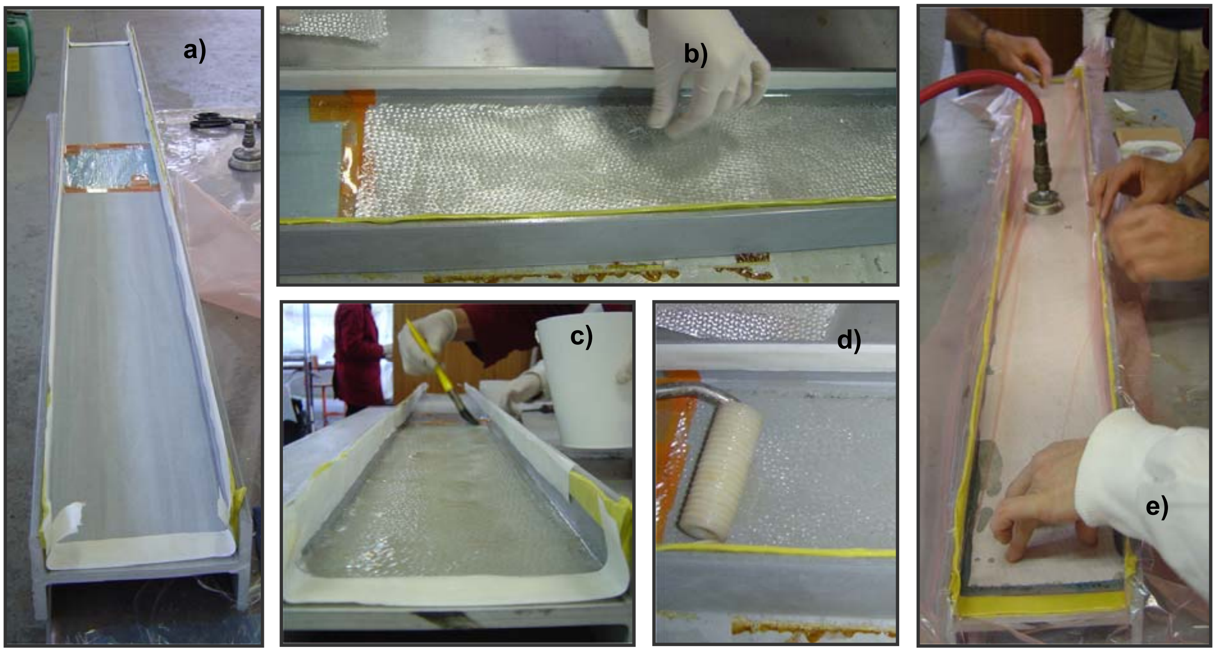

Figure 2 – Main steps of manufacturing process of FRP laminates for shear reinforcement.

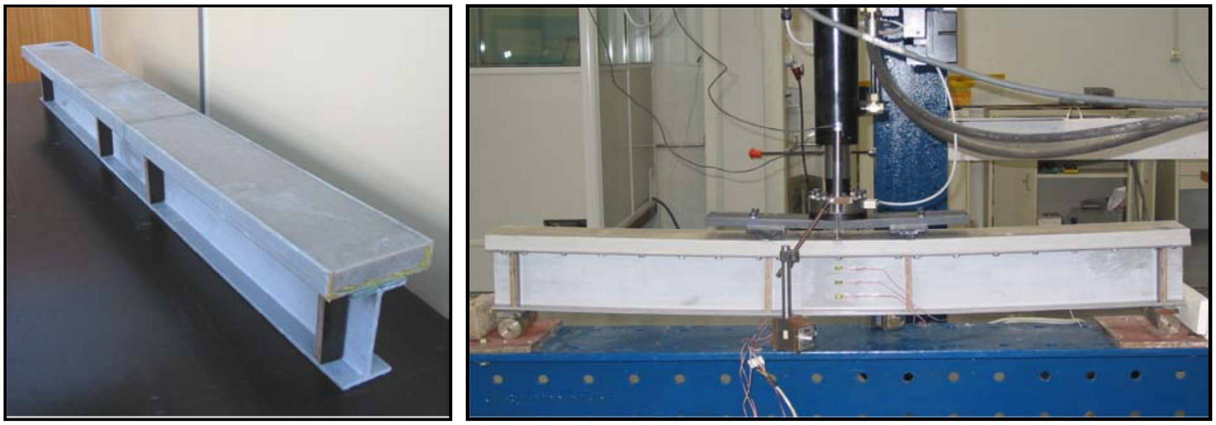

Figure 3 – aspect of HB2 composite beam after curing of PC. Test set-up used for bending tests.

2.3 Bending Tests Procedure

Beam specimens were tested in four-point bending over a 1.40 m simply supported span, with a constant moment length of 0.30 m. At mid-span section, test beams were instrumented with electrical strain gauges mounted on the top concrete surface and on the bottom flange of h-profile. Additionally, three extra strain gauges were also mounted on both sides of the web. Deflection was measured by two LVDTs placed at both sides of mid-span section, so that the complete load-displacement curve could be recorded. Load was applied under a constant stroke rate of 3 mm/min by means of a hydraulic actuator with a load cell of 200 kN. Load, LVDT and strain data were recorded at a rate of one sample per second, until specimen failure. A continuous data acquisition system with 16 channels was used. Fig. 3 shows the test set-up, as well HB2 beam specimen before being tested.

3. TEST RESULTS AND ANALYSIS

3.1 Experimental Results

Load-deflection curves corresponding to both specimens are plotted in Fig. 4. Respective failure modes are also illustrated in this figure. Load-strain relationships and longitudinal strain profiles, for various load levels, are displayed in Fig. 5. From the presented results, as well as the observed behaviour of the test specimens, the following remarks could be concluded.

HB1 specimen collapsed due to web shear failure. Shear crack started at one of the shear spans, approximately at 80-85 mm from the beam bottom, and rapidly spread to the mid-span. HB2 beam specimen failed, at a higher load, due to delamination at the interface between the web and top flange of h-profile. Flange/web junctions are critical points, as they constitute the most likely zones to be richer in resin and poorer in fibres. This well-known phenomenon, already noticed by other researchers [14], was probably the main reason for failure location.

No loss of bond was observed on either specimens, nor between concrete and the u-channel, or between this last one and the h-profile. Shear connectors and treatment of bond surfaces revealed to be efficient, allowing the composite action between components to be kept until failure.

In both composite beams, applied load increased linearly with deflection almost until failure. For HB1 specimen, a perfect elastic behaviour is observed till a load level of 40 kN, while for HB2 specimen, the linear behaviour remains longer, till the load level of 70 kN. After these points, the load-deflection curves diverge slightly from the initial straight lines, but remained not far away. The observed behaviour is also confirmed by recorded load-strain relationships.

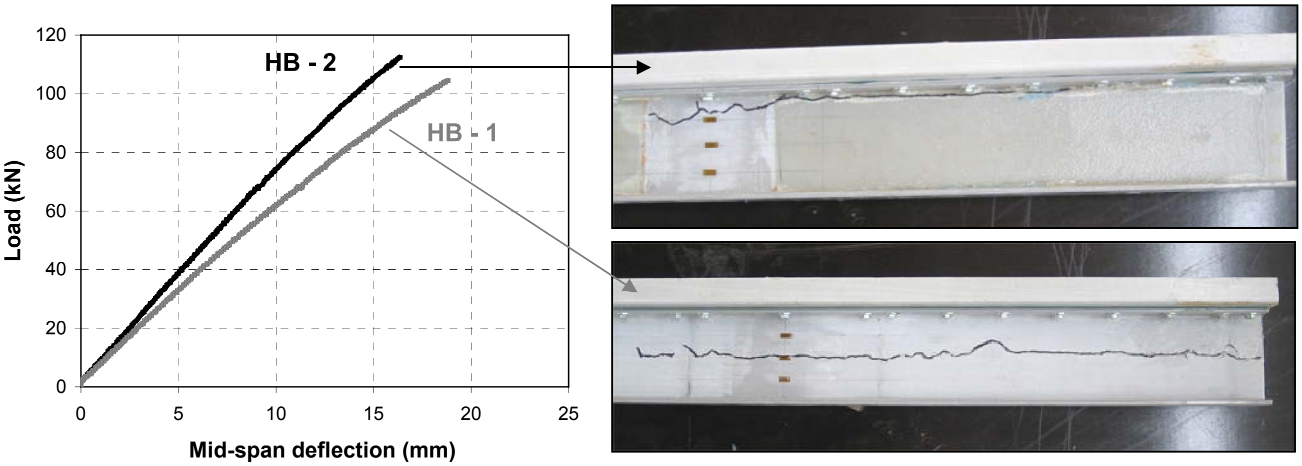

Figure 4 – Load-deflection curves corresponding to both test specimens and respective failure modes.

