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Pultrusion of thermoplastic composites

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To the memory of my father

To my mother and my brother

À memória do meu Pai

Para a minha Mãe e o meu Irmão

ABSTRACT

The use of thermoplastic matrix in continuous fibres composites is relatively recent and the number of its applications is growing. However, it involves great challenges since thermoplastics polymers present much higher viscosity than thermosets, making much difficult and complex the impregnation of reinforcements and consolidation tasks. Sometimes, thermoplastic compatibilizers are added to the matrices to improve their adhesion and facilitate the impregnation of reinforcements. For this reason, the successful application of the thermoplastic matrix composites in commercial markets is still largely dependent on the development of new processes of transformation and/or the adaptation of the equipment currently used for the production of thermossets matrix composites.

In this work, it has been addressed the pultrusion of thermoplastic composites by referring the advantages of using this type of matrix compared with the thermoset polymers, as well as the benefits of applying composite parts over more traditional materials, without neglecting some of its drawbacks. In this sense, it was analysed, globally, the market where these composites are applied and their high performance, indicating the main characteristics and properties that set them apart.

Two major technologies are being used to allow impregnate reinforcing fibres with thermoplastic polymers: i) direct melting of the polymer and, ii) intimate fibre/matrix contact prior to final composite fabrication. Continuous fibre reinforced thermoplastic matrix pre-impregnated tapes (PCT´s and tapes) are, for example, produced by direct melting processes (in the present work, by the co-extrusion process). Alternatively, intimate contact processes allow producing cheap and promising pre-impregnated materials, such as, commingled fibres and powder coated towpregs.These pre-impregnated materials may be processed into final composite parts by compression moulding, filament winding and pultrusion.

In this work, four different thermoplastic matrix fibre reinforced pre-impregnated materials were used: towpregs and pre-consolidated tapes (PCT´s), both produced in our manufacturing lines and commingled fibres (TWINTEX®)) and tapes (CompTape®) supplied by external companies. Glass and carbon fibres and two different thermoplastic matrices (polypropylene and PRIMOSPIRE®) were selected for the production of the pre-impregnated materials.

Pultrusion and heated compression moulding were the manufacturing technologies used to obtain composite profiles and plates for study.

The optimization of the manufacturing processes used (production of towpregs, pultrusion and heated compression moulding) was made by studying the influence of the most relevant processing parameters in the final properties of the produced fibres and thermoplastic matrix pre-impregnated materials and composites. The method of Taguchi / DOE (Design of Experiments) was used to achieve this aim as it allowed making more rational choices of processing windows established.

Using pultrusion and heated compression prototype equipments, profiles from four different pre-impregnated-materials (comingled system, powder coated towpregs, PCT´s and tapes) and composite plates from pultruded profiles were produced.

The raw-materials, the pre-impregnated materials and the produced composites (profiles and plates) were characterized by various mechanical tests (tensile, bending, ILSS and DMA), microscopy, calcination and thermogravimetric analysis, and the mechanics of composites concepts were applied for the final products in order to predict its main properties and the evaluation of their behaviour.

RESUMO

O uso de matrizes termoplásticas em compósitos de fibras contínuas é relativamente recente e o seu número de aplicações está a crescer. No entanto, envolve grandes desafios devido a que os polímeros termoplásticos apresentam muito maior viscosidade que os termoendurecíveis, o que torna muito mais difícil e complexa a impregnação dos reforços e as tarefas de consolidação. Às vezes, compatibilizadores termoplásticos são adicionados às matrizes para melhorar a sua adesão e facilitar a impregnação dos reforços. Por esta razão, o sucesso da aplicação dos compósitos de matriz termoplástica em mercados comerciais ainda é largamente dependente do desenvolvimento de novos processos de transformação e/ou a adaptação dos equipamentos atualmente utilizados para a produção de compósitos de matriz termoendurecível.

Neste trabalho, foi abordada a pultrusão de compósitos termoplásticos referindo-se as vantagens de usar este tipo de matriz em comparação com os polímeros termoendurecíveis e os benefícios de aplicar as peças em compósito em relação aos materiais mais tradicionais, sem negligenciar alguns dos seus inconvenientes. Neste sentido, foi analisado, globalmente, o mercado onde estes compósitos são aplicados e o seu elevado desempenho, indicando as principais características e propriedades que os distinguem.

Duas principais tecnologias estão a ser usadas para permitir impregnar fibras reforçadas com polímeros termoplásticos: i) a fusão directa do polímero e, ii) o contato íntimo da fibra/matriz antes da fabricação final do compósito. Fitas pré-impregnadas de matriz termoplástica reforçada com fibras contínuas (PCT´s e Tapes) são, por exemplo, produzidas por processos de fusão directos (no presente trabalho, pelo processo de co-extrusão). Alternativamente, processos de contato íntimo permitem produzir materiais pré-impregnados baratos e prometedores, tais como, “commingled yarns” e “towpregs”. Estes materiais pré-impregnados podem ser transformados em peças finais em compósito por moldação por compressão, por enrolamento filamentar e por pultrusão.

Neste trabalho, foram utilizados quatro diferentes materiais pré-impregnados de matriz termoplástica reforçada com fibra: “towpregs” e “pre-consolidated tapes” (PCT´s), ambos produzidos por linhas de fabrico internas e “commingled fibres” (TWINTEX®) and tapes (CompTape®) fornecidos por empresas externas. As fibras de vidro e de carbono e duas matrizes termoplásticas diferentes (polipropileno e PRIMOSPIRE®) foram as matérias-primas selecionadas para a produção dos materiais pré-impregnados.

A pultrusão e moldação por compressão a quente foram as tecnologias de fabricação utilizadas para se obter perfis e placas em compósito para estudo.

A otimização dos processos de fabricação usados (produção de towpregs, pultrusão e moldação por compressão a quente) foi realizada estudando a influência dos parâmetros de processamento mais relevantes nas propriedades finais dos materiais pre-impregnados de fibra e matriz termoplástica e dos compósitos produzidos. O método Taguchi / DOE (Design of Experiments) foi utilizado para atingir este objectivo assim como permitiu fazer escolhas mais racionais no estabelecimento de janelas de processamento.

Utilizando os equipamentos protótipos de pultrusão e de moldação por compressão a quente, foram produzidos perfis com origem em quatro materiais pré-impregnados diferentes (sistema “commingled”, towpregs, PCT´s e tapes) e placas em compósito de perfis pultrudidos.

As matérias-primas, os materiais pré-impregnados e os compósitos produzidos (perfis e placas) foram caracterizados por diversos ensaios mecânicos (tração, flexão, ILSS e DMA), microscopia, calcinação e análise termogravimétrica, e os conceitos da mecânica dos compósitos foram aplicados aos produtos finais para prever as suas principais propriedades e a avaliação do seu comportamento.

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NOMENCLATURE

LIST OF ABBREVIATIONS AND ACRONYMS

AFM	Atomic Force Microscope
ANOVA	Analysis of Variance
BMC	Bulk Moulding Compound
CAGR	Compound Annual Growth Rate
CC	Carbon Composites
CFC	Carbon Fibre Reinforced Carbon
CFRP/CRP	Carbon Fibre Reinforced Plastics
CFRT	Continuous Fibre Reinforced Thermoplastic
CFs	Carbon Fibres
CI	Confidence Interval
CLT	Classical Laminate Theory
CMC	Ceramic Matrix Composites
CTE	Coefficient of Thermal Expansion
DMA	Dynamic Mechanical Analysis
DOE	Design of Experiments
DRA	Discontinuously Reinforced Aluminium
DRIFT	Direct ReInforcement Fabrication Technology
DRTi	Discontinuously Reinforced Titanium
DSC	Differential Scanning Calorimetry
ESA	European Space Agency
FIT	Fibre Impregnated Thermoplastic
FM	Fibre/Matrix
FPF	First Ply Failure
GDP	Gross Domestic Product
GMT	Glass Mat Reinforced Thermoplastic
GRP	Glass Fibre Reinforced Plastics
HDPE	High Density Polyethylene
IACS	International Annealed Copper Standard
ILSS	Interlaminar Shear Strength
JEC	Trade show and conference
LFRT/LFT	Long fibre Reinforced Thermoplastic
MMC	Metal Matrix Composites

PA	Polyamide
PAI	Poly(amide imide)
PAN	Polyacrylonitrile
PAS	Poly(aryl sulfone)
PBT	Poly(butylene terephthalate)
PC	Polycarbonate
PCT	Pre-consolidated tape
PE	Polyethylene
PEEK	Poly(ether ketone ketone)
PEI	Poly(ether imide)
PEK	Poly(ether ketone)
PES	Poly(ether sulfone)
PET	Poly(ethylene terephthalate)
PI	Polyimide
PMC	Polymer Matrix Composites
PMMA	Poly(methyl methacrylate)
PP	Polypropylene
PPP	Poly(para-phenylene)
PPS	Poly(phenylene sulfide)
PSU	Polysulfone
Q/I	Quasi-Isotropic
R&D	Research and Development
ROM	Rule of Mixtures
S/N	Signal to Noise
SRP	Self-reinforced polyphenylene
SEM	Scanning Electron Microscopy
SFRT	Short Fibre Reinforced Thermoplastic
SGL	Carbon fibre manufacturer
SMC	Sheet Moulding Compound
TC	Thermal Conductivity
TGA	Thermogravimetric Analysis
Thsd	Thousand
TMC	Titanium Metal Composites
Tons	Tonnes
UTS	Ultimate Tensile Strength

LIST OF SYMBOLS

A_t	Cross-sectional area of the profile, (m^2)
$[a]$	Membrane compliance matrix (of a laminate)
$[a^*]$	Normalized membrane compliance matrix (of a laminate)
$[A]$	Membrane stiffness matrix (of a laminate)
$[A^*]$	Normalized membrane stiffness matrix (of a laminate)
$[b]$	Compliance matrix of membrane-bending coupling (of a laminate)
$[b^*]$	Normalized compliance matrix of membrane-bending coupling (of a laminate)
$[B]$	Stiffness matrix of membrane-bending coupling (of a laminate)
$[B^*]$	Normalized stiffness matrix of membrane-bending coupling (of a laminate)
$[d]$	Bending compliance matrix (of a laminate)
$[d^*]$	Normalized bending compliance matrix (of a laminate)
$[D]$	Bending stiffness matrix (of a laminate)
$[D^*]$	Normalized bending stiffness matrix (of a laminate)
D_p	Distance to impregnate by the polymer, (mm)
$d_{lin.pe}$	Linear weight per unit length of pre-impregnated material, (TEX (g/km))
E	Elastic modulus, (GPa)
E_f	Fibre elastic modulus, (GPa)
E_p	Matrix elastic modulus, (GPa)
E_x	Elastic modulus in the x-axis direction, (GPa)
E_y	Elastic modulus in the y-axis direction, (GPa)
E_1	Modulus of the layer in the direction of the fibres, (GPa)
E_2	Elastic modulus of the layer in the transverse direction to the fibres, (GPa)
E_x^f	Bending elastic modulus in the x-axis direction, (GPa)
E_y^f	Bending elastic modulus in the y-axis direction, (GPa)
F	Force, (N)