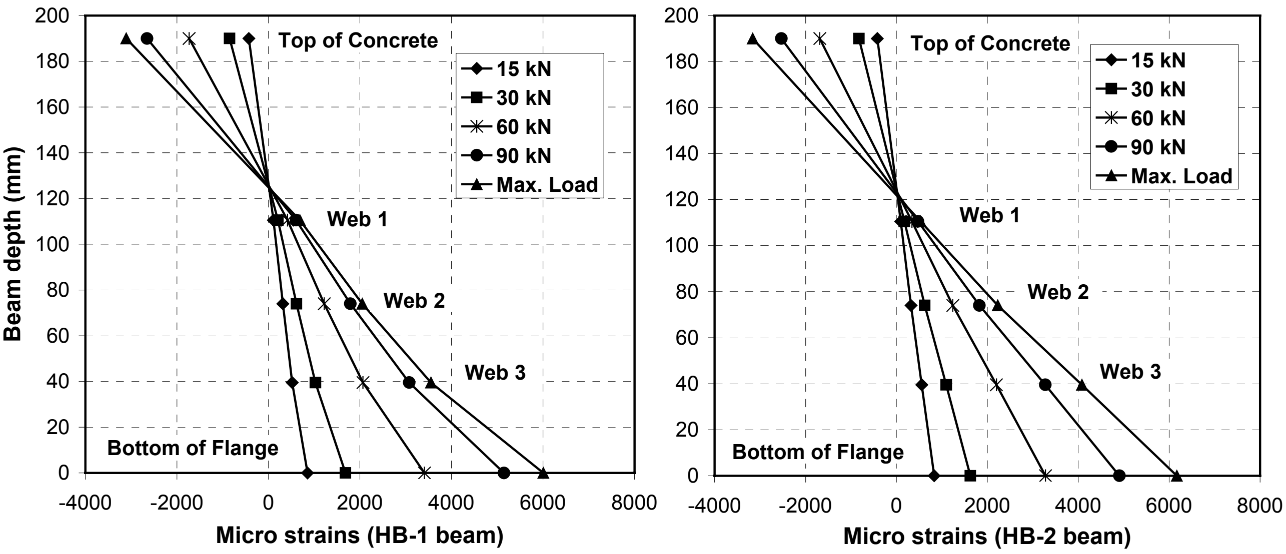

Figure 5 – Load-strain relationships and longitudinal strain profiles at mid-span section.

At all loading stages, the web shear reinforced beam, HB2, is stiffer than the un-reinforced one, HB1. This is due to the composite action between the FRP laminates and the h-profile, which improved the strength and the stiffness of the beam. This is also confirmed by load-strain curves. This reduction in strain, corresponding to a higher load capacity, arises from the already mentioned composite action. In both specimens, the neutral axis remains practically at the same location (at the web of h-profile near the upper flange), until failure took place.

3.2 Analytical Analysis

The hybrid section loaded in bending can fail in a number of possible ways. However, the theoretical analysis herein presented only considers two failure modes: flexural failure and web shear failure. In the analytical analysis the following assumptions were considered:

- Navier-Bernouilli hypothesis is assumed;
- Material behaviour of both FRPs (pultrusion profiles and laminates) is assumed to be linear elastic up to failure, while for PC, the non-linearity is considered for compressive strains beyond 5‰;
- Flexural failure prediction is defined by the maximum strain criterion (10‰ for both PC and GFRP)
- Shear connectors provide both a complete shear interaction and a full shear connection.
- A perfect bond is assumed between FRP laminate and the web of h-profile.

Flexural Failure Analysis: Hybrid beam sections were homogenised with respect to the stiffness of GFRP profile E_{gfrp}.(25 GPa) This methodology allowed a simplified calculation of the neutral axis position and the value of second moment of area. The ultimate flexural capacity was dependent on the two possible failure modes: PC crushing due to compression or tensile fracture of GFRP profile flange. However, attending to both estimated position of neutral axis and strain compatibility equations, failure due to PC crushing was eliminated. Hence, flexural capacity was calculated assuming GFRP tensile fracture. A triangular stress block was assumed under the constraint that PC was still working in the elastic zone. Contribution of u-channel's walls was ignored in the theoretical analysis. The effective depth of neutral axis was then established from internal force equilibrium and strain compatibility equations, using an iterative process. Finally, ultimate flexural capacity was given by the moment equilibrium equation. FRP laminate properties were taken into account on the theoretical analysis of HB2 beam, through its homogenisation on GFRP material and considering the web of h-profile with an equivalent thickness. Obtained results are presented in Table 4.

Web Shear Failure Analysis: As the neutral axis lies within the web, maximum shear stress occurs at the neutral axis level. Maximum shear stress in the web may be taken, approximately, to be equal to 1.5 times the average shear stress. Shear fracture occurs when the maximum shear stress equals the shear strength of the webs. EuroComp Design Code recommends that the in-plane shear strength should be considered to characterize web shear strength of pultrusion profiles. However, resin burn-off process showed that continuous strand mat layers in the web of h-profile were insignificant when compared to roving. Moreover, E-glass roving arrangement in the web could be considered as preferentially positioned by longitudinal layers perpendicular to the load plan. Under this point of view, it seems to be more reasonable to consider the interlaminar shear strength of h-profile as the effective shear resistance of the web, instead of the in-plane shear strength. Attending to the above, during the analytical analysis, the interlaminar shear strength of h-profile was considered to estimate the shear load capacity. Obtained results are also shown in Table 4. Web shear strength of reinforced beam (τ_{comp}) was determined considering a simple weighed average of shear strengths for both materials involved (FRP laminate and web of h-profile) by the respective thickness (t_i), as showed by the following equation:

$$\tau_{comp} = \frac{\tau_{lam}\, t_{lam} + \tau_{web}\, t_{web}}{t_{lam} + t_{web}} \qquad (1)$$

where τ_{lam} is the experimentally determined in-plane shear strength of FRP laminate; τ_{web} is the web shear strength of h-profile; and t_{lam}, t_{web} are the respective thickness.

Table 4. Analytical results versus experimental results.

Beam Type	Neutral Axis Depth^a (mm)		Ultimate Moment (kN.m)			Failure mode	
	Anal.	Exp.	Anal. Fl^b	Anal. Sh ^{c}	Exp.	Pred.	Exp.
HB 1	124.9	125.2	38.50	27.51	28.32	Web shear failure	Web shear failure
HB 2	124.5	124.0	39.05	31.49	31.08	Web shear failure	Web/flange junction shear failure

a) Measured from beam bottom; b) Bottom flange tensile failure; c) Web shear failure

Theoretical versus Experimental Results: Being aware of the lack of knowledge on result's reproducibility, due to the reduced number of tested specimens, as well as the difficulty in controlling GFRP properties, the analysis of obtained results will be generic.

A very good agreement was found between analytical and experimental values. The analytical method seems to be efficient in predicting failure mode and ultimate capacity load of hybrid composite beams. The use of interlaminar shear strength as the effective shear resistance of the web revealed to be wise. If the in-plane shear strength had been used, the shear load capacity of web's composite beams would have been underestimated. Ultimate moments of 9.82 and 13.80 kN.m would be obtained, respectively, for the HB1 and HB2 beams. It is believed that shear failure of reinforced beam was due to a weak point in the web/flange interface, and therefore, providing an h-profile with homogenized distribution of fibers, a higher ultimate load should be expected. A larger anchorage of FRP laminates in width could be a solution to prevent this kind of failure.

4. CONCLUSIONS

GFRP-PC hybrid beams, with two different model designs, reinforced and un-reinforced for shear, were manufactured and tested in four-point bending. Flexural behaviour of such structures was analysed and discussed. Based on experimental results, the following conclusions are put forth:

- GFRP-PC hybrid beams have a high potential as structural members, presenting an excellent load bearing capacity to self-weight ratio. Brittle failure and relative low stiffness are negative points associated.
- Web shear reinforcement with FRP laminates provides a significant extra stiffness. This parameter and load capacity can still be improved using a thicker laminate.
- Shear connectors and treatment of bond surfaces are an efficient method to ensure a full composite action between components.
- Web shear resistance of pultrusion profiles cannot be systematically assessed by the in-plane shear strength. Layer arrangement within the web must be firstly evaluated.
- The used analytical method can be applied with success to predict load capacity of this new type of hybrid beams.

It is realized, that the present work forms a promising feasibility study but has not considered a number of important issues that should be addressed before the hybrid systems can have engineering applications. Significant future work will be needed to develop GFRP-PC hybrid beams that are efficient, cost-effective and reliable structural members.

5. ACKNOWLEDGEMENTS

The support of 'Fundação e Ciência e Tecnologia' under POCTI/EME/42820/2001 is gratefully acknowledged.

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APPENDIX B

PC Modified with Natural Lightweight Aggregates

i) ‘*Mechanical characterization of lightweight wood-modified polymer concrete’*, Ciência & Tecnologia dos Materiais, Vol. 16, n.º 2-3, 2004, 81-87........ B-3

ii) *Mechanical characterization of lightweight polymer mortar modified with cork granules’*, Composites Science and Technology, Vol. 64, Issues 13-14 (2004), 2197-2205 .... B-11

MECHANICAL CHARACTERISATION OF LIGHTWEIGHT WOOD-MODIFIED POLYMER CONCRETE

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Resumo: O betão polimérico é um material onde um polímero é utilizado como ligante de agregados naturais ou sintéticos. Este material alia uma elevada resistência à compressão a uma forte resistência à corrosão. Contudo, o seu comportamento mecânico é globalmente frágil. No presente trabalho, aparas de madeira são introduzidas na formulação com o intuito de promover a ductilidade e simultaneamente diminuir o peso do material, tirando partido das suas baixas rigidez e densidade, respectivamente. A madeira também exibe elevada compressibilidade o que potencia uma eventual melhoria das propriedades de absorção de energia do betão. Foram realizados ensaios de flexão e de compressão com registo das curvas de carregamento carga vs. deslocamento até à rotura. Foram investigadas a influência no comportamento mecânico da fracção mássica de agregado orgânico e do tipo de resina polimérica utilisadas. Os resultados obtidos permitem algumas conclusões interessantes no que respeita ao desenvolvimento de betões poliméricos mais leves modificados com agregados de origem vegetal, exibindo um comportamento menos frágil.

Palavras chave: betão polimérico, resina de poliéster insaturado, resina de poli-epóxido, agregados orgânicos leves, madeira, propriedades em flexão, resistência à compressão.

Abstract: Polymer concrete is a material where a polymer binds together natural or artificial aggregates. This material combines high compressive strength with very high corrosion resistance. However its general mechanical behaviour is brittle. In this work, wood shavings are added to the formulation in order to improve the ductility and reduce weight, taking advantage of its low stiffness and low density, respectively. In addition, wood is an organic material that also exhibits large compressive strains, which may lead to a more energy absorbing concrete material. Flexural and compressive tests were performed and load vs. displacement curves were plotted up to failure. Both the influence of organic aggregate weight fraction and organic aggregate type were considered in the mechanical behaviour. The results anticipate a very interesting expectation in terms of lighter modified polymer concretes with a less brittle behaviour.

Keywords: polymer concrete, unsaturated polyester resin, epoxy resin, lightweight organic aggregates, wood, flexural behaviour, compressive strength.

1. Introduction

The research on polymer concrete (PC) has been steadily increasing over the past years driven by its ability to serve many applications in civil construction [1-4].

In this class of materials, a polymer is used as binder of natural or artificial aggregates in place of the traditional Portland cement found in conventional hydraulic concretes. By far the most used polymers have been thermoset resins based on unsaturated polyester and epoxy prepolymers but other thermoset polymers (e.g., vinyl esters and polyurethanes) have also been tested as binder alternatives.

The first applications of PC in the late 50's were the production of building cladding and cultured marble, but its excellent properties lead to its widespread use in other fields. The fast cure characteristics, excellent bonding to concrete and steel reinforcement, high strength, and durability made it a very attractive choice as a repair material. Overlays in PC, for bridge surfaces and industrial floors, have also become widely used due to the ability to use thin layers combined with low curing time, very low permeability, and high resistance to chemical and frost attacks. Precast components are another excellent use of the material. The high strength to weight ratio, good damping properties, moldability and ability to form complex shapes make PC particularly suitable for these applications [1].

The main limitation of concrete-polymer materials lies in their cost. Even considering that the density of cement is about 2 ½ times that of most polymers, the cost per unit volume of polymer concretes is still higher than Portland cement concrete. The higher cost of polymer concrete makes its use almost prohibitive for high volume applications, except in specialty ones where durability is paramount and renders cement concrete unusable. One way to minimize this limitation is the development of a lighter polymer concrete. In addition to lower dead load, insulating properties are also improved.

The two traditional ways for the development of a lightweight concrete material involve the use of: (i) an alternative binder to cement and (ii) lightweight aggregates. In the case of PC, we are already in presence of an alternative binder with weight savings with respect to cement. So, in order to further weight reduction we are essentially limited to the second option: the use of lighter aggregates.

The general class of lightweight aggregates encloses a wide range of products. From natural products, either organic (*e.g.*, wood, cork or rice husk) or mineral (*e.g.*, products from volcanic source), to artificial products specially manufactured for the effect (*e.g.,* expanded clay, shale or slate), as well as industrial sub-products and wastes (*e.g.,* fly ashes, expanded slag and civil construction debris), a large spectrum of lightweight aggregates has been produced and/or applied in the last years for construction purposes.

The use of lightweight aggregates in building construction is not a recent practice as shown by the Basilica of Saint Sophie in Constantinople, made with diatomite. Artificial lightweight aggregates have been produced since the beginning of the 20th century in the U.S, and from the 60's onward examples of concrete structures made with light aggregates have multiplied throughout the world [5]. But it was only in the 70's that a significant research effort in lightweight aggregate concrete was achieved [6-8]. Since then, several investigations on Portland cement concrete and mortars with lightweight aggregates have been reported and there are worldwide environmental, economic and technical impetuses to encourage the structural use of these materials [9-13].

In this study, an effort is undertaken to develop a new type of polymer concrete material, being both lighter and with improved ductility. Previous work on polymer concretes, where polyester and epoxy concrete behaviour was measured under various chemical and mechanical conditions [14-16], was the basis for this research. The strategy in the present work consisted in keeping the binder-to-sand weight ratio and adding increasing amounts of wood shavings resulting in a series of formulations with changing aggregate composition, characterized by the organic aggregate-to-sand weight ratio. Considering the low density and low stiffness of wood [17,18], its introduction in the concrete formulation was expected to reduce the material weight and brittleness, respectively. The light organic aggregate also exhibits large compressive strains, which may lead to a more energy-absorbing material. The low thermal conductivity and high sound absorbing properties of wood may also introduce these features in the modified polymer concrete. These features are expected to be the subject of a future work.

The main challenge consists in developing a material with the above benefits while minimizing strength and cost changes. The wood shavings used in this work are a by-product in the wood industry. They are produced from scrap of cutting and trimming operations, and are subsequently used in the production of agglomerated products, hence its cost is considerably lower compared with that of virgin wood.

The mechanical performance of polymer concrete modified with wood was evaluated by flexural and compressive tests performed at room temperature. The influences of both organic aggregate weight fraction and resin type were considered in the analysis of results.

2. Experimental Program

Polymer concrete formulations were prepared by mixing an epoxy or polyester resin with foundry sand, which had been previously mixed with the wood shavings.

The polyester resin used in this investigation, designated by S226E (NESTE®), is a low viscosity mixture of an orthophtalic unsaturated polyester prepolymer and styrene (44% by weight), which acts both as solvent and reactive monomer. The resin system is pre-accelerated by the manufacturer with a cobalt (II) salt and the catalyst used consisted of a methyl ethyl ketone peroxide solution (2 phr).

The chosen epoxy resin, EPOSIL 551 (SILICEM®), is based on a diglycidil ether of bisphenol A and an aliphatic amine hardener. This resin system is processed with a weight mix ratio to the hardener of 2:1.

The foundry sand is of siliceous nature, with rather fine uniform granulometry and a mean diameter, (D_{50}), of 242 μm. The wood shavings, a by-product of the planed lumber industry, resulted from pine timber and had the appearance of small flakes (Fig.1).

Physical properties of the aggregate materials are presented in Table 1. Both aggregates, mineral and organic, were previously dried before being added to polyester or epoxy resin in an automatic mixer.

Table 1. Physical properties of aggregates

Aggregates	Density [g.cm^{-3}]	Bulk Density [g.cm^{-3}]	Average Particle Dimensions [mm]
Sand	2.65	1.56	0.24 (Ø)
Wood	0.55	0.08	15 : 7.5 : 0.3 (l:w:t)*

* - Length, width and thickness

Two series of lightweight polymer concrete formulations modified with pine wood shavings were studied: (i) series 'EW', wood-modified epoxy concrete formulations, and (ii) series 'PW', wood-modified polyester concrete formulations. In each series, sand was partially replaced by equivalent weights of wood shavings, ranging from 0% (unmodified formulation) up to 6% of total aggregate weight. Previous works by the authors, on lightweight polymer concretes modified with cork granules [19, 20], established the different amounts of wood shavings used in the present work – *i.e.*, the organic aggregate mass fraction was kept in the formulations. Mix proportions of polymer concrete formulations are presented in Table 2.

Table 2. Weight mix proportions of concrete formulations

Resin Type	Test Series	Resin : Sand [w:w]	Wood : Sand [w:w]
Epoxy	EW-0	20 : 80	0 : 100
	EW-1		2.6 : 97.4
	EW-2		4.2 : 95.8
	EW-3		6.2 : 93.8
Polyester	PW-0	20 : 80	0 : 100
	PW-1		2.6 : 97.4
	PW-2		4.2 : 95.8
	PW-3		6.2 : 93.8

With the above formulations and mix proportions, polymer concretes were mixed and moulded to prismatic specimens (4 x 40 x 160 mm), as illustrated in Fig.1, according to RILEM standard CPT PC-2 [21].

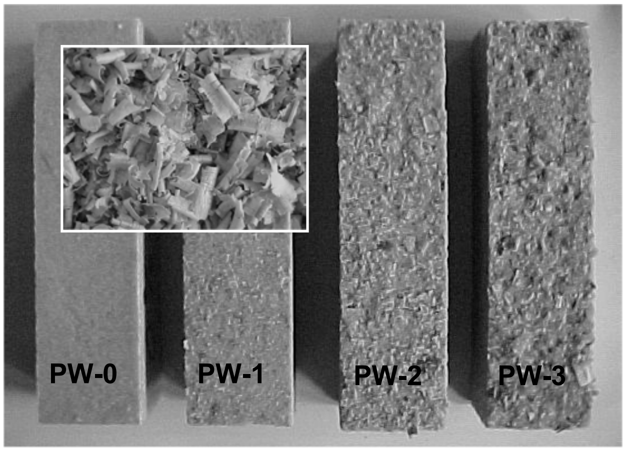

Fig. 1. Some examples of prismatic specimens of polyester PC modified with wood aggregates. Pine wood shavings used in this investigation work.

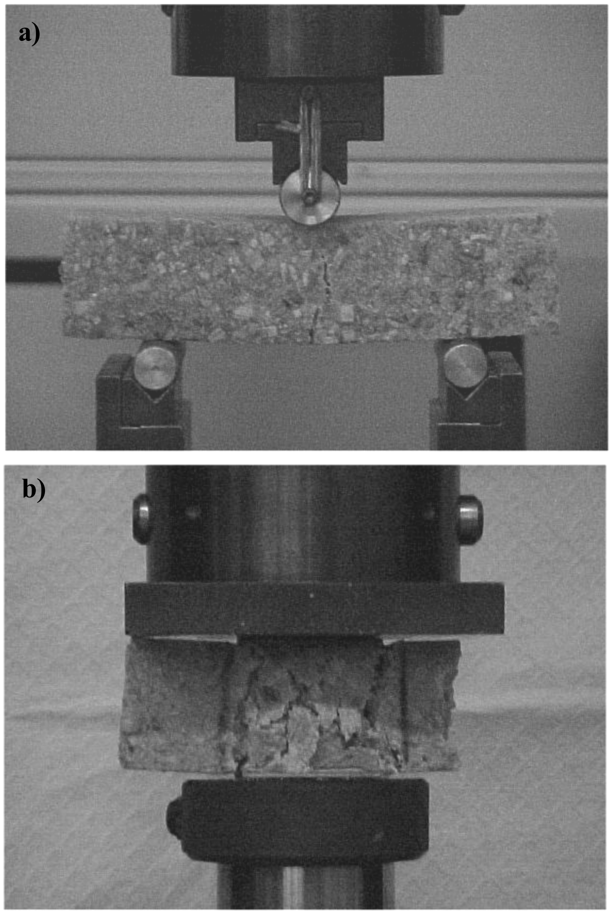

Fig. 2. Flexural (a) and compressive (b) test set-up. Bending and compression failure of one specimen of wood-modified PC (EW-3).