G_f	Fibre shear modulus, (GPa)
G_p	Matrix shear modulus, (GPa)
G_{xy}	Shear modulus in plane x-y, (GPa)
G_{12}	Shear modulus in plane 1-2, (GPa)
h	Total thickness of the laminate, (mm)
h_i	Thickness of each layer i of the laminate, (mm)
K	Permeability, (m^2)
$\{M\}_{xy}$	Bending loads matrix (bending moments) (of a laminate)
n_c	Number of layers of the laminate
Nreq	Number of pre-impregnated materials required
$\{N\}_{xy}$	Membrane loads matrix (of a laminate)
P	Pressure, (MPa)
$[\overline{Q}]_i$	Stiffness matrix of layer i in the global coordinate system (x, y, z) (of a laminate)
$[Q]_i$	Stiffness matrix of each layer in the main coordinate system (1, 2, 3) (of a laminate)
r	Radius, (m)
r_f	Fibre radius, (μm)
r_p	Polymer particle radius, (μm)
S	Shear strength, (MPa)
t	Time, (s)
t_{imp}	Time to ensure the full impregnation of reinforcement, (s)
T	Absolute temperature, (°K)
$[T]$	Transformation matrix of the coordinated system
u	Displacement in x-axis direction, (m)
u_p	Polymer flow velocity, (m/s)
u_0	Displacement in the middle plane of the laminate in the x-axis direction, (mm)
v	Displacement in y-axis direction, (m)
v_f	Fibre volume fraction
v_p	Matrix volume fraction (polymer)

v_v	Voids content of a composite laminate
v^0	Displacement in the middle plane of the laminate in the y-axis direction, (mm)
w	Displacement in z-axis direction, (m)
w_f	Fibre mass fraction
w_p	Matrix mass fraction (polymer)
w^0	Displacement in the middle plane of the laminate in the z-axis direction, (m)
X	Mechanical strength of the layer in the direction of the fibres, (MPa)
X_f	Fibre strength (tensile strength), (MPa)
X_p	Matrix stress at a strain equal to fibre strength, (MPa)
y	Deflection, (mm)
Y	Mechanical strength of the layer in the transverse direction to the fibres (transverse tensile strength) (MPa)
z_i	Coordinate in the z axis of the outer surface of the layer i, (mm)
ε	Longitudinal strain
ε_{xz}	Tensorial shear strain in plane x-z
ε_{yz}	Tensorial shear strain in plane y-z
ε_x	Strain in x-axis direction
ε_y	Strain in y-axis direction
ε_z	Strain in z-axis direction
$\{\varepsilon\}_{xy}$	Strain matrix (of a laminate), in the global coordinate system
$\{\varepsilon^f\}_{xy}$	Bending strain matrix on the outer surface in the global coordinate system (of a laminate)
$\{\varepsilon^o\}_{xy}$	Membrane strain matrix of the middle plane in the global coordinate system (of the laminate)
η	Viscosity, (Pa×s)
$\{\kappa\}_{xy}$	Curvatures matrix in the global coordinate system (of a laminate)
ν	Poisson's ratio
ν_f	Fibre Poisson's ratio
ν_p	Matrix Poisson's ratio

ν_{xy}	Major Poisson's ratio in the x-y plane
ν_{yx}	Minor Poisson's ratio in the x-y plane
ν_{12}	Higher Poisson's ratio in the 1-2 plane
ν_{21}	Lowest Poisson's ratio in the 1-2 plane
θ	Angle between the x-axis and the 1-axis, measured counterclockwise and at layer plan, (rad)
ρ	Density, (Mg/m^3)
ρ_f	Fibre density, (Mg/m^3)
ρ_p	Matrix density, (Mg/m^3)
ρ_c	Composite density, (Mg/m^3)
σ	Normal stress, (MPa)
$\left\{\sigma^o\right\}_{xy}$	Normalized membrane stresses matrix in the global coordinate system (of a laminate)
$\left\{\sigma^f\right\}_{xy}$	Normalized bending stresses matrix in the global coordinate system (of a laminate)
σ_1	Stress in the layer in 1-axis direction, (MPa)
σ_2	Stress in the layer in 2-axis direction, (MPa)
σ_x^f	Bending stress in x-axis direction, (MPa)
σ_y^f	Bending stress in x-axis direction, (MPa)
τ	Shear stress, (MPa)
τ_{12}	Shear stress in the layer in plane 1-2, (MPa)
λ	Coefficient of thermal conductivity (W/m×ºK)
λ/ρ	Specific termal conductivity ((W/m×º)/ (Mg/m^3))
α	Coefficient of thermal expansion (1/ºK*10^{-6})

Chapter 1

INTRODUCTION

Although only not long ago thermoplastic matrices have been used in long and continuous fibre reinforced composites as alternative to thermoset matrices, the number of their applications is increasing due to their better ecological and mechanical performance [1.1]. Composites with thermoplastic matrices offer increased fracture toughness, high damage tolerance, short processing cycle times and excellent environmental stability. They are recyclable, post-formable and can be joined by fusion welding. However, the use of continuous fibre reinforced thermoplastic matrix composites involves great technological and scientific challenges, since thermoplastics present much higher viscosity than thermosets, which makes more difficult and complex the impregnation of reinforcements and consolidation tasks [1.1-1.6].

Today, two major technologies are being used to allow wetting reinforcing fibres with thermoplastic polymers [1.1, 1.4-1.10]: i) the direct melting of the polymer and, ii) the intimate fibre/matrix contact prior to final composite fabrication. Continuous fibre reinforced thermoplastic matrix pre-impregnated tapes are, for example, produced by direct melting processes. Alternatively, intimate contact processes allow producing cheap and promising pre-impregnated materials, such as, commingled fibres and powder coated towpregs. Sometimes, thermoplastic compatibilizers are added to the matrices to improve their adhesion and facilitate the impregnation of reinforcements [1.11].

This thesis presents and compares the processability of final composite parts by using four different pre-impregnated materials produced by each one of the above mentioned wetting techniques. Two are a pre-consolidated tape - PCT and tape that were produced by the melting process (cross-head extrusion) [1.12]. The other two were produced by fibre/matrix intimate contact methods, being one a commercially available commingled fibres product and the other a towpreg produced by our own developed dry coating line [1.13]. All studied pre-impregnated materials were based on a continuous carbon and glass fibres reinforced polypropylene and PRIMOSPIRE® matrix system. Pultrusion was the selected manufacturing method for processing all these pre-impregnated materials into composite parts. It is a versatile continuous high speed production technology, allowing the production of fibre reinforced complex profiles. Nowadays, crucial challenges in thermoplastic pultrusion exhist, such as developing of modelling and simulation processes. Also, the improvement of the most common process (using various types of prepregs), promising process techniques like reaction injection pultrusion (in-situ pultrusion) or multi-die vacuum assisted pultrusion are being studied. Different raw-materials and pre-imprenated materials used (namely natural fibres or braided and parallel hybrid yarns) may bring new challenges, like residual stresses in the product, which may induce damage or premature cracks and delamination [1.14-1.38].

The heated compression moulding was a selected manufacturing process to transform pultruded profiles into composite plates. Compression moulding is very popular for its high reproducibility, easy handling, low maintenance and capability of manufacturing complex geometry structures. Compression moulding is designed to produce a part with essentially no final trimming required.

Different compression processes of thermoplastic materials reinforced by continuous fibres (heated, cold or *in situ* polymerisation compression moulding) have been used to manufacture various types of raw materials (fibres, including natural and thermoplastic matrices), dry fibres preforms by reactive impregnation, prepregs/preforms (powder impregnated tows, commingled yarns, solution/direct melt impregnation tapes/tows, film stacking and fabrics or other textile forms of previous prepregs), semi-products (thermoplastic composite preconsolidated sheets or profiles made from prepegs) into final products. Some pre-impregnated materials need a final impregnation prior the consolidation of composite during shaping (powder impregnated tows, commingled yarns, film stacking) [1.3, 1.5, 1.38-1.57].

Many previous researchers have developed models for flow of a resin in a composite and their consolidation manufacturing by compression moulding. Typically and like pultrusion, these models originate from the use of Darcy’s Law and extend from there with the addition of relating empirical and constitutive equations. One of the ways the various models diverge from each other is in how they approach the issue of permeability [1.57-1.65].

The optimization of the towpregs manufacturing and pultrusion and heated compression processes was made by studying the influence of the most relevant processing parameters in the final properties of the produced pre-impregnated materials and composites. The method of Taguchi / DOE (Design of Experiments) was used to achieve this aim.

The possibility of using maleic anhydride as compatibilizer of carbon and glass fibre reinforced polypropylene composites was also analysed in the present research.

Towpregs were characterized by scanning electron microscopy (SEM), visual analysis and their polymer mass contents were determined. The final composite parts were also submitted to tensile, interlaminar and flexural tests, as well as calcination and SEM/optical microscopy tests and the results were compared with theoretical ones that can be predicted by using the ROM (Rule Of Mixtures) and other engineering traditional materials (steel, aluminium and several polymers).

Considering the context presented above, this thesis has been organized into eight parts, including the present chapter (Chapter 1). Chapter 2 is the state of art which describes the bibliographical review conducted on the pultrusion system of thermoplastic matrix composites and all related subjects and includes the objectives to be achieved in the work. Chapter 3 exposes the main theoretical concepts to be used in later chapters of the thesis. The last part corresponds to the work carried out, which will be presented by a collection of papers under each chapter. In Chapter 4, which presents a collection of three international conference papers, there will be a description of processing technologies for the production of intermediate products i.e. towpregs and PCTs, as well as the charcaterization of these semi-products and also the commingled yarns. Chapter 5, which is the main focus of the thesis, gathers four journal papers and two international conference papers and describes the manufacturing of towpregs, PCTs and commingled yarns using the pultrusion process. Besides, considering the processing parameters and using the Taguchi method for Design of Experiments, the final products were tested for mechanical characterization, microscopic analysis and fibre content determination. The prediction of properties was made using the rule of mixtures. In chapter 6, which presents two international conference papers and one submitted journal paper, a similar methodology has been used to manufacture pultruded rectangular profiles using the heat compression process.

Finally, conclusions were drawn (in Chapter 7) and ideas for future work are presented (in Chapter 8).

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Chapter 2

STATE OF ART

2.1. Introduction

This thesis will address the theme pultrusion of thermoplastic composites by referring the advantages of using this type of matrix compared with the thermosets polymers and the composite parts with more traditional application materials, without neglecting some drawbacks. In this sense, it will be analysed globally the market where these composites are applied and their high performance, indicating the main characteristics and properties that set them apart [2.1].

A composite material results from the combination of two or more distinct materials. A study of its constituents, with emphasis on the types of fibres and in polymeric matrices (thermoset and mainly thermoplastic) will be done to verify how their properties affect the mechanical and technical characteristics of the final product [2.1].

Some typical manufacturing processes for the production of thermoplastic matrix composites will be described, in particular pultrusion and heated compression moulding. The raw-materials, the equipment's/moulds, the most significant processing variables (and their optimization) and the technical characteristics of the final parts will be also presented.

The polymeric composites with thermoplastic matrix present a higher rate of growth in the consumer markets, an elevated fracture toughness, a reduced cycle time, an excellent corrosive resistance and are more recyclable than thermoset matrix ones. Thus, more attention will be given to study them, in particular the process used for the production of pre-impregnated materials as well as some promising manufacturing technologies for their transformation into composite structures. [2.2-2.3].

The use of thermoplastic matrix composites reinforced with long or continuous fibres involves, however, large technological and scientific challenges due the thermoplastic matrices presents much higher viscosity than the thermosettings, making very difficult and complex the impregnation of the reinforcement and the consolidation tasks [2.2-2.3].

The production of thermoplastic matrix composite materials by pultrusion and heated compression moulding (from pultruded profiles) will be the subject of detailed analysis. The raw-materials, the pre-impregnated materials and the produced composites (profiles and plates) will be characterized by various mechanical tests, microscopy, calcination and thermogravimetric analysis, being applied mechanics of composites concepts for the final products to predict its main properties and the evaluation of their behaviour [2.2-2.3].

2.2. Composites materials

Many applications in the field of engineering require materials with specific characteristics in terms of weight and mechanical stiffness and strenght which are difficult to obtain using simple polymeric, ceramic or metallic materials. In such situations, rather than developing a new material, which may or not have the desired properties for a certain application, engineers can modify a given pre-existing material by incorporating another component, thus obtaining a composite material [2.4].

A composite material is a macroscopic combination of two or more distinct materials phases, having a recognizable interface between them, with a significantly different physical or chemical properties that, when combined, produce a material with different characteristics from the individual components. Given the vast range of materials that may be considered as composites and the broad range of uses for which composite materials may be designed, it is difficult to agree upon a single, simple and useful definition. However, as a common practical definition, composites materials may be restricted to emphasize those materials that contain a continuous matrix constituent that binds together and provides form to an array of a stronger and stiffer reinforcement constituent. The resulting composite material has a balance of structural properties that is superior to either constituent material alone [2.5-2.7].