For each formulation 5 prismatic specimens were cast. All specimens were allowed to cure for seven days at room temperature and then post-cured at 80ºC for three hours before being tested in bending and compression.

Prismatic polymer concrete specimens were tested in bending up to failure at the loading rate of 1 mm.min-1, according to RILEM CPT PCM-8 standard test method [22]. The two parts, of each broken specimen in bending, were tested afterwards in compression at the loading rate of 1.25 mm.min-1, following the procedure described in UNE 83821:1992 test standard [23]. Both, flexural and compressive testing set-up, are presented in Fig. 2.

3. Test Results and Discussion

Mechanical properties obtained from flexural and compressive tests performed on specimens of all formulations of wood-modified polymer concrete are presented in Table 3.

In order to better compare mechanical behaviour of both test series, retained compressive and flexural strengths are plotted against wood content in Fig. 3. For better visualization, trend lines are shown on the right side of the figure.

Table 3. Mechanical properties of wood-modified PC formulations. Average values and standard deviation.

Test Series	Density [g.cm^{-3}]	Flexural Strength [MPa]	Compressive Strength [MPa]
EW-0	1.832	45.52 (1.68)	76.19 (0.85)
EW-1	1.779	39.37 (1.59)	71.94 (0.69)
EW-2	1.695	34.08 (2.14)	54.97 (0.96)
EW-3	1.593	24.87 (0.40)	43.32 (1.36)
PW-0	1.846	22.44 (0.19)	61.72 (0.90)
PW-1	1.803	18.83 (0.68)	55.78 (2.41)
PW-2	1.690	14.78 (0.69)	41.43 (2.67)
PW-3	1.516	5.21 (0.13)	10.68 (0.54)

It is clear from the experimental results that both compressive and flexural strength of wood-modified polymer concrete formulations decrease with increasing addition of wood shavings.

Since resin-sand ratio was kept constant and increasing amounts of wood aggregates were added throughout each test series, the effective resin volume content was successively reduced. Insufficient binder to wet increasing amounts of wood shavings exhibiting high specific surface, together with the relative low resistance of wood, appear to be the most relevant factors leading to the above trend in properties.

For both test series, the decay of mechanical properties with the increasing amounts of wood shavings follows similar trends in compression and bending. In general, compressive resistance is somewhat less affected with regard to the first addition of wood shavings. Further incorporation of wood leads to similar relative behaviour in both properties.

Polyester resin based formulations are more sensitive to the incorporation of wood aggregate than those with epoxy resin binder. Strength properties decrease is particularly impressive for the last formulation in the series of polyester based concretes. Decreases of 77% and 83% occurred for bending and compression, respectively. For epoxy formulations the observed values were less pronounced: strength decreases of 45% and 43% were obtained.

In an attempt to explain this behaviour, void contents were determined for all formulations. Calculation procedure took into consideration the difference between expected densities, based on the density of individual constituents, and experimentally measured concrete densities. An unexpected high void content was found for the last polyester based formulation, which corresponds to an increase of 56% relatively to the previous formulation in the test series. By contrast an increase of only 11% was found for the epoxy based formulations. This observation is consistent with, and may explain, the steeper loss of properties between W-2 and W-3 for polyester formulations.

Since the mixing procedure and casting process were rigorously the same for all test formulations, an insufficient adhesion between polyester binder and wood aggregate could be the cause for the unusual high void content found in PW-3 formulation, and, globally, for the higher sensibility of this test series to wood incorporation.

In order to access the effect of binder type and wood organic aggregate content on ductility and stiffness of polymer concretes, typical shapes of the obtained stress-deflections curves were determined and plotted in Figs. 4 and 5.

From the experimental curves it seems clear there is no significant gain in strain to failure in the case of wood-modified polyester PCs, particularly in bending. In compression, a higher ultimate strain occurs for the first formulation, PW-1, with lowest wood content. However, this increase declines throughout the other formulations, as wood content rises and ultimate load capacity drops off.

Opposite behaviour is shown by epoxy resin based formulations. In fact, except for the first formulation that presents equal ultimate compressive strain as the unmodified one, all other wood-modified epoxy PCs yield higher ultimate strain values, presenting an improved ductility.

A less brittle failure was observed for both test series, either in compression or in bending, in particular for the last formulations with higher content of organic aggregate.

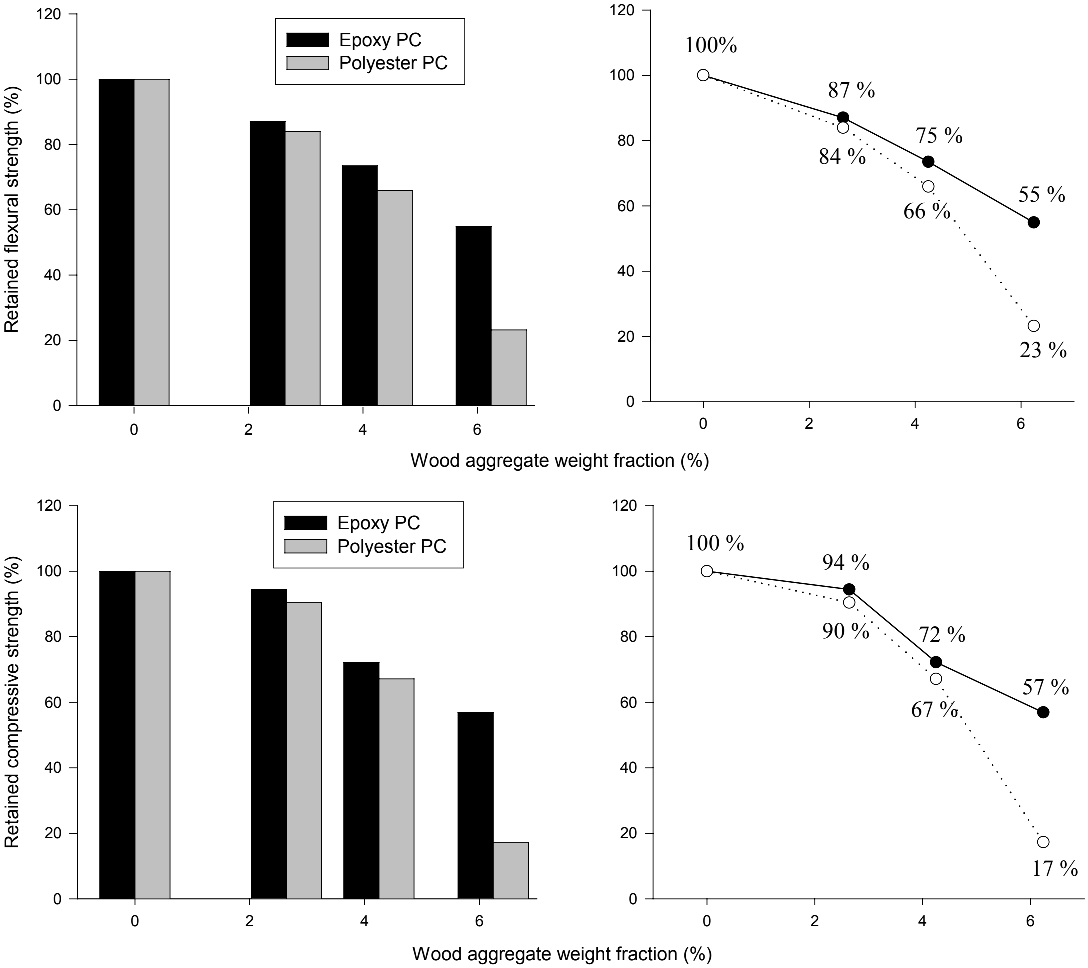

Fig. 3. Retained flexural and compressive strength of both test series as function of wood aggregate weight fraction.

In order to verify if there is some benefit in mechanical performance, considering the reduction in density as light aggregate weight fraction rises along test series, specific properties should be examined. In Fig. 6, both specific and absolute values of mechanical strengths are plotted against wood aggregate weight fraction.

While it is true that even specific strengths decrease with wood content, the density factor smoothes the loss in resistance when specific values are considered. As a consequence, plot lines can be extrapolated beyond interception points, where specific properties will exceed absolute ones, or put in another way, where PC formulations with sub-unitary density will be achieved. Wood content values corresponding to the interception points are around 6.6 to 6.9% and 8.8 to 9.2% for polyester and epoxy resin based formulations, respectively. It is, however, not certain if those points can be attained in practice, as larger amounts of wood may result in unworkable mixes. In particular, in the case of polyester test series, where bond between wood and resin is less efficient, such increase in wood content will lead to a concrete material with no significant load carrying capacity (1.5 MPa and 3.0 MPa, respectively, for bending and compressive resistance).

So far, the lack of binder, the low resistance of wood shavings and the relative weak adhesion between this organic aggregate and the resin binder, appear to be the main causes for loss in resistance.It is, nevertheless, clear that the observed mechanical strengths are globally still higher than those shown by an ordinary Portland cement concrete prepared with the same siliceous size aggregate (commonly named by mortars). Compressive and flexural strength of normal cement mortars usually range from 10 to 35 MPa and from 4 to 7 MPa, respectively, as function of cement type, cement dosage and water-cement ratio [24].Higher resin content and/or the use of interfacial modifiers that promote organic aggregate/resin adhesion might be the solution to improve the mechanical behaviour of this new class of lightweight polymer concretes.

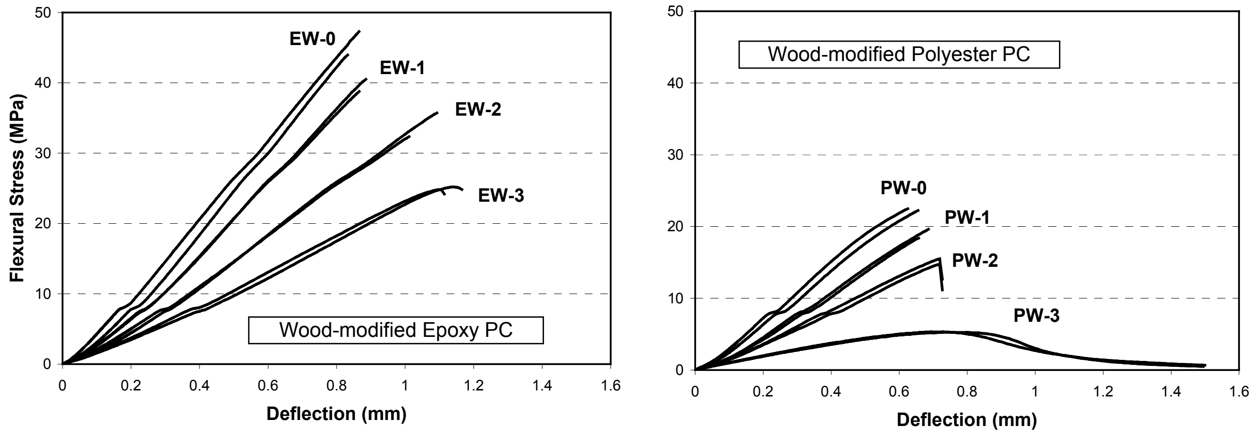

Fig. 4. Representative stress-deflection curves obtained from flexural tests performed on specimens of epoxy and polyester PC modified with wood organic aggregate.

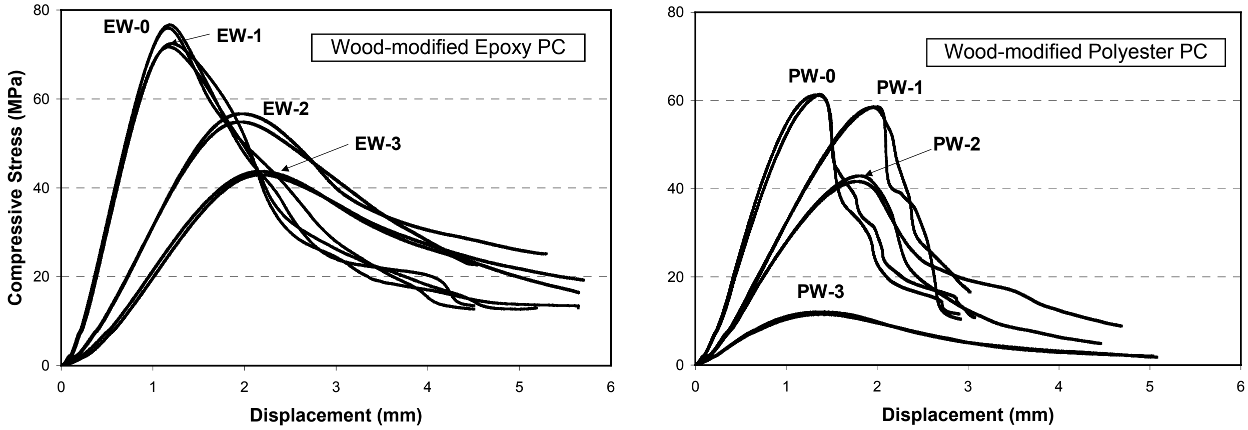

Fig. 5. Representative stress-displacement curves obtained from compressive tests performed on specimens of epoxy and polyester PC modified with wood organic aggregate.

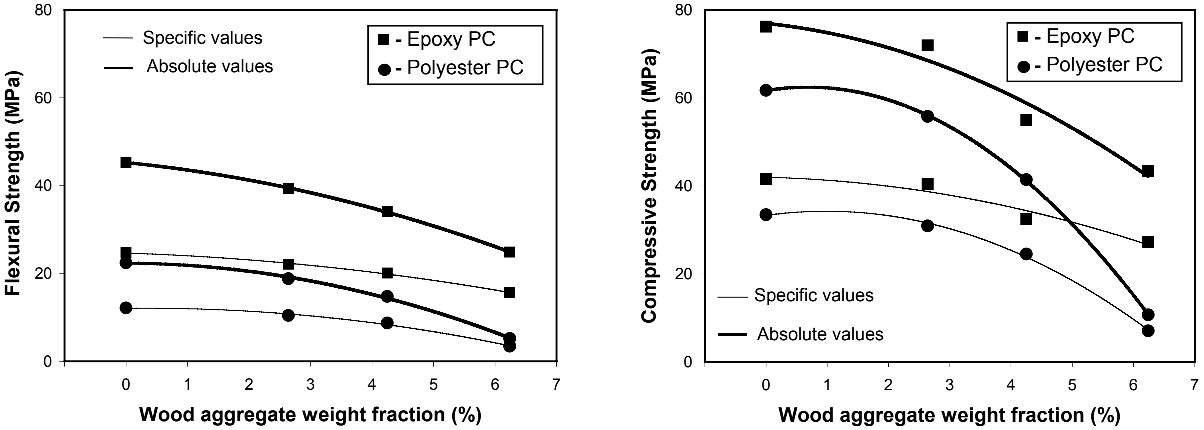

Fig. 6. Absolute and specific mechanical strengths of both series of polymer concrete formulations as function of wood aggregate weight fraction

4. Conclusions

The following conclusions can be drawn considering the mechanical behaviour of epoxy and polyester polymer concretes modified with wood shavings.

- Compression and bending strengths are both adversely affected by the introduction of any level of wood organic aggregate.
- Some of the main factors responsible for the decay in properties are the insufficient binder, the low resistance of wood shavings and the relative weak adhesion between this organic aggregate and the resin binder.
- Polyester based concretes are more sensitive to the incorporation of wood aggregate than epoxy based formulations due to a poorer interface between resin and wood.
- Wood-modified epoxy concretes yield higher ultimate strain values, presenting an improved ductility.
- A less brittle failure occurs for both resin based concretes, either in compression or in bending, in particular for the last formulations with higher content of organic aggregate.
- Low material density with good retention of properties is achieved for epoxy based concrete (EW-3).

The results of the present work anticipate interesting developments in research of lighter polymer concretes modified with organic aggregates. Other works on PC modified with wood are foreseen, in order to exploit other features brought by the incorporation of organic aggregate such as improved thermal and acoustic isolation properties.

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Mechanical characterization of lightweight polymer mortar modified with cork granulates

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Abstract

The mechanical behaviour of a cork modified polymer mortar was investigated. Two series of mortar formulations were studied, with different resin/sand (i.e., binder/fine aggregate) weight ratios. In each series, cork ranged from 0% to 45% of the total aggregate volume. Flexural and compressive tests were performed at room temperature and load vs. displacement curves were plotted up to failure. In the study, both the influence of the cork volume fraction and the resin/sand weight ratio were considered relative to the mechanical behaviour of the cork-modified polymer mortars. A linear decrease in properties was observed as function of cork volume content. When specific properties were considered, this tendency was kept. However, the lower density of the cork-modified mortars lead to a smoother loss in specific properties. The modified mortar properties seem to follow a rule of mixtures in terms of their components. The overall results anticipate interesting expectations in terms of lighter modified polymer concretes.

Keywords: A. Polymer–matrix composites; Cork; B. Mechanical properties; C. Elastic properties; E. Casting

1. Introduction

Polymer concrete (PC) and mortars (PM) have gained an increasing research interest due to their wide range of possible applications in civil construction [1–4]. In this class of materials, a thermoset resin is used as binder of natural or artificial aggregates, replacing the paste of Portland cement/water of conventional hydraulic concretes. The most commonly used resins have been unsaturated polyesters, acrylics and epoxies, but vinyl ester, furan and urethane, have also been applied.

The initial applications of PC, in the late 1950s, were the production of building cladding and cultured marble, but its excellent properties rapidly widespread its application fields. Its rapid curing, excellent bond to concrete and steel reinforcement, high strength and durability made it a very attractive repair material. As a mortar it can be placed with thickness less than 10 mm. Overlays in PC, for bridge surfaces and floors, have also become widely used because of the ability to use thin layers, fast curing time, very low permeability, and high resistance to chemical and frost attack. Precast components are another excellent use of the material. The high strength to weight ratio, good damping properties, moldability and ability to form complex shapes make PC and PMs particularly attractive for these applications [1].

The main limitation of concrete polymer materials is their cost. Even considering that the specific gravity of cement is about 21/2 times that of polymer, the cost per unit volume of polymer concretes is still significantly higher than Portland cement concrete. The higher cost of polymer concretes makes its use almost forbidden for high volume applications except in cases where durability renders cement concrete unusable. One way to minimize this limitation is the development of a lighter polymer concrete.