Composite materials are the most advanced and adaptable engineering materials known to man. In load-bearing or structural applications, composites in most cases comprise a bulk phase enclosing a fibrous reinforcing phase; in a conventional terminology one talks of matrix and reinforcement. The objective of the matrix is to bind the reinforcement together so as to effectively transfer external loads to the reinforcement and to protect it from adverse environmental effects. While the matrices gives a composite its shape, surface appearance, environmental tolerance (to high temperature, water, ultra-violet light, etc), and overall durability, it is the fibrous reinforcement that carries most the structural loads and thus largely dictates macroscopic stiffness and strength [2.4-2.6].

The matrices may be metallic, ceramic or polymeric in origin and the composite materials can be classified according to the type of matrix that is used, notably Polymer Matrix Composites (PMC´s), Metallic Matrix Composites (MMC´s) and Ceramic Matrix Composites (CMC´s).

2.2.1. Ceramic Matrix Composites (CMCs)

Ceramic Matrix Composites generally consist of ceramic fibres or whiskers in a ceramic matrix. CMCs are designed to overcome the main drawback of monolithic ceramics (specially conventional technical ceramics like alumina, silicon carbide, aluminium nitride, silicon nitride or zirconia, namely their brittleness. To increase the crack resistance or fracture toughness, particles (so-called monocrystalline whiskers or platelets) were embedded into the matrix. However, the improvement was limited, and the products have found application only in some ceramic cutting tools. So far, only the integration of long multi-strand fibres has drastically increased the crack resistance, elongation and thermal shock resistance, and resulted in several new applications. The most common reinforcement embodiment is a continuous-length ceramic fibre, with an elastic modulus that is typically somewhat higher than the matrix. The functional role of this fibre (1) is to increase the CMC stress for progress of micro-cracks through the matrix, thereby increasing the energy expended during crack propagation; and then (2) when thru-thickness cracks begin to form across the CMC at a higher stress, to bridge these cracks (this mechanism works only when the matrix can slide along the fibres) without fracturing, thereby providing the CMC with a high ultimate tensile strength (UTS).

Carbon (C), special silicon carbide (SiC), alumina (Al_2O_3) and mullite (Al_2O_3–SiO_2) fibres are most commonly used for CMCs. The matrix materials are usually the same, that is, C, SiC, alumina and mullite. The important commercially available CMCs are C/C, C/SiC, SiC/SiC and Al_2O_3/Al_2O_3.

CMCs are referred to as inverse composites, which is to say that the failure strain of the matrix is lower than the failure strain of the fibres, whereas it is the reverse in most polymer or metal matrix composites. Hence, under mechanical or thermo-mechanical loads it is the matrix which fails first, that is, fracture easily because the cracks initiated by small defects or scratches. In order to prevent an early failure of the brittle fibres when the matrix starts to microcrack, the fibre/matrix (FM) bonding should be controlled during processing. CMCs are tough materials and display a high failure stress when the FM bonding is not too strong or too weak, which is usually achieved through the use of a fibre coating referred to as the interface. Unlike the goal of metal matrix and polymer matrix where high strength is desired, the objective in CMCs is to create a tough material that fails ductily instead of catastrophically. The CMCs exhibits a high strain capability before ultimate failure when compared with monolithic ceramic, which is highly desirable in any structural material. Ductile failure is achieved by allowing the fibres to debond from the matrix as a crack propagates causing energy to be absorbed by this event and by the eventual fibre fracture and fibre pull-out. The requirement is that the energy to fracture the interface must be significantly lower than the energy to fracture the fibre. This requirement has led to much research focused on finding interface materials that can meet this requirement. CMCs are used as thermo-structural materials under severe service conditions, for example, high temperatures under load and in corrosive atmospheres, such as combustion gases. [2.8-2.10]

The desirable characteristics of ceramic matrix composites include high-temperature stability, high thermal shock resistance, high hardness, high corrosion resistance, light weight, elongation to rupture up to 1%, improved dynamical load capability, anisotropic properties following the orientation of fibres, non-magnetic, and versatility in providing unique engineering solutions. The thermal and electrical properties of the composite are a result of its constituents, namely fibres, matrix and pores as well as their composition. The orientation of the fibres yields anisotropic data. Oxide CMCs are very good electrical insulators, and because of their high porosity their thermal insulation is much better than that of conventional oxide ceramics. The use of carbon fibres increases the electrical conductivity, provided the fibres contact each other and the voltage source. Silicon carbide matrix is a good thermal conductor and electrically, it is a semiconductor, and its resistance therefore decreases with increasing temperature. The combination of these characteristics makes ceramic matrix composites attractive alternatives to traditional processing industrial materials such as high alloy steels and refractory metals. For the processing industry, related benefits of using ceramic composites include increased energy efficiency, increased productivity, and regulatory compliance. Key barriers to the broad application of ceramic matrix composites include the lack of specifications, databases, attachment concepts, in-service repair methodology, high cost, and scale-up [2.10].

CMCs are widely used in structural parts, such as gas turbines for power plants, heat treatment furnaces, rocket and jet engines, heat shields for space vehicles, fusion reactor first wall, aircraft brakes, etc [2.11].

2.2.2. Carbon Fibre/Carbon Matrix Composites

Carbon Fibre/Carbon Matrix composites are often considered a subclass of CMCs family. The promise of reaching service temperatures up to 2000 ºC is one of most attractive aspect of carbon matrices reinforced with carbon fibres and tend to have continuous, three-dimensional reinforcement. Among the advantages of carbon fibre/carbon matrix composites are high strength, high modulus, low creep, high thermal conductivity, high specific heat, low coefficient of thermal expansion (CTE), low density, high wear-resistance, and biocompatibility. The major disadvantages are high cost and the fact the carbon stars oxidize around 400ºC. Thus, where the service conditions involve elevated temperatures in oxidizing ambient, the carbon materials cannot survive, and oxidation-resistant matrix materials with oxidation-resistant fibres must be used. Really high service temperatures may thus only be realized in inert atmosphere (e.g. space) or if oxygen-impermeable surface coating is applied to the composite. High-temperatures applications are in rocket engines and in “re-entry conditions”, i.e. as heat shields or leading edges on space craft and rockets re-entering the earth´s atmosphere. A reasonably common low temperature application is as brake disks in aircraft, race cars, etc., where thermal and wear properties are major advantages that allow substantial improvements in wear resistance and weight savings [2.5, 2.9].

2.2.3. Metal Matrix Composites (MMCs)

One of the most prominent material systems in the past few decades is Metal Matrix Composites (MMCs), where two or more constituents are used to fabricate a new material. By formulating a composite, it is possible to use the unique advantages of different constituents in a complementary manner to suppress the limitations of each constituent. For example, the need for lightweight structural material for the applications in automotive and aerospace industry is paramount these days. This is partly due to enforcement of new emission regulations and the rising fuel costs. Traditional materials such as aluminum or titanium are failing to overcome current challenges of ordinary materials are facing today. The properties of materials deteriorate significantly at relatively low temperatures, which limit their use in critical components. However, by combining inherent ductility of matrix and toughness with high stiffness and high specific strength materials, such as ceramic filaments or carbon fibres, it is possible to fabricate materials that can overcome performance issues and also being used in high-tech applications like nanoelectronic, structural and medical applications. The incorporation of such reinforcements into metal matrices significantly improves the hardness, tensile strength, elastic modulus and other mechanical properties. Few other properties, such as thermal conductivity (TC), coefficient of thermal expansion, coefficient of friction, wear resistance, corrosion and fatigue resistance can also be tailored according to application requirements in metal matrix composites [2.12].

MMCs have found enormous application in aerospace, automotive and other structural applications due to their superior properties namely, low density, low coefficient of thermal expansion, high thermal conductivity, high stiffness, high strength and high wear resistance. However, on the other hand, toughness of MMCs is inferior as compared to monolithic metals. Two different developments may be assigned to MMCs; as a mean of improving the properties over unreinforced metals or as a way to increase the temperature tolerance of continuous-fibre reinforced composites. In the former and more common case, discontinuous fibres, whiskers, or particles are used and MMC basically is viewed as an improved metal with macroscopically isotropic properties. In the case manufacturing methods typically are modified versions of conventional metal forming operations, e.g. casting and sintering. When comparing MMCs to metals, the addition of reinforcement yields improved high temperature properties, such strength, stiffness, fatigue, wear, etc. In the latter case, continuous and aligned fibres are used and the resulting properties are anything but isotropic. In this case, fibre preforms are impregnated with the liquid metal [2.5, 2.13, 2.14].

Historically, it was wrongly assumed that the matrix's only role was to hold reinforcements in place. Along with the properties of the reinforcement, it is also very important to understand the interaction between the matrix and the reinforcement. The interface or the region between the matrix and the reinforcement actually plays a significant role in stress transfer between the matrix and the reinforcement. If the bonding between the two is weak, which can occur due to wettability issues or lack of interaction in-between, the final composite will have poor mechanical properties. As an example, carbon fibres do not usually have any chemical interaction with Al/Cu metals. The lack of interaction results in inferior final properties of the composite. In a broader sense, reinforcements could be classified in two major categories, i.e. continuous/discontinuous fibres and particulates. Fibres are the filamentary materials for which lengths are often greater than 100 μm. The properties of various fibres and particulates used as reinforcement for different metal matrix composites are given in Table 2.1. Continuous fibre reinforcement provides the most effective strengthening, while particulate reinforcement provides cost effectiveness and isotropic properties. In applications requiring high loading or extreme thermal conditions, continuous fibre reinforced MMCs are better choice [2.12].

Table 2.1 - Properties of different reinforcements used in metal matrix composite systems [2.12]

Reinforcement	Nominal size (µm)	Density (g/cm^3)	UTS (MPa)	Modulus (GPa)
Boron, single fibre, SiC coated	100–150	2.70	3100	400
a-Alumina, tow	20	3.95	1380	379
c-Alumina, tow	17	3.25	1800	210
Carbon, high modulus, tow	8	1.85	2300	400
SiC, tow	13	2.55	2550	196
SiC, single fibre	100–140	3.5	2700	400
SiC	15–340	3.2		324 (1090 °C)
SiO_2	40–60	2.66		73
MgO	40–60	2.7–3.6	41 (1090 °C)	317 (1090 °C)
Si_3N_4	40–60	3.18		207
TiC		4.93	55 (1090 °C)	269 (24 °C)
B_4C	40–300	2.52	2759 (24 °C)	448 (24 °C)
ZrO_2	75–180	5.65–6.15	83 (1090 °C)	132 (1090 °C)
BN_2	40–50	2.25		
Graphite	40–250	1.6–2.2		
TiB_2		4.5		414 (1090 °C)
ZrB_2		6.09		503 (24 °C)
ZrC		6.73	90 (1090 °C)	359 (24 °C)
ZrO_2		5.89	83 (1090 °C)	132 (1090 °C)
K_2TiO_3	0.5	3.30	7000	280
AlN		3.26	2069 (24 °C)	310 (1090 °C)
VC		5.77		434 (24 °C)
HfC		12.20		317 (24 °C)
WSi_2		9.40		248 (1090 °C)
WC		15.63		669 (24 °C)
NbC		7.60		338 (24 °C)
ThO_2		9.86	193 (1090 °C)	200 (1090 °C)
Mo_2C		8.90		228 (24 °C)

A vast range of MMC materials has been conceived and studied. This diversity comes from the large number of permutations of metal matrices and reinforcements and the almost endless combinations of reinforcement size, morphology and distribution. MMCs of commercial importance represent a much smaller subset, but still cover a broad range. Matrices based on Ag, Al, Be, Co, Cu, Fe, Mg, Ni and Ti are all commercially produced and used. By far the largest commercial volumes are for discontinuously reinforced Al (DRA), which accounts for 69% of the annual MMC production by mass. Reinforcements most often used in commercial applications are Al_2O_3, B_4C, BeO, C (chopped and continuous fibre), graphite, Mo, NbC, SiC, TaC, TiB, $TiBl_2$, TiC, W and WC. The reinforcement of largest commercial volume is SiC by a significant margin, followed by Al_2O_3 and TiC. Nearly all MMCs in commercial use rely on discontinuous reinforcements, although applications exist for MMCs with continuous graphite, SiC and Al_2O_3 fibres [2.15].