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The two traditional ways for the development of a lightweight concrete material involve the use of:

(i) an alternative binder to cement,
(ii) lightweight aggregates.

An example of the first option is the use of fly ash as a replacement for cement. It is an attractive solution since it consists of an inexpensive pozzolanic material that can reach half the density of cement. Its use in concrete industry is currently common practice and well documented [5]. Besides lowering cost and density of concrete it can lead to improved strength, durability and corrosion resistance.

In the case of polymer concrete and mortars, we are already in presence of an alternative binder with weight savings with respect to cement. So, in order to further weight reduction we are somewhat limited to the second option: the use of lighter aggregates.

The general class of lightweight aggregates encloses a wide range of products. From natural organic/mineral products (wood, cork, rice husk and products from volcanic source), to artificial products specially manufactured for the effect (expanded clay, shale or slate), as well as industrial sub-products and wastes (expanded slags and civil construction debris), a large spectrum of lightweight aggregates has been produced and/or applied in the last years for construction purposes.

The use of lightweight aggregates in building construction is not a recent practice as shown by the Basilica of Saint Sophie in Constantinople, made with diatomite. Artificial lightweight aggregates have been produced since the beginning of the 20th century in the US, and since the 1960s, the examples of concrete structures made with lightweight aggregates have multiplied throughout the world [6]. But only in the 1970s, a broad research effort in lightweight aggregate concrete was achieved [7–9]. Since then, several investigations on Portland cement concrete and mortars with lightweight aggregates have been reported and there are worldwide environmental, economic and technical impetuses to encourage the structural use of these materials [10–14].

A recent example of lighter aggregate substitute is a study by McBride and Shukla [15] where porous thin-walled particles called *cenospheres*, a byproduct during fly ash formation, are used in the development of lightweight concrete material. A 22% reduction in concrete density, while maintaining acceptable strength values, was obtained. A significant improvement on the mechanical behaviour was reached using interfacial modifiers.

1.1. Research significance

In this study an effort is undertaken to develop a new type of polymer mortar material, being both lighter and with improved ductility. Previous work on polymer mortars where polyester and epoxy mortar behaviour was measured under various chemical and mechanical conditions [16–18] was the basis for this research.

The strategy in the present work consisted in keeping the binder-to-sand weight ratio and adding increasing amounts of cork granulate resulting in a series of formulations with changing aggregate composition, characterized by the cork-to-sand volume ratio. With this procedure, it is clear that the binder-to-total aggregate ratio will decrease as we proceed along the series. For this reason, in addition to a series of formulations based on a binder-to-sand ratio optimized for unmodified polymer mortars determined in previous work [16], a higher ratio was also used.

Considering the low density and low stiffness of cork [19], its introduction in the mortar formulation was expected to reduce the material weight and brittleness, respectively. Cork also exhibits low strength, and large compressive strains, which may lead to a more energy-absorbing material. The low thermal conductivity and high sound absorbing properties of cork may also introduce these features in the cork-modified polymer mortar. These features are expected to be the subject of a future work.

The main challenge consists in developing a material with the above benefits while minimizing strength and cost changes. The cork granules used in this work are a by-product in the cork industry. They are produced from scrap of cutting and trimming operations, and are subsequently used in the production of agglomerated products; hence its cost is considerably lower compared with that of virgin cork.

The mechanical performance of the cork-modified polymer mortar was evaluated by flexural and compressive tests performed at room temperature. The influence of both cork volume fraction and resin/sand weight ratio was considered in the analysis of results.

2. Experimental program

2.1. Materials and mortar formulations

Polymer mortar formulations were prepared by mixing an epoxy resin with a siliceous sand with rather fine uniform granulometry and granulated cork. The chosen epoxy resin (Eposil-552), based on a diglycidil ether of bisphenol A and an aliphatic amine hardener, has low viscosity (500–600 mPa s) and flexural strength of 70 ± 5 MPa. Physical properties of the aggregate materials are shown in Table 1. Both aggregates, sand and cork granulates, were previously dried before the addition to epoxy resin in an automatic mixer.

Two series of mortar formulations were studied, where different resin/sand weight ratio values were used.

Table 1
Physical properties of aggregates

Aggregate	Density ($g\,cm^{-3}$)	Apparent density ($g\,cm^{-3}$)	Average particle diameter (mm)
Sand	2.65	1.56	0.24
Cork	0.22	0.12	2.75

In each series, sand was partially replaced by equivalent volumes of cork, ranging from 0% to 45% of aggregate volume. Mix proportions of polymer mortar formulations are presented in Table 2.

With these binder formulations and mix proportions, polymer mortars were mixed and moulded to prismatic ($40 \times 40 \times 160$ mm) and cylinder ($\varnothing$ 50×100 mm) specimens, as illustrated in Fig. 1, according to the RILEM standard CPT PC-2 [20]. For each formulation five prismatic and three cylinder specimens were cast. All specimens were allowed to cure for 7 days at room temperature and then post-cured at 70 °C for 3 h, before being tested in bending and compression.

2.2. Flexural and compressive testing procedures

Prismatic polymer mortar specimens were tested in three-point bending up to failure at the loading rate of 1 $mm\,min^{-1}$, with a span length of 100 mm, according to RILEM CPT PCM-8 standard test method [21]. The specifications of this standard, in terms of specimen geometry and span length, are similar to those specified in ASTM C348-02, standard test method for flexural strength of hydraulic cement mortars [22]. In both mentioned standards, shear effect is not taken into account on calculation procedure of flexural strength. Despite the very short span length compared with specimen thickness, shear effect is disregarded and it is not considered. Mortar is assumed as an isotropic material and the theory of plane cross-sections is used. Flexural strength, considered as the strength under normal stresses, was determined applying the following equation known from the strength of materials:

Table 2
Mix proportions of mortar formulations

Test series		Resin:sand (m/m)	Cork:sand (v/v)	Resin:sand:cork (v/v/v)
A	A-0	20:80	0:100	36.0:64.0:0.0
	A-25		25:75	29.8:52.9:17.3
	A-35		35:65	26.8:47.7:25.5
	A-45		45:55	23.8:42.3:33.9
B	B-0	25:75	0:100	42.8:57.2:0.0
	B-25		25:75	36.1:48.2:15.7
	B-35		35:65	32.8:43.8:23.4
	B-45		45:55	29.4:39.2:31.4

$$\sigma_f = \frac{3Pl}{2bh^2}, \tag{1}$$

where σ_f is the flexural strength; P is the maximum load recorded; l is the span length; and b and h are, respectively, the width and the height of the prismatic specimens.

Cylinder polymer mortar specimens were tested in compression at the loading rate of 1.25 $mm\,min^{-1}$ according to ASTM C469-94 standard [23]. All specimens were instrumented with wire strain gages bonded to two diametrically opposite gage lines parallel to the axis of the specimen. In order to obtain Poisson's ratio, one specimen of each series was also instrumented with two bonded strain gages mounted circumferentially at diametrically opposite points at the specimen mid-height. Longitudinal and circumferential strains, as well as LVDT data, were recorded continuously using a data logger with a continuous acquisition system.

Compressive strength, chord modulus of elasticity in compression and Poisson's ratio were calculated according the following equations:

$$\sigma_c = \frac{P}{A}, \tag{2}$$

where σ_c is the compressive strength; P is the maximum load recorded; and A is the cross-sectional area of cylinder specimens.

$$E = \frac{S_2 - S_1}{\epsilon_2 - 0.000050}, \tag{3}$$

where E is the chord elasticity modulus; S_2 is the stress corresponding to 40% of maximum load; S_1 is the stress corresponding to a longitudinal strain of 50 millionths; and ϵ_2 is the longitudinal strain produced by S_2.

Fig. 1. Some examples of cylinder and prismatic specimens produced of cork-modified polymer mortars.

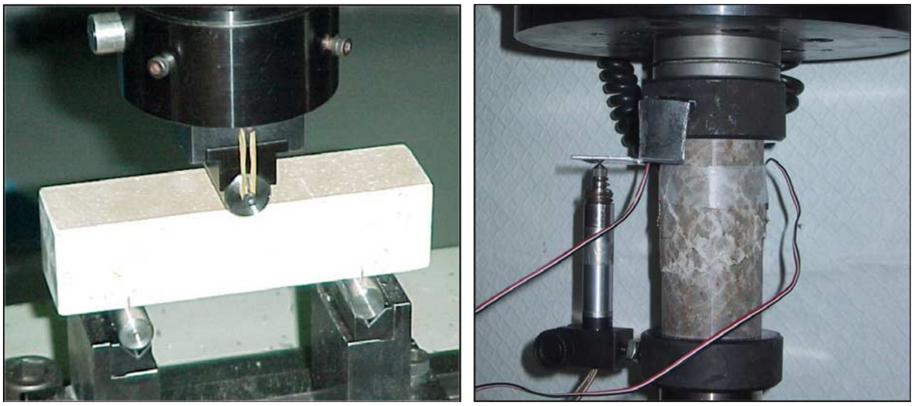

Fig. 2. Flexural and compressive test set-up.

$$v = \frac{\epsilon_{t2} - \epsilon_{t1}}{\epsilon_2 - 0.000050}, \tag{4}$$

where v is the Poisson's ratio; and ϵ_{t2} and ϵ_{t1} are the transverse strains at mid height of the specimen produced, respectively, by stresses S_2 and S_1.

Both, flexural and compressive testing set-up, are presented in Fig. 2.

3. Test results and discussion

Mechanical properties obtained from flexural and compressive tests performed on specimens of all formulations of cork-modified polymer concrete, are presented in Table 3.

In order to assess the effect of resin and cork content on ductility and stiffness of polymer mortars, typical shapes of the obtained stress–deflection and stress–strain curves were determined and plotted in Figs. 3 and 4.

3.1. Influence of cork volume content

The results in Table 3 show that both compressive and flexural strength of cork-modified polymer concrete formulations decrease with the increasing addition of cork granulates.

Considering test series A in compression, decreases of 45% and 38% are observed in strength and modulus, respectively, for the A-25 mix in relation to A-0, the unmodified mortar mix. A decrease in flexural strength close to 44% is observed for the same formulation. As we continue along the series, mechanical properties versus cork content relationships are quite linear. In fact, as cork volume in total aggregate increases by 10% between consecutive formulations, property relative values decrease by a similar amount.

In series B, the initial drop in properties, i.e., from B-0 to B-25, is less pronounced. Decreases close to 36% and 34% are observed for strength and modulus in compression, respectively. Flexural strength decrease is again inferior and around 29%. The following formulations in this series reveal the same trend in properties found for series A, as already described. The fact that series B is less affected by cork introduction appears to be related with the binder/sand ratio, which is higher in this series. This feature shall be discussed further ahead in the paper.

The values of Poisson's ratio do not show a clear trend. Although cork is a highly anisotropic material [19], its use in this study in the form of granules masks that property. The random distribution of granules means that any anisotropic feature has its value aver-

Table 3
Mechanical properties of cork-modified polymer mortar formulations: average values and standard deviation

Test series	Mechanical properties				
	Density (g cm^{-3})	Compressive strength (MPa)	Flexural strength (MPa)	Elastic modulus (GPa)	Poisson ratio
A-0	1.81	67.81 ± 0.64	37.37 ± 1.34	12.60 ± 0.32	0.25
A-25	1.57	37.28 ± 0.89	20.95 ± 0.79	7.79 ± 0.44	0.25
A-35	1.51	31.17 ± 0.84	18.53 ± 0.72	6.61 ± 0.01	0.23
A-45	1.37	22.47 ± 0.98	14.18 ± 1.02	5.12 ± 0.47	0.27
B-0	1.73	58.47 ± 2.21	35.87 ± 2.67	9.73 ± 0.28	0.27
B-25	1.50	37.63 ± 1.20	25.50 ± 1.40	6.41 ± 0.27	0.27
B-35	1.45	32.98 ± 0.71	22.36 ± 1.11	5.81 ± 0.19	0.24
B-45	1.36	27.83 ± 0.86	19.11 ± 0.58	5.51 ± 0.08	0.25

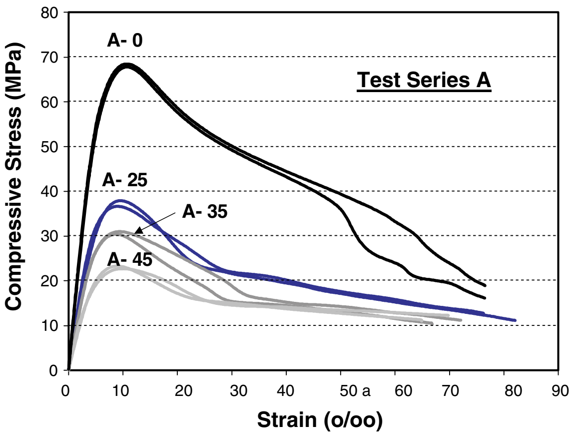

Fig. 3. Some representative stress–strain curves obtained from compressive tests performed on cork-modified polymer mortar specimens.

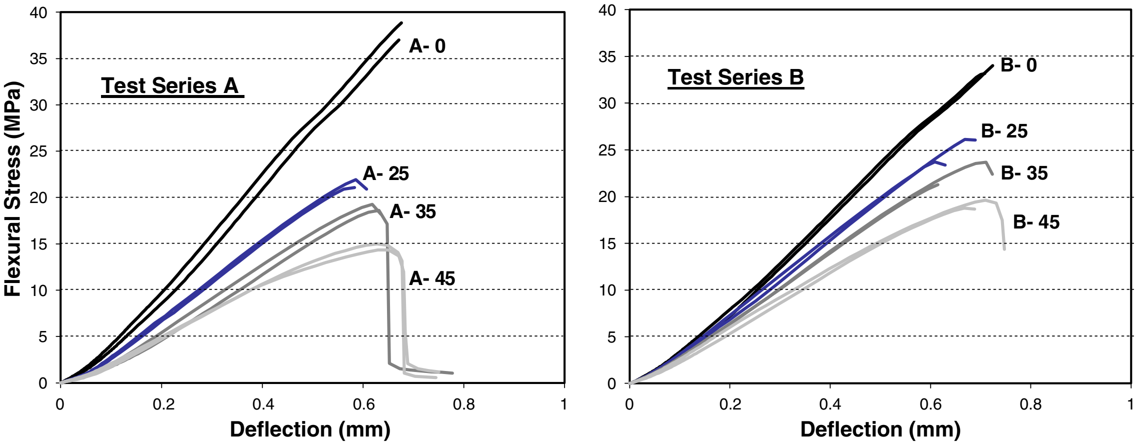

Fig. 4. Some representative stress–deflection curves obtained from flexural tests performed on cork-modified polymer mortar specimens.

aged through all possible orientations. This explains why Poisson's ratio is randomly affected by the inclusion of cork.

From the experimental curves in Figs. 3 and 4 it seems clear that there is no gain in strain to failure. The main difference in behaviour is in compression, where a smaller drop in resistance occurs after maximum load capacity is overcome, followed by a very smooth decrease in resistance, and this clearly relates to cork content. In bending, failure also becomes less brittle as cork content is progressively increased in the series formulations.

In order to better understand the influence of cork, mechanical properties of polymer mortar formulations are plotted as function of cork content in Figs. 5 and 6, respectively, for compressive and bending strength, and for elasticity modulus. In addition Fig. 6 also includes the predicted elasticity modulus based on the Kelvin–Voigt model for the rule of mixtures:

$$E_{\mathrm{comp}} = E_{\mathrm{c}} V_{\mathrm{c}} + E_{\mathrm{m}} V_{\mathrm{m}}, \qquad (5)$$

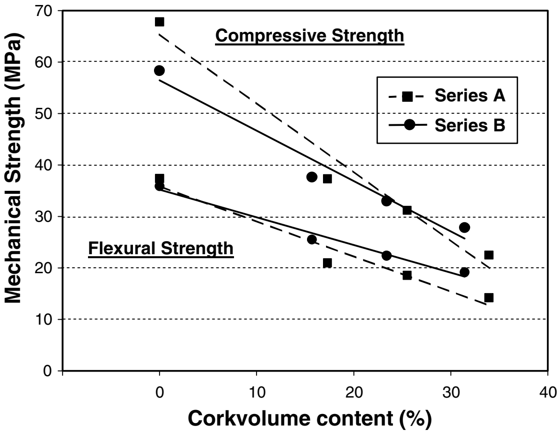

Fig. 5. Compressive and flexural strengths of both series of polymer mortar formulations as function of cork volume content.

where E and V refer to elasticity modulus and volume fraction; and the indexes comp, c and m, are relative to final composite, cork and matrix (unmodified mortar formulations). Elasticity modulus values obtained

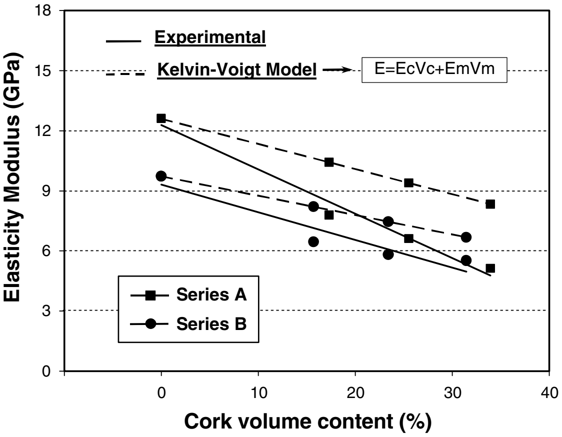

Fig. 6. Experimental and predicted elasticity modulus (by Kelvin–Voigt Model) of both series of polymer mortar formulations as function of cork volume content.

experimentally for the unmodified mortar formulations, A-0 and B-0, were assumed for E_m values.

It is clear that concrete strength and modulus are quite linear with respect to cork volume content. In addition to confirming the trends stated initially, these plots clearly show that the loss in properties is more pronounced in series A, where binder volume fraction is comparatively smaller, leading to poorer inter-particle bonding.

It seems likely there is a critical point beyond which, further additions of cork, promoting an increase on total specific surface [1] of aggregates, leads to an insufficient wetting ability by the available binder. This feature had already been noticed during the casting process.

The predicted values given by the simple Kelvin–Voigt model constitute only an upper bound for the composite modulus variation. A possible source of discrepancy could be the occurrence of premature microcracking starting at matrix/cork interface.

In order to verify if there is some benefit in mechanical performance, considering the reduction in density when cork is used, specific properties should be examined. In Fig. 7, both specific and absolute values of mechanical strengths are plotted against cork volume in aggregate. While it is true that even specific strengths decrease with cork content, the density factor smoothes the loss in resistance when specific values are considered. As a consequence, plot lines can be extrapolated beyond interception points, where specific properties will exceed absolute ones, or put in another way, where mortar formulations with sub-unitary density will be achieved. Cork content values corresponding to the interception points are around 40% and 42% for series A and B, respectively, which correspond to cork volume fraction on aggregate of 55% and 64%. It is, however, not certain if those points can be attained in practice, as larger amounts of cork may result in unworkable mixes, particularly in the case of series A, where binder relative content is smaller.