The reinforcement is in the form of wires, whiskers or particulates, continuous/discontinuous fibres that are distributed in different volume fraction percentages according to their properties. Except the reinforcements that are in the form of wires, others are provided of ceramics that are oxides, carbides, and nitrides having excellent properties like specific strength and stiffness at both high and ambient temperatures. It is possible to tailor their properties as per the requirement of various industrial applications by suitable combinations of matrix, reinforcement and fabrication method. These reinforcements are known for their lower coefficient of thermal expansion with higher strength and modulus [2.14].

Strength and stiffness are the two most important characteristics for structural applications. The specific stiffness and specific strength are shown for fibre-reinforced alloys of Al and Ti (the latter are often denoted as TMCs), discontinuously reinforced Al (DRA), discontinuously reinforced Ti (DRTi), conventional metals and graphite/epoxy composites (Figure 2.1) [2.15].

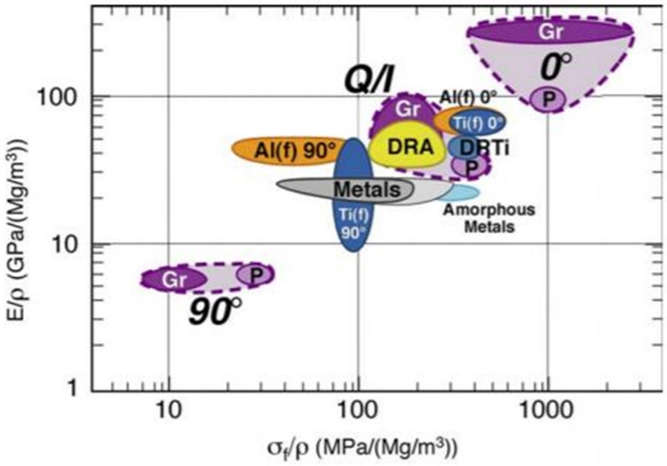


Figure 2.1 - Specific stiffness vs. specific strength for structural materials. Aerospace organic matrix composites are shown as graphite/epoxy (Gr) or PAN/epoxy (P) in the longitudinal (0), transverse (90), and quasi-isotropic (Q/I) configurations. The longitudinal and transverse properties for fibre-reinforced Al (Al(f)) and fibre-reinforced Ti (Ti(f)) are also shown. Conventional aerospace metals (Metals), including Al, Mg, Ti, Ni and steel alloys, are shown, and the extension of this envelope indicates a few specialty metals such as b-Ti and ultra high strength steels [2.15]

While graphite/epoxy provides the best uniaxial strength and stiffness, it simultaneously provides the poorest response in the transverse direction (Figure 2.1). Since structures must typically support multi-axial loads, these uniaxial composites have only restricted applications. Quasi-isotropic (Q/I) properties are produced in two dimensions by various cross-ply architectures, vastly expanding the applications of graphite/epoxy composites at more modest levels of specific strength and stiffness (Figure 2.1). It is in this range of specific strength and stiffness that MMCs best compete.

Discontinuously reinforced MMCs provide competitive levels of specific strength and stiffness (Figure 2.1), and provide the additional advantages of improved affordability and isotropy in three-dimensions. Further, structures often impose requirements in addition to excellent specific stiffness and strength. These requirements can include high bearing strength for attachments, resistance to aggressive environments (including chemicals, cryogenic or organic fluids, atomic oxygen, and ultraviolet radiation), resistance to outgassing, good through-thickness thermal conductivity; good wear resistance, high dimensional stability, good impact, erosion resistance, resistance to burning and high temperature application. MMCs typically provide superior response relative to organic matrix composites in these areas.

From the structural viewpoint, a main limitation to the industrial application of MMCs has been the embrittlement associated with the addition, to the metal, of brittle ceramic reinforcements.

Fracture properties, such as ductility, toughness, impact resistance and fatigue response, are often of primary importance for structural applications. While the open literature abounds with reports of poor fracture properties in MMCs, a critical interpretation is necessary. Nevertheless, the growing use of MMCs in fracture-sensitive and fracture-critical applications provides sufficient evidence of the confidence placed in the fracture properties of MMCs by the engineering design community. Recent scientific studies are establishing the fundamental importance of reinforcement size, shape and especially distribution in achieving the full potential of MMCs for fracture-sensitive structural applications. In general, the best fracture properties are achieved in MMCs with a more uniform distribution and finer particulate sizes. In addition, fracture properties also depend sensitively on fibre volume fraction (v_f), and some bounds must be established for materials used in fracture-sensitive applications. In DRA, the current state of the art limits v_f to less than about 20% for fracture-critical components, although attractive properties can be provided in material with v_f values of $\geq$25% with careful control over particulate size, shape and distribution [2.15].

Thermal management is important in a wide range of applications, including substrates for computer processor chips, power semiconductor devices and packaging for microwave devices used in telecommunications. A high coefficient of thermal conductivity (λ) is required, and specific thermal conductivity (λ/ρ) is a useful property of comparison for components that are part of a moving system, such as sub-components in aerospace systems. CTE (α) is the second primary property for thermal management. Candidate electronic packaging materials must have values between 4 and 7 $x \cdot 10^{-6}/^{o}K$ to match the CTE of semiconductor materials and ceramic substrates, thereby avoiding build-up of residual stresses in this critical region. Thermal management materials that perform best are those that possess a CTE from 4 to 7 x 10^{-6}/ºK (indicated by the horizontal shaded band in Figure 2.2) and which have the highest value of λ/ρ [2.15].

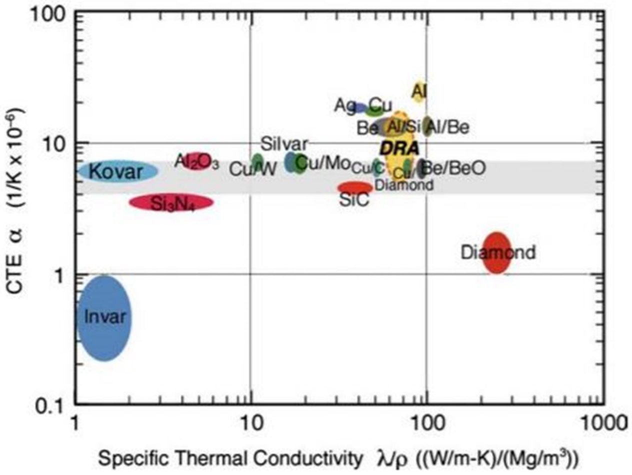


Figure 2.2 - Materials comparison for thermal management applications. The best materials are those that have the highest values of k/q and fall within the band of an illustrated by the horizontal shaded band [2.15]

Although the specific thermal conductivity of Al is higher than any other metallic material, the CTE is too high to be useful (23 x 10^{-6}/ºK). SiC additions decrease α without significantly degrading λ/ρ, and at $V_f \geq 55\%$, the CTE of DRA provides a good match with semiconductor materials and ceramic substrates. Diamond particle reinforced copper MMCs has also been studied to replace bulk metal heat sinks. Although, these MMCs were found to have improved thermo-mechanical properties, the required volume fraction of the reinforcement for property enhancement is as high as 60%. This, in turn, makes the diamond and SiC reinforced MMCs very difficult to machine for industrial applications. In search of the balance between machinability and thermo-mechanical properties, carbon fibres reinforced MMCs have also been explored for heat sink application. That only 30% carbon fibre reinforcement could reduce the CTE of aluminium and copper. Owing to the very low CTE in the longitudinal direction (-1 x 10^{-6}/ºK) carbon fibre reinforced aluminum and copper MMCs have been found to offer great promise as heat sink material. [2.15, 2.16]

Many applications require exceptional resistance to distortion from thermal or mechanical loads. Examples include hard disk drives, video recording heads, atomic force microscope (AFM) sample support frames, robotic arms, inertial guidance systems, satellite antennae, optical benches and high speed manufacturing equipment. Propulsion systems may also be viewed as precision device, since exacting dimensional tolerances must be maintained under operating conditions that impose high thermal gradients and mechanical stresses. The stiffness depends upon material characteristics such as elastic modulus (E) and density (ρ) as well as component geometry and the loading mode. Many precision components are well approximated as a beam under self-loaded mechanical bending and, for this arrangement, materials with higher values of $E^{1/2}/\rho$ possess higher stiffness to elastic deflections for a given mass. Thermal expansion generates stresses that can cause distortion. A large coefficient of thermal conductivity (λ) reduces thermal gradients and hence reduces thermally induced stresses. Thus, increasing λ/α ratio decreases the magnitude of thermally induced distortion. Figure 2.3 compares different materials against these two figures of merit.

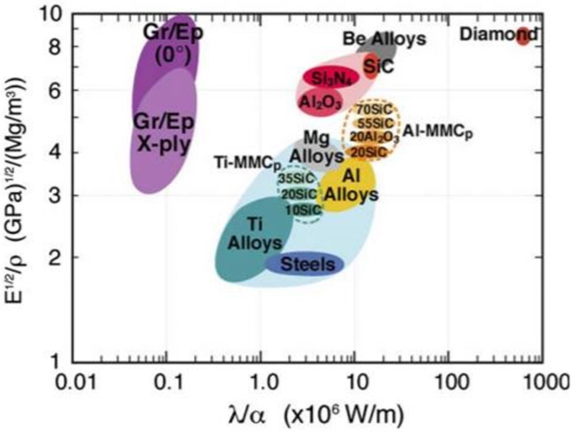


Figure 2.3 - Materials comparison for resistance to mechanical (vertical axis) and thermal (horizontal axis) distortions required for precision devices. Vibrational frequencies are well below the natural frequency of the device [2.15]

Ceramic particle additions to a metal alloy produce only a modest decrease in λ and a small change in ρ, but provide a significant decrease in α and a large increase in stiffness. Thus, MMCs provide improved resistance to distortion from both thermal and mechanical loads over unreinforced matrix alloys. As a class of materials, DRA exceeds all of the common structural metals in resistance to distortion. In addition, DRA competes with graphite/epoxy with respect to mechanical distortion, but has a resistance to thermal distortion that is two orders of magnitude higher [2.15].

Wear resistance is an important function in the balance of properties provided by MMCs. The addition of hard reinforcements intrinsically improves the wear resistance of the host metal.

Chemical compatibility between matrix and reinforcement is of fundamental and practical significance. Compatibility is needed so that the matrix and reinforcement retain their separate identity and properties during extreme thermal exposures of primary and secondary processing and application. Extensive chemical interaction degrades the mechanical and thermal properties and needs to be understood and controlled within bounds. Thermal compatibility is also required. A large difference in a between matrix and reinforcement will introduce deleterious residual stresses and deflections upon cooling from processing and forming temperatures and during application at elevated temperatures. Finally, differences in density can play an important role during liquid metal processing, as a large difference can lead to segregation.

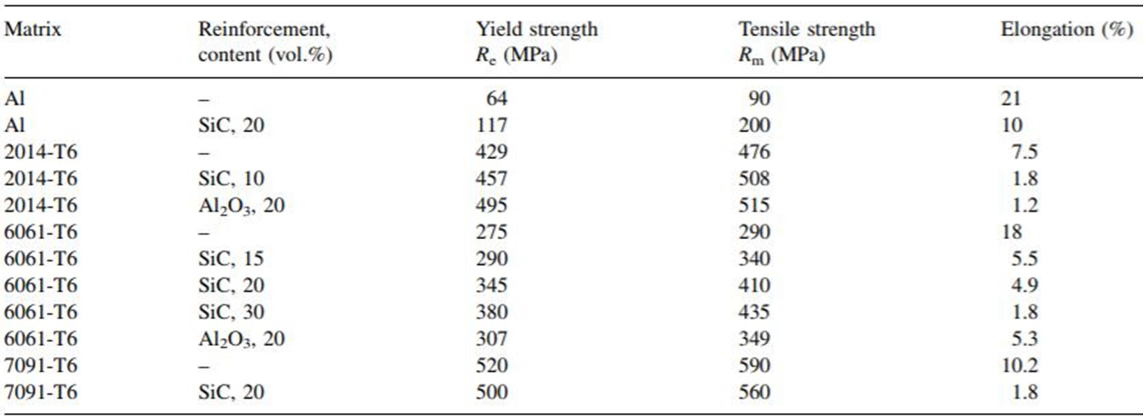
Currently produced and applied practically are composite materials based *on light metal alloys*, especially on magnesium alloys, aluminium alloys and titanium alloy matrices, as well as high temperature superalloys based on nickel reinforced by stable ceramic dispersion particles. Composite materials based on light metal alloy are characterised by very good mechanical properties and find applications in the production technology of aircraft and cars, in defence technology and in astronautics. Composite materials based on light metal alloys are reinforced with dispersion particles, platelets, short and continuous fibres [2.16].

The physical properties of *magnesium alloys* and especially the combination of mechanical properties, Young's modulus and density make them very useful for applications as the matrix of composite materials. Composite materials based on magnesium alloys reinforced by dispersion particles of silicon carbide (SiC) having very low density of 2.0-2.1 g/cm^3 and are characterised by 30-40% better mechanical properties than unreinforced magnesium alloys [2.16].

Composite materials based on magnesium alloys reinforced with ceramic particles presently find practical applications; composite material Melram 072 developed by Magnesium Elektron, is produced as composite pipes and application is foreseen in aircraft and car technology [2.16].

The mechanical properties of composite materials reinforced with ceramic particles depend on the matrix properties, mutual wettability at interphase, and the amount of reinforcing phase and the diameter of the reinforcing particles. In Table 2.2 are shown the mechanical properties of pure *aluminium and chosen aluminium based composite materials*, from which it is clear that the largest increases of mechanical properties are noted in the case of matrices characterised by low tensile strength. On the other hand, in the case of reinforcing of aluminium alloy 7091 characterised by high mechanical strength and reinforced by dispersion particles SiC of 5 and 13 mm diameter, ascertained even worsening of mechanical properties, which was explained by the weak bonding at the matrix/reinforcement interfaces [2.16].

Table 2.2 - Mechanical properties of aluminium based composite materials [2.16]

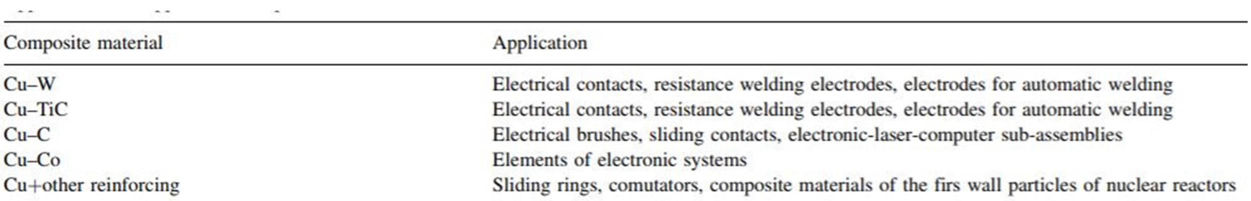


Matrix	Reinforcement, content (vol.%)	Yield strength R_e (MPa)	Tensile strength R_m (MPa)	Elongation (%)
Al	–	64	90	21
Al	SiC, 20	117	200	10
2014-T6	–	429	476	7.5
2014-T6	SiC, 10	457	508	1.8
2014-T6	Al_2O_3, 20	495	515	1.2
6061-T6	–	275	290	18
6061-T6	SiC, 15	290	340	5.5
6061-T6	SiC, 20	345	410	4.9
6061-T6	SiC, 30	380	435	1.8
6061-T6	Al_2O_3, 20	307	349	5.3
7091-T6	–	520	590	10.2
7091-T6	SiC, 20	500	560	1.8

The advantages of composite materials on aluminium alloy matrices such as high resistance to wear, good strength, and relatively good heat conduction, resulted in their practical application as discs of car brakes made, for example, by Alcan from A359 aluminium alloy reinforced with 20 vol.% of SiC particles [2.17].

Due to the fact that small additions of alloying elements to copper and existing impurities lower considerably its electrical conductivity (the addition of 0.3% Zn to copper lowers the electrical conductivity to 85% International Annealed Copper Standard (IACS), of 1.25% Al to 70% IACS and of 0.1% P to 50% IACS, taking into account that the electrical conductivity of pure copper is 58 MSm^{-1} = 100% IACS) the increase of its mechanical properties by conventional alloying methods is associated with considerable lowering of its electrical conductivity. On the other hand *composite materials on a copper basis* reinforced with dispersion particles having good mechanical properties are characterised by relatively good electrical conductivity. A recently developed method of mechanical alloying of copper powders makes possible the introducing of different dispersion particles such as tungsten, metal oxides and carbides into a copper matrix. The main applications of copper base composite materials by reinforced with dispersion particles are shown in Table 2.3 [2.16].

Table 2.3 - Applications of copper base composite materials reinforced with dispersion particles [2.16]



Composite material	Application
Cu–W	Electrical contacts, resistance welding electrodes, electrodes for automatic welding
Cu–TiC	Electrical contacts, resistance welding electrodes, electrodes for automatic welding
Cu–C	Electrical brushes, sliding contacts, electronic-laser-computer sub-assemblies
Cu–Co	Elements of electronic systems
Cu+other reinforcing	Sliding rings, comutators, composite materials of the firs wall particles of nuclear reactors

The dispersion particles that reinforced the *composite materials on titanium alloys* are mainly the titanium borides and carbides (TiB, TiC). Saito, Furuta and Yamaguchi from Toyota

Central Research and Development Laboratories produced powder metallurgy titanium based composite materials and ascertained a considerable increase of mechanical properties in comparison with sintered titanium [2.18]. Moreover, the mechanical high temperature properties of the titanium-based alloy composite materials were higher than those of the heat resistance steels. Taking into account the relatively low density of titanium alloys, very high specific mechanical properties of titanium-based composite materials are achieved. There are foreseen applications of titanium-based composite materials for the inlet and exhaust valves and connecting rods of internal combustion engines and gears. Mentioned parts, besides having very good mechanical properties, are characterised by very reasonable production costs in comparison with conventionally produced titanium parts and can be competitive against parts made of steel [2.16].

Nickel-based superalloys produced by powder metallurgy methods are characterised by better high temperature mechanical properties than conventional high temperature alloys. They find applications especially in jet engine technology and industrial turbines. Composite material produced by mechanical alloying is based on nickel alloy (INCONEL alloy MA6000) reinforced with very stable dispersion yttrium particles (Y_2O_3). The composite is characterised by very good mechanical properties at elevated temperatures, is resistant to creep and is of special importance in jet engines production technology [2.19].

Relatively little work has been published in the open literature on the class of *Fe-based and Ni-based MMCs* now used in a significant number of industrial applications. A wide range of matrix alloys is used, including a variety of tool steels (medium alloy, high chrome, hot work and impact resistant), martensitic stainless steels, maraging steels, and Ni-based superalloys. These super-hard MMCs typically use rounded particulate TiC reinforcements with $25 \leq v_f \leq 45\%$. TiC is thermodynamically stable in Fe and Ni matrices and has a low coefficient of friction, giving good lubricity and outstanding galling resistance.

Cast composite materials are mainly reinforced with *alumina fibres, carbon fibres and hybrid reinforcement* composed of ceramic alumina fibres and SiC particles.

Degischer et al. [2.20] produced composite materials based on magnesium and aluminium alloys reinforced with continuous carbon fibres, alumina fibres and silicon carbide fibres. The specific mechanical properties of composite materials produced by Degischer et al. are shown in Figure 2.4.

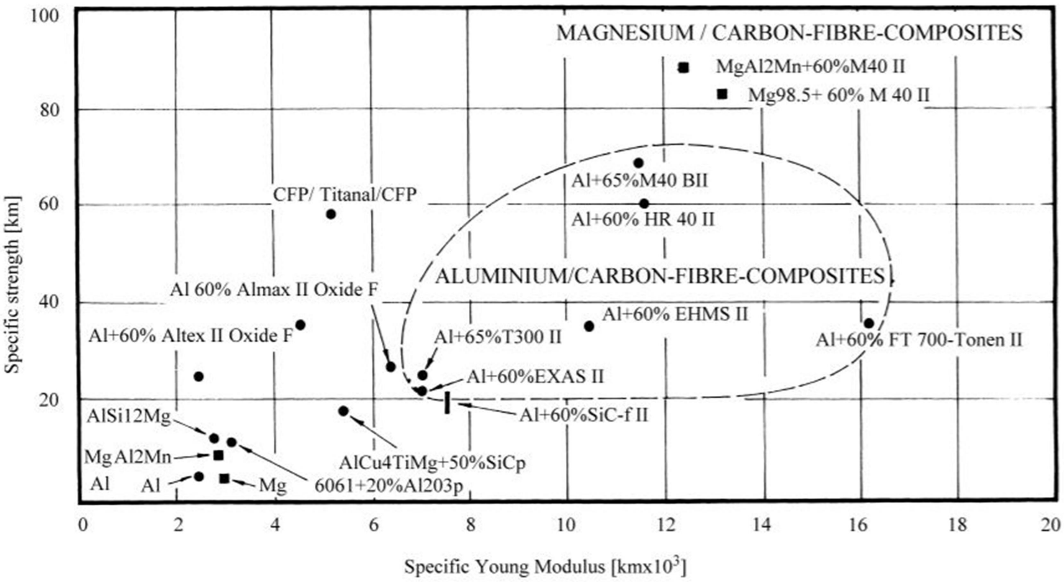


Figure 2.4 - Specific mechanical properties of magnesium and aluminium based composite materials [2.16]

Aluminium-based composite materials are now produced on a large scale by squeeze casting methods of porous preforms made of ceramic fibres. Figure 2.5 is shown the structure of porous preform made of alumina oxide ceramic fibres ``SAFFIL" [2.21]. As mentioned earlier, reinforcing of the matrix results in increase of mechanical properties and in Figure 2.5 the considerable effect of the reinforcing fibres content on the tensile strength is shown. Other development properties are improved, such as fatigue strength and resistance to wear. On the other end, the thermal stability of the composite materials is improved due to the effect of the reinforcing fibres content on thermal expansion [2.22].

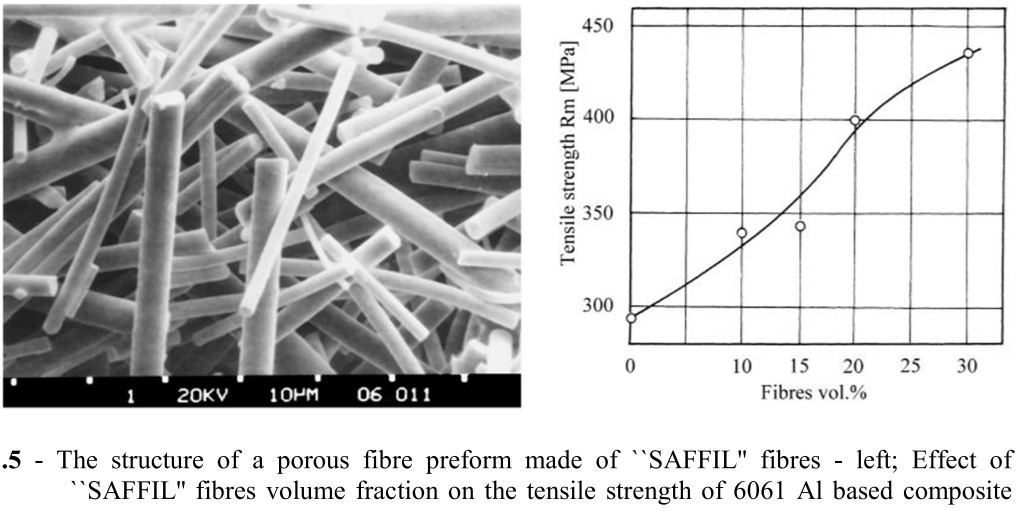


Figure 2.5 - The structure of a porous fibre preform made of ``SAFFIL" fibres - left; Effect of ceramic ``SAFFIL" fibres volume fraction on the tensile strength of 6061 Al based composite material produced by squeeze casting - right [2.21-2.22]

Aluminium-alloy based composite materials reinforced with ceramic fibres in the form of tubes are manufactured by GKN Automotive (USA) and are applied as Cardan shafts in passenger cars [2.17].