Observing the lines for specific mechanical strengths of both series in Fig. 7, other theoretical conclusions can be drawn:

(i) For polymer mortar mixes with cork volume contents above 17% (cross-point lines), the higher resin–sand ratio of series B matrix is always preferable, as a higher strength to weight ratio is expected to be achieved by resultant mortar formulations.
(ii) For cork contents below that value, the option between series A or B matrix, will depend of which mechanical behaviour (in compression or bending) is intended to be improved.

3.2. Influence of effective resin volume content

Since resin–sand ratio was kept constant and increasing amounts of granulate cork were added throughout each test series, the effective resin volume content was successively reduced. In an attempt to assess the influence of binder content, the mechanical properties were plotted against binder effective volume content in each formulation (Fig. 8).

The binder content values were corrected for void content in the specimens, taking into consideration the material densities (Table 1), and the experimentally determined densities of mix formulations presented in Table 3. The following expression was used to determine the effective resin volume contents:

$$V_r(\%) = \frac{(m_r/\rho_r)}{\sum_{i=1}^{3} m_i/\rho_{\text{exp}}} \times 100, \tag{6}$$

where V_r is the effective resin volume fraction; m_r and ρ_r are, respectively, the resin mass and the resin density ($\rho_r = 1.18$); m_i is the mass of constituent materials (resin, sand and cork granules); and ρ_{exp} refers to experimentaly determined density of mix formulations.

Again, it seems reasonable to assume a linear trend in the plots. The main observations seem to be

(i) Series A is more sensitive to effective resin volume content, i.e., mechanical properties variation with effective resin volume content is higher.
(ii) Series B exhibits an overall smaller change in property absolute values.
(iii) In both series, compressive strength is more affected by resin volume content than flexural strength.

The lack of binder and the very low resistance of cork, appear to be the most relevant factors of the above trend

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[1] Ratio between total surface and volume of aggregate particles.

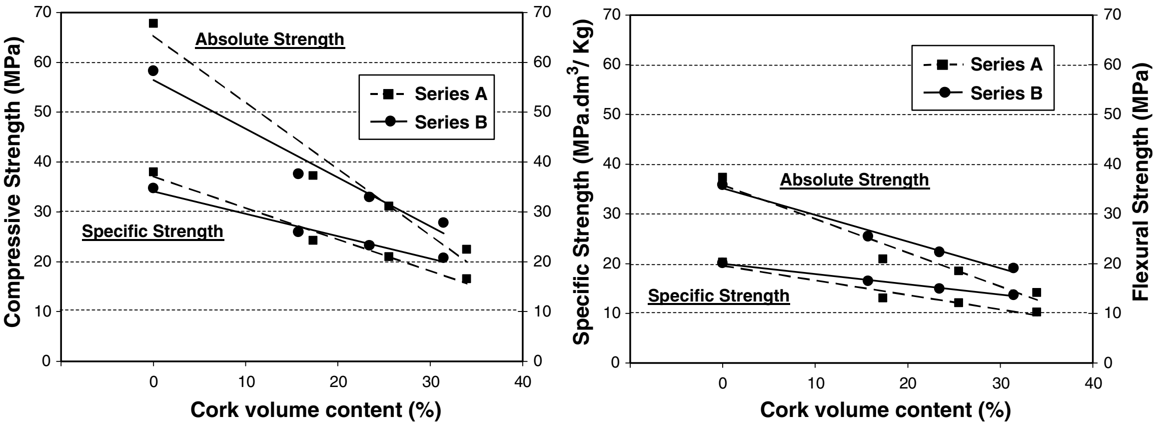

Fig. 7. Absolute and specific mechanical strengths of both series of polymer mortar formulations as function of cork volume content.

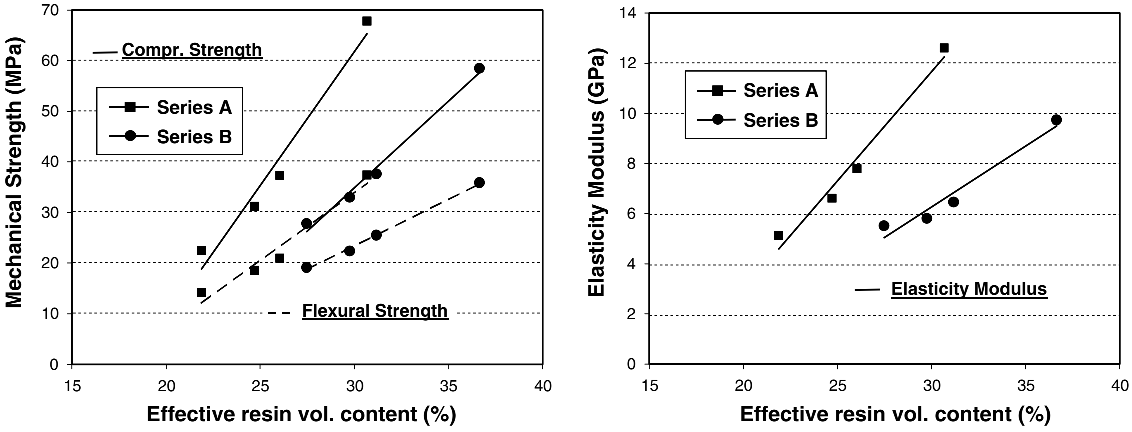

Fig. 8. Compressive and flexural properties of both series of polymer mortar formulations as function of effective resin volume fraction.

in properties. Higher resin content and the use of interfacial modifiers that promote cork/resin adhesion might be the solution to improve the mechanical behaviour of cork-modified polymer mortars.

It is, nevertheless, clear that the observed mechanical strengths are globally still higher than those shown by an ordinary Portland cement mortar, particullary in bending. Compressive and flexural strength of cement mortars range from 10 to 35 MPa, and 4 to 7 MPa, respectively, as function of cement type, cement dosage and water/cement ratio [24].

3.3. Flexural strength and compressive elasticity modulus vs compressive strength

Two important design parameters for concrete and mortars are both the flexural tensile strength and compressive modulus to compressive strength, relationships. These are depicted in Fig. 9. For comparison, similar relationships for normal weight Portland cement concrete were also included. These last ones were derived from empirical relationships, given by Eurocode 2, which are usually applied for design data of normal weight concrete with strength classes between C12/15 (cylinder average compressive strength of 20 MPa) and C50/60 (cylinder average compressive strength of 58 MPa) [25].

As can be seen from Fig. 9, flexural tensile/compressive strength ratio values found for both series of lightweight polymer mortars modified with cork exceed largely those of normal weight cement concrete. On the other hand, mainly due to viscoelasticity properties of polymers, elastic modulus of cork-modified polymer mortars is less than that of conventional material, for the same compressive strength.

Comparing the two series of cork-modified formulations, the highest flexural tensile/compressive strength ratio is presented by series B, while series A, with lower resin content, shows a higher elasticity modulus/compressive strength ratio. For both series, the above relationships are linear with cork content, i.e., the ratio values are kept constant for the cork-modified formulations.

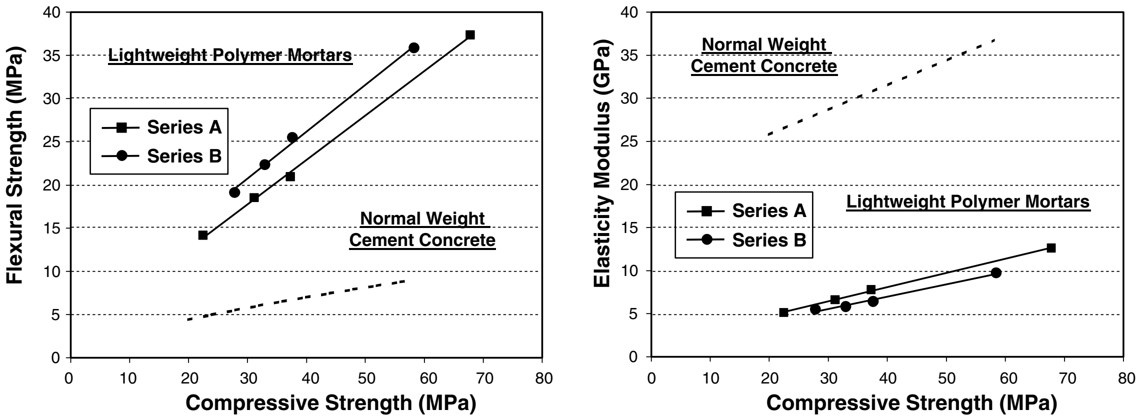

Fig. 9. Flexural strength and compressive elasticity modulus to compressive strength relationships of lightweight polymer mortars and normal weight cement concrete.

4. Conclusions

The following general conclusions may be drawn concerning the properties of cork-modified polymer concrete formulations considered in the present work:

- Strength and elasticity modulus, in both compression and flexion, are adversely affected by the introduction of any level of cork considered in the present work. Formulations in series A, where binder content is comparatively lower, are more severely affected by cork content.
- The decrease of relative resin volume along each test series and the low resistance of cork are main factors responsible for the observed loss in properties.
- The mechanical behaviour is altered by cork. As cork content rises throughout each test series, material becomes more ductile, particularly in compression, and shows less brittle failure.
- Comparatively with conventional cement materials, elasticity modulus of cork-modified polymer mortars is quite low, but flexural/compressive strength ratio is remarkably higher.
- The results demand future work with increased cork content, on a quest for a class of very lightweight formulations, i.e., with densities below unity.

The results so far obtained allow for a very interesting expectation in terms of lighter modified polymer concretes with improved compressive ductility. Further investigations are foreseen in order to optimize resin content and to exploit other features induced by cork introduction such as higher energy-absorbing, and improved thermal and acoustic properties.

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