Carbon fibre reinforced metal matrix composites also possesses high wear resistance, and thus found application in bearings and wear part (40 vol% of short carbon fibres not only improves the wear resistance of Cu, but also improves the friction coefficient). Owing to the high temperature strength and self-lubricating effect of carbon fibres, other chemical and physical properties such as, modulus, strength, toughness, electrical conductivities of these MMCs also tend to be superior. As a result, carbon fibres MMCs have received great attention from the aircraft, aerospace, automobile and electronics industries.

Important MMC applications in the ground transportation (auto and rail), thermal management, aerospace, industrial, recreational and infrastructure industries have been enabled by functional properties that include high structural efficiency, excellent wear resistance, and attractive thermal and electrical characteristics. MMCs are now an established materials technology [2.15].

The major applications served by MMCs in the *automotive sector* include selectively reinforced pistons for diesel engines, selectively reinforced cylinder bores in Al engine blocks, intake and exhaust valves, driveshafts and propshafts, brake components (discs, rotors and calipers) and power module components for hybrid and electric cars. Honda developed a simple process for producing the cylinder bore ceramic preform from chopped Saffil and graphite fibres and for integrating the preform infiltration with the engine block casting process (Figure 2.6).

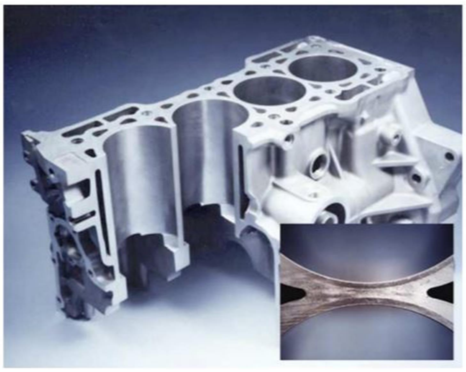


Figure 2.6 - Honda Prelude 2.0 l cast aluminum cylinder block with an inset showing the selective reinforcement for the cylinder liner. The cylinder liner and the engine block are cast in a single operation, eliminating the need for separate inserts and the additional processing steps associated with inserting separate liners [2.15]

The most commonly used MMCs for *thermal management* include Cu/Mo and Cu/W. Be/BeO MMCs are used in high performance applications. Over 1 million MMC thermal management piece parts are produced annually. The largest market segment is for radio frequency (RF) microwave packaging used in telecommunications and radar systems.

Aeronautical MMC applications have been established in the aerostructural, aeropropulsion and subsystem categories.

Industrial applications include cemented carbide and cermet materials, electroplated and impregnated diamond tools, Cu and Ag MMCs for electrical contacts, erosion-resistant cladding for the petrochemical industry, Cu-infiltrated steel components, and TiC-reinforced Fe and Ni alloys. While most of these materials and markets are established and stable, this last class of MMCs represents a new market of growing importance, where exceptional hardness and resistance to wear are of primary importance. These TiC-reinforced Fe and Ni MMCs are used in wide range of industrial operations such as cutting, rolling, pelletizing, stamping, piercing, warm metalworking, drawing, forming and punching. Components include hammers, impact dies, canning tools, crimp rollers, check valves, extruder nipples, bending dies, extrusion dies and hot forging die inserts.

MMCs components used in the *recreational market* include bicycle tubing, track spikes and lacrosse stick shafts. *Infrastructure applications* include Al/B_4C MMCs for nuclear waste containment and continuously reinforced Al/Saffil MMCs for overhead power transmission conductors.

When they were first entering commercial applications, MMCs were viewed as niche materials. This characterization was often used as pejorative, suggesting that MMCs applications were intrinsically limited to a narrow set of specialized requirements. In these early niche applications, MMCs were selected because they offered the best overall solution in a competition between different materials for the particular application. These applications can typically be characterized as point insertion, where a material substitution was made to overcome some deficiency of the original material while maintaining the overall form, fit and function of the initial design. The growing commercial importance of MMCs results less from any fundamental shift in the nature or capabilities of MMCs, and more from the fact that they compete successfully in the broad range of applications and markets described above, some of which are sizeable [2.15].

2.2.4. Polymer Matrix Composites (PMCs)

Polymer Matrix Composites are based on the combination of stiff, strong reinforcement fibres with either thermoset or thermoplastic polymer matrices and are used in structural composite applications (are currently by far the most significant matrix category in this field) [2.23].

In order to be used as a matrix the polymers must present the following requirements:

- Good mechanical properties – the matrix must be as resistant as possible and be characterised by a high strain capacity.
- Good adhesive characteristics at the interface with reinforcement so as to guarantee effective load transfer.
- Capacity to resist environmental conditions, specifically water, chemical reactions, radiation, temperature, etc. [2.2, 2.4].

However, thermosets clearly dominate in structural composite applications, although thermoplastics have lately received increased attention also in continuous-fibre reinforced composite applications due to a number of attractive potential advantages.

The variables to take into account when selecting a polymer for use as a composite matrix are reinforcement-matrix compatibility in terms of bonding, mechanical properties, thermal properties, cost, etc., though perhaps the most important aspect may be its processability, i.e. how easy it is to deal with it in manufacturing situations. Among the many issues that may be considered part of processability are, viscosity, processing temperature, processing time and health concerns. Low viscosity is important in achieving reinforcement impregnation, where each reinforcing fibre ideally should be surrounded by the matrix without voids present. Not yet crosslinked thermosets have shear viscosities at processing temperature on the order of 10^{0} Pa·s, while melt viscosities at processing temperature of thermoplastics are on the order of 10^{2} Pa·s or higher (for comparison the shear viscosity of water at room temperature is 10^{-3} Pa·s), meaning that it is much easier to complete the impregnation with thermosets than thermoplastics. While some thermosets may be crosslinked at room temperature, other thermosets and all thermoplastics require an increased processing temperature that in general must be well controlled and may be as high as several hundred degrees Celsius for some polymers. While thermoplastics only need to be melted, shaped and then cooled to achieve dimensional stability in a matter of seconds at one extreme, thermosets may take several days to fully crosslink at the other extreme. The very nature of thermosets makes them unpleasant to work with from health point of view, since chemical reactions involving volatile and potentially toxic substances are require to crosslink the polymer. Table 2.4 presents the principal characteristics of thermoset and thermoplastic polymers [2.5].

Table 2.4 –Main characteristics of thermosetting and thermoplastic polymers [2.4, 2.5]

Property	Thermosets	Thermoplastics
Cost	+	
Temperature tolerance	+	
Thermal expansion	+	
Volumetric shrinkage	+	
Stiffness	+	
Strength	+	
Toughness		+
Fatigue life	+	
Creep	+	
Chemical resistance		+
Available material data	+	
Raw material storage time (shelf life)		+
Simplicity of chemistry		+
viscosity	+	
Processing temperature	+	
Processing pressure	+	
Processing time		+
Processing environment		+
Mould requirements	+	
Reformability		+
Recyclability		+

Characteristics of thermosetting and thermoplastic polymers	
Thermoset	**Thermoplastic**
Limited store time	Recyclable
Low viscosity	Grater chemical simplicity
Greater stiffness and mechanical strength	Unlimited store time
High level creep and fatigue resistance	High viscosity
Processing with chemical reaction (curing)	Require high processing pressures and temperatures
Require low processing pressures and temperatures	High toughness
Processing requires simple moulds	Low creep resistance
	Low thermal and dimensional stability
	Processing without chemical reaction
	Processing requires complex moulds
	Faster production cycles

In polymer-matrix composites, the common reinforcement types are (in order of decreasing importance) glass, carbon and polymer. The composite reinforcement may be discontinuous ("short fibres") or continuous ("endless fibres") and randomly oriented or aligned (Figure 2.7). The composites can be also particulate reinforcement, by spheres, rods, flakes and many other shapes of roughly equal axes (Figure 2.7) [2.5].

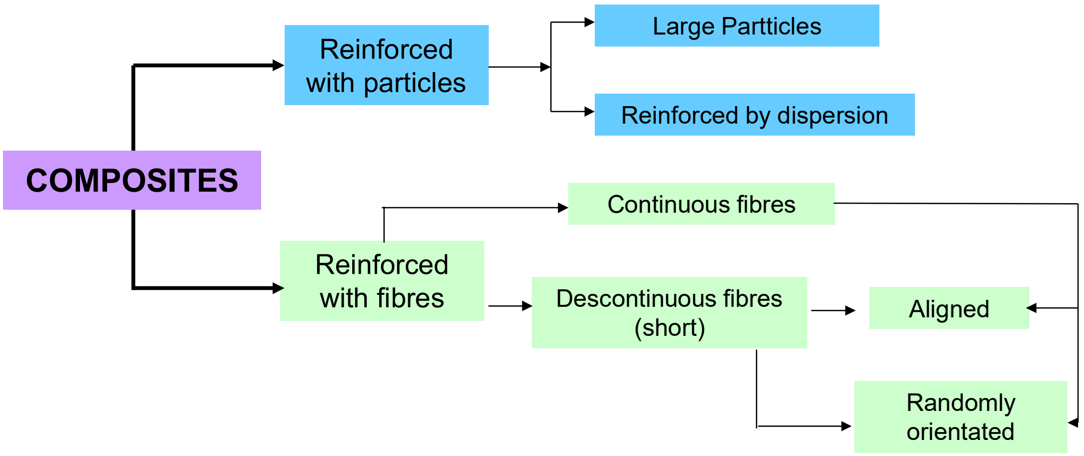


Figure 2.7 - Classification of composites in terms of reinforcement type [2.4]

It should be understood that the individual fibres have a diameter of the order of 10 μm and that it would be inconvenient, to say the least, to build a substantial structure starting with single filaments. In practice, the fibres are assembled in bundles, known as tows (textile nomenclature) or strands (glass terminology); these may contain anything from a few hundred to several thousand filaments. It is sometimes necessary to create even larger bundles by bringing together a number of tows (strands) into rovings. These provide a linear reinforcement which may be used directly in processes such as filament winding and pultrusion. In most cases, it is more convenient to produce an intermediate sheet-like reinforcement format. These include random mats, prepreg, woven and knitted fabrics, braids and some newer non-crimp fabrics in which essentially uniaxial layers are stitched, or bonded, together to form a multi-layer, multi-axial fabric. Fabrics are now available which incorporate a layer each of fibres in the 0°, 90° and ±45° orientations. Fabrics are also now being developed in which a proportion of the fibres run in the direction normal to the plane of the fabric to provide a measure of three-dimensional reinforcement. There is inevitably a limit to the amount of fibre that may be packed into a given available space. Thus, by placing fibres in multiple directions, the proportion in any one direction must be reduced. A balanced plain woven cloth has 50% of the fibres in each of two directions, whilst geometric and processing considerations limit the overall fibre fraction to about 0.5. There will then be an equivalent of 0.25 v_f in each of the directions; however, the reinforcing efficiency is further reduced by the crimp induced by the weaving process. A random mat is a rather inefficient method of packing fibres. Overall fibre fraction cannot exceed about 0.3, and as these are aligned in all directions the stiffening effect in any one is less than 10% of what might be obtained from a uniaxial arrangement. The advantage of a random mat lies in its low initial cost and ease of processing [2.23].

Since the reinforcement is the primary load-bearing constituent, its configuration (form and degree of orientation in the matrix) is critical to the macroscopic properties of the composite. It should therefore come as no surprise that the most impressive mechanical properties are found with continuous and aligned reinforcement. In order to provide a useful increase in mechanical properties, the composites generally must have a substantial volume fraction (~10% or more) of the reinforcement [2.5-2.6].

Probably the most common reason why polymer composites are used in structural applications is that they offer a given property, often stiffness, at lower weight more than the competitor, which most of time is a metal, but sometimes also plastic, wood or concrete. One therefore talks of excellent specific stiffness and strength, i. e. property normalized with density. There are numerous potential advantages of composites other than their excellent structural capabilities, including corrosion resistance, electric insulation and reductions in tooling and assembly costs, and any more. Modern composite materials are usually optimized to achieve particular balance properties for a given range of applications and are also used for electrical, thermal, tribological and environmental applications [2.5-2.6].

While it is easy to become impressed with the potential advantages of composites, the disadvantages must not be ignored. It is probably essentially true that if one disregards cost, a polymer composite can outperform any other engineering material in all respects except temperature tolerance. It is, nevertheless, rare that the cost is not important, thus one also has to take into account less desirable traits of composites, such as high raw material cost, lack of knowledge and experience and difficult manufacturing. Composites are, therefore, certainly not appropriate in all applications; a critical assessment of the materials alternatives must always be made in terms of performance-to cost ratio. The performance of composites is determined by the properties of the fibre, the fraction of fibre in the composite and the structure, or fibre architecture. Processing technologies have been developed which maximise fibre content and precisely control the fibre architecture allowing for the manufacture of components with mechanical properties tailored to service requirements. This makes them attractive for applications where high mechanical performance and minimum weight are important. However, the wider acceptance of composites is based on their ability to offer a more cost-effective alternative. In particular, composites also allow a dramatic reduction in the parts count in many applications, which leads to significant manufacturing advantages and greater economy [2.5, 2.6, 2.23].

2.3. Thermoplastic matrix composites market

2.3.1. Introduction

Rapid industrialization in developing economies from Asia Pacific and increasing demand for wind energy are expected to augment market growth. High demand from automotive industry is anticipated to further propel market growth. Rising fuel prices have triggered the need for fuel-efficient vehicles. This factor is projected to positively influence market growth in near future [2.24].

Composites are most widely used as a replacement for steel on account of their higher strength to weight ratio. Presently, a substantial number of vehicles use conventional fuel technologies such as petrol and diesel. This has led to a rise in demand for fuel-efficient vehicles. Increasing environmental concerns and stringent regulations regarding pollution control have forced automotive manufacturers to use advanced technologies and develop vehicles to reduce pollution.

Extensive R&D activities in Japan and Europe have led to emergence of numerous market players, which in turn, is expected to drive the market demand. For example, presence of key industry players such as Toray Industries Inc., Teijin Limited, and Mitsubishi Rayon Co., Ltd. in Japan has boosted regional product demand.

Growing aerospace industry in North America and Europe is also anticipated to fuel the market. Escalating demand for commercial aviation on account of increased disposable income and globalization is driving aerospace industry over the last few years. This key trend is expected continue over the forecast period as well.

Due to increasing concerns about the weight of aircraft, greater demand for light composites by the aeronautical industry is expected to reduce fuel consumption. Commercial aviation has increased the usage of composites to around 50% of total weight of the aircraft. Airbus A350 is built utilizing 52% CFRP, while Boeing 787 Dreamliner is built using 50% CFRP in terms of weight. Surge in commercial aviation is expected to drive the global CFRP market over the forecast period.

Glass fibre composites emerged as the largest product segment in the global composites market. Also known as fibreglass, this composite is made of fibre glass filaments. Fibreglass is robust, lightweight, and strong material, but has lower stiffness than carbon fibre. Glass fibres weight properties and bulk strength are very favourable compared to metals.

Carbon fibre is expected to register fastest growth next years. Carbon fibres are combined with other materials to form a composite. Carbon fibre reinforced polymer is formed when carbon fibre is moulded with polymeric matix. Properties of carbon fibres such as low weight and thermal expansion, high stiffness, temperature tolerance, and high chemical resistance makes it very popular in industrial and other applications.

Thermoset resin was estimated to be the largest market globally, with a share of 83.3% in 2015. Thermoset or thermosetting composites are synthetic materials that get strengthened when heated. They cannot be remoulded after the initial heating. Thermosets products are stronger owing to cross linking and are also suited for high temperature.

Thermoplastics harden when cooled down without losing their plasticity. They can be re-melted and reshaped when reheated above their processing temperature. Thermoplastics are less expensive, fusion weldable, extra tough, non-toxic, and recyclable for other processes.

Layup was the dominant market globally, with a share of 30.9% in 2015. Layup is the most basic method for production. The process involves placing a layer of fibre in a sequence by using a matrix of resin and hardener. The layup is then allowed to set at room temperature. The curing process can be accelerated by applying heat with an oven. Hand layup process is a low cost tooling technique and includes a wide choice of material types and suppliers.

Asia Pacific is expected to continue its dominance over the forecast period. Increasing production of boats, wind turbine blades and architectural mouldings are expected to fuel the growth of layup product market in Asia Pacific.

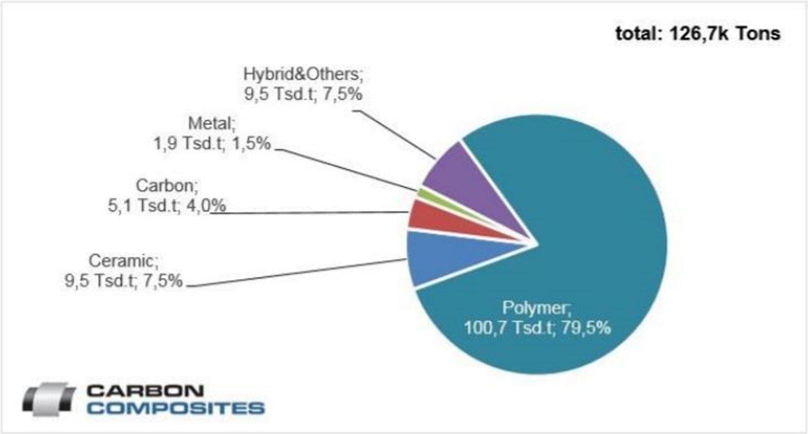
Transportation accounted for the largest share of 20.8% in 2015. Advantages of durable and lightweight materials are appreciated in design, manufacturing efficiencies, and fuel savings for autos to buses to trains, across the transportation spectrum. Manufacturers in the bus and light rail markets use composites to enhance fuel efficiency and interiors. Top suppliers require corrosion resistant, fire retardant, and durable products to fulfil demand for adhesives, resins, putties, reinforcements, and gels in transportation applications.

The market has observed backward as well as forward integration from various raw material manufacturers. Self-procurement of raw materials along with production and utilization of carbon fibre helps manufacturers cut down logistics cost and cater to end-use product manufacturers directly to increase profitability. CFRP applications depend on the grades used and ultimately on the quality of precursor. Various manufacturers have developed their own manufacturing technique to gain competitive advantage. CFRP is manufactured as per client requirement for special applications such as aerospace and high performance cars.

Key market players such as Cytec Industries, Toray industries, Mitsubishi Rayon Corporation, Hexcel, and Hyosung have integrated major part of their value chain ranging from production and raw material supply to CFRP distribution. High level of integration enables companies to cut down on cost associated with raw material procurement and strengthens their market share with development of specialty products. Key market players have their own patented technologies and they have presence across all levels of a value chain [2.24].

2.3.2. The global Carbon Composites Market

Almost all of the carbon fibres produced are further processed into composites. In each case, the fibres are embedded in a matrix material to combine the best properties of the two diverse material classes into a single material. Along with many other advantages, carbon fibre composites have above all a particularly high potential in lightweight design. Depending on the application, various metal alloys (Metal Matrix Composites; MMC), ceramic materials (Ceramic Matrix Composites; CMC) or also Carbon (Carbon Fibre Reinforced Carbon; CFC) can serve as a matrix material. However, the majority of composites are assembled with a polymer matrix (carbon fibre reinforced polymer, CFRP). Figure 2.8 depicts a breakdown of carbon composites (CC) according to matrix material and is itemised according to demand volume and quantity. The largest market segment CFRP (by turnover) is again further broken down regarding the polymer matrix employed. Here a more detailed description of turnover could be shown based on data provided. It is evident that the majority of carbon composites, based on turnover generated (approx. US $13.23 billion; 70%) as well as regarding to volumetric amount (approx. 109,6k tons; 86.5%), fall under the CFRP sector. Thermoset matrix systems dominate this market with around 71.5% (approx. US $9.46 billion). However, over the past few years, a steady increase in the proportions of thermoplastics from approx. 24% (2014), over 25% (2015) and up to 26.3% (2016) can be seen. All other polymer matrix materials currently only appear in a very small market volume. In the future, the area of elastomers could prove to be interesting, for example for hinge-free elastic connecting elements or as form-variable adaptive structural components. Non-polymer matrix materials occupy around 20% of the whole market and with that, generate a relatively high turnover. This is mainly due to the fact that these material combinations are frequently applied to individual niche applications (e.g. aerospace) and a particularly high price is paid for such special solutions [2.25].



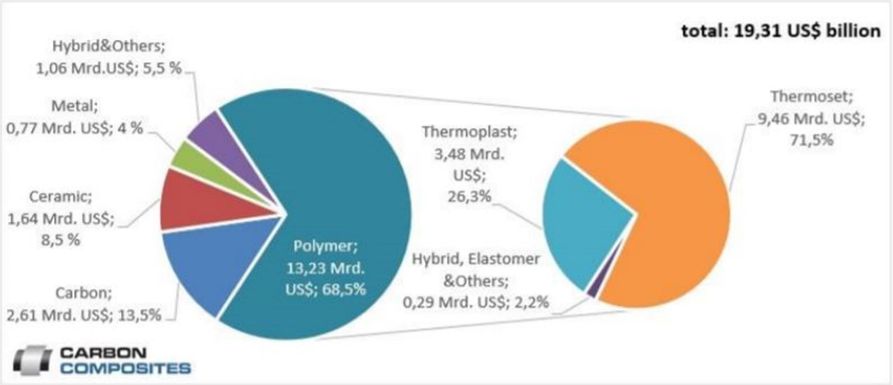


Figure 2.8 - Distribution of the global Carbon-Composites market by matrix-materials with reference to demand (above) and turnover (below; 09/2017) [2.25]

As seen in Figure 2.9, the material class CFRP currently represents the most relevant segment for the carbon composites market. This material combination, primarily based on its excellent lightweight design potential, will be considered as an essential growth engine within the industry for the next few years. Correspondingly, the global demand volume for the CFRP sector in 2016 is around 101k tons so that this year the significant benchmark of 100k tons CFRP demand volume was successfully exceeded. This corresponds to a growth of 10.99% based on the previous year (91k tons) and lies just above the predicted development. This results in annual growth rate (CAGR) of around 11.98% from the year 2010. A further positive development with double-digit growth figures in the range from 10 to 13% is also expected for the following years. The overall worldwide turnover, for CFRP in 2016, totals to approx. US $13.23 billion. This corresponds to a growth rate of approx. 14.05% compared to the previous year (US $11.6 billion).

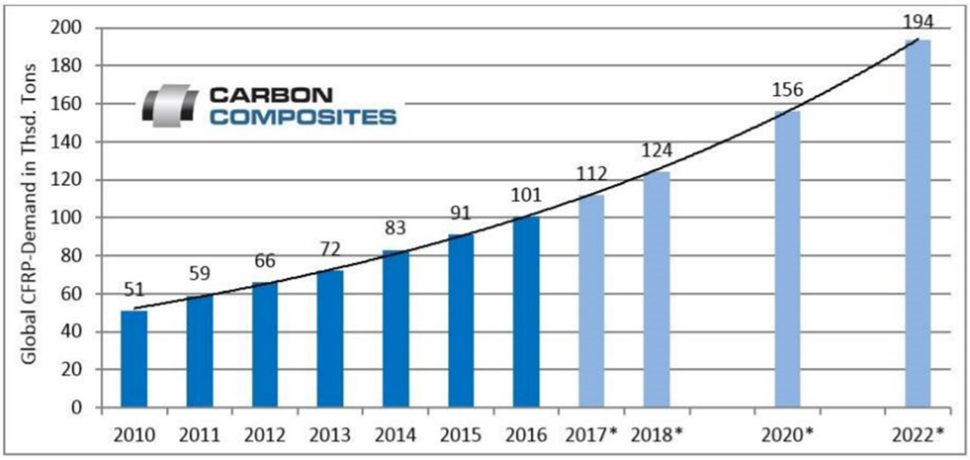


Figure 2.9 - Development of the global CFRP-Demand in Thsd. Tons from 2010 until 2022 (*Estimation; 09/2017) [2.25]

A variety of different production processes are used in the manufacture of CFRP materials/components (see Figure 2.10). Layup processes using prepregs (37%) continue to account for a major proportion of processes employed. However, pultrusion and filament winding are gaining importance and now represent a combined total of 40% of the market as they capture market share from prepregs. As well as easy-to-automate pressing and injection processes (e.g. RTM), the manual processes of wet lamination and vacuum infusion/infiltration are also frequently used [2.26].

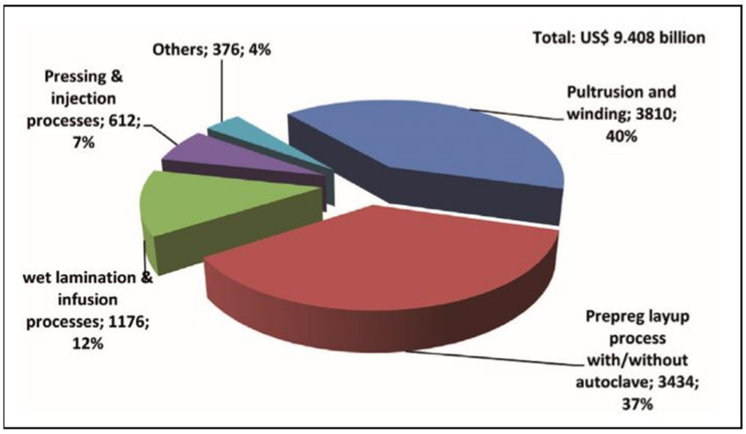


Figure 2.10 - CRP market share in US$ million by manufacturing process (2013) [2.26]

It can be seen in Figure 2.11 that the turnover generated worldwide in the CC sector is distributed almost equally between the three regions shown. In comparison to the previous year and referring to demand volume, a particularly strong growth rate of 13.06% (2015: 26.9k tons) for the Asian region can be determined. Other regions also boast significant growth rates of 7.67% (North America; 2015: 44.3k tons) and 7.8% (Western Europe; 2015: 40.8k tons). For the rest of the world, there is a smaller growth rate of roughly 4.2% (2015: 4.6k tons). It is assumed that this development is attributed to the Asian economic structure within the entire carbon market. At the same time, large carbon fibre production capacities are already being established in the respective countries in 2016, of which clearly exceed their own requirements. Accordingly, it is assumed that the domestic demand for composite materials on this basis only increases somewhat over time. On top of that comes strong government programs, such as activities in South Korea (economic hub of Northeast Asia), and especially those connected with the announced investments from Hyosung. Furthermore, it can also be assumed that an economic protectionist strategy could lead the subsequent manufacturing industry to settle domestically or to fix it by means of strategic partnerships in Asian locations. Therefore, given the current status, this trend is expected to continue further into the following years.

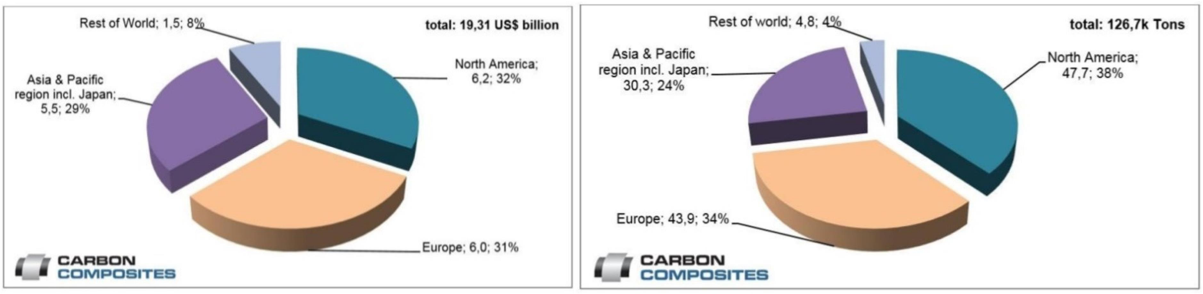


Figure 2.11 - Global CC-Turnover in US$ billion by region (09/2017) - left; Global CC-Demand in Thsd. Tons by region (09/2017) – right [2.25]

It is clear in Figure 2.12 that the aviation and aerospace sector, as in previous years, currently represents the most significant market segment in terms of turnover. Even though the requested demand volume (37,93k tons; 30%) only just lies above the demand volume of the automotive sector (27,88k tons; 22%), the turnover, which is roughly 60% of the total worldwide turnover for the CC market, is considerably higher. This is due to the higher quality expectations and approval costs, which lead to comparably higher prices per kilo. The establishment of the A350XWB, A380, B787 and B777X programs in the commercial aviation sector is a major contributor to this development, with growth rates of around 8% between 2015 and 2016 recorded. Furthermore, there are also currently activities in the area of carrier rockets in the space travel segment. Both the Falcon9 (SpaceX) as well as Ariane 6 (ESA/ASL) will be designed in large proportions with the aid of CC. There are also increasing efforts in the Asian region to expand the national aerospace segment considerably. In addition to new large-scale activities in India, the development in China is particularly interesting. In the commercial aviation sector, the Comac C919, which successfully conducted its maiden flight in Mai 2017, should act as a direct competitor to Airbus A320 and Boeing

B737. Aside from this, the space travel program is also being strongly propelled forward by the construction of China’s own space station.

The automotive sector makes up the second largest segment for the demand volume and turnover. Here, the joint venture between BMW and SGL take on a leading role. Within the scope of the i-series project, it has already been successfully demonstrated that the use of carbon fibre composites in automotive serial applications is possible, whereby the achieved high lightweight design potential synergises very well with the emerging trend of E-mobility. Approximately 24.000 units of the i3 and 5500 i8 were sold in 2015, for 2018 a sell-off of approx. 33.000 i3 is expected. It can be anticipated that by 2021, the i-Portfolio will be expanded to the new iNext model, whose format up until now strongly resembles that of the BMW 5er series and is expected to close the existing gap for to an electric car. Electric or hybrid versions of the X3 and Mini models are also expected to be released onto the market, with the latter model ready by 2019. While no complete composite structural vehicle body is planned at this stage, it is however probable from today's point of view that the experience from the i-series projects will also be transferred over to individual assemblies. Such a transfer has already been successfully performed in the 7er series by BMW through the skillfull combination of metal and CFRP called “Carbon Core Technology”, whereby 64.000 saled units have already been achieved in 2016 and a 100k order of magnitude is conceivable on long-term. An exciting development is also expected for Volvo in the upcoming years. For their XC90, S90 and V90 models, a composite transverse-leaf spring will be put into service. Through collaboration between Benteler-SGL and Henkel, an innovative high-speed RTM process based on the two component polyurethane resin system Loctite MAX2 has been developed for this specific application. At present, the spring is implemented with glass fibre reinforcement. A transfer to carbon fibre reinforced structures seems possible and offers the potential for a high-volume application in the automotive industry with over 500.000 units per year from 2018. In addition, the activities of Hyundai in collaboration with their Intrado model (Crossover/SUV) are of particular interest for the ongoing development in the following years. The associated concept car was already presented in 2014 and exhibits a significant amount of CFRP, whereby large assemblies are to be implemented in a braiding process with the help of the Axontex system. The assigned carbon fibres will be coming from Hyosung (Tansome fibre) out of South Korea. In light of the announced investments, an earlier entry into the market seems possible here. In summary, a growth rate of 12.5% (turnover related) and 9.4% (based on demand volume) could be determined for the automotive sector between the years 2015 and 2016. The wind energy sector also experienced a strong upswing of around 11.5% (turnover) and 12.7% (demand volume) with reference to the previous year. This development is presumably due to the further intensified ambitions of energy transition, and the growing interest in large wind power plants. Particularly in Europe and Asia, there is a growing willingness towards the comprehensive implementation of climate change objectives, and here renewable energies will always play an important role in the future. Virtually all of the latest generation of large design wind power models implement significant volumes of carbon fibre composites, especially in the tension- and compression-chords.

Based on the given data sets, not all fields of application can be represented in detail and as a result the “Medical Technology" sector (primarily prostheses and X-rayboards) has been intergraded into the category "Other".

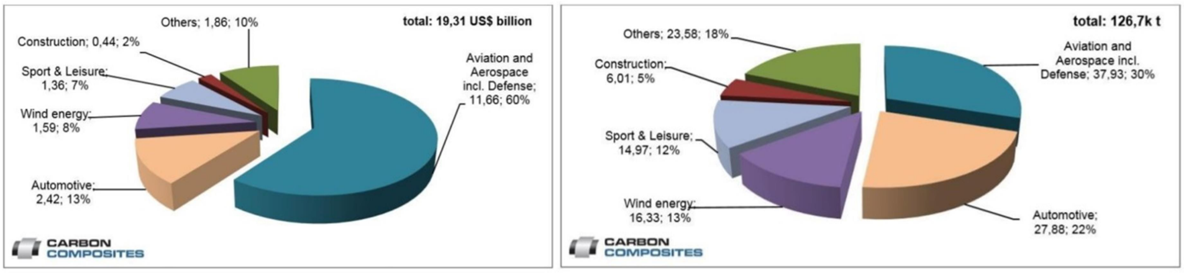


Figure 2.12 - Global CC-Turnover in Thsd. Tons by application field (09/2017)- left; Global CC-Demand in Thsd. Tons by application field (09/2017) – right; [2.25]

Figure 2.13 shows a forecast of CC demand worldwide in thousands of tons by 2022, broken down by field of application. Assuming that the growth within the automotive sectors will continue to be relatively high, the corresponding demand of the aviation and aerospace sector (incl. defence) will be exceeded by the end of 2020. In this scenario, approximately 30% of the global demand of approximately 239k tons is attributable to the automotive sector. The three following fields of application exhibit very similar growth potential and maintain their fundamental allocation. The “Sports & Leisure” and “Construction” fields show a somewhat weaker growth here and must provide new innovations for a higher evaluation. It should be noted here that, in principle, very large application potentials with comparatively very large numbers and quantity are available, especially in the construction sector. Therefore, as soon as only a few application points are passed through, the conservative benchmark shown here can be clearly exceeded.

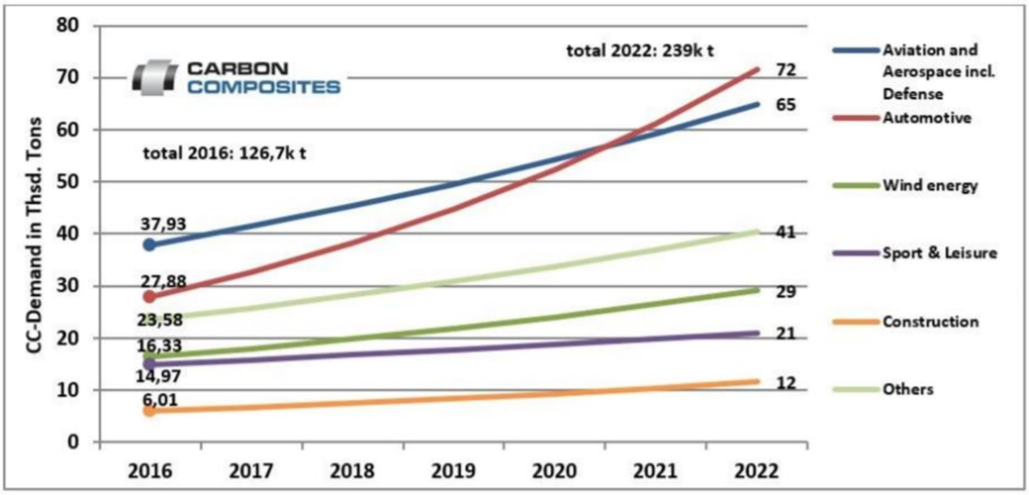


Figure 2.13 - Global CC-Turnover in Thsd. Tons by application field (09/2017)- left; Global CC-Demand in Thsd. Tons by application field (09/2017) – right; [2.25]

If you were to divide the worldwide turnover of CFRP generated in 2016 of US $19,31 billion by the worldwide CC demand in 2016 of 126,7k tons, you would receive an “imaginary” weight-based CC price – averaged across all sectors and applications – of 152 US$/kg. A corresponding calculation alone for the CFRP sector (turnover: US $13.23 billion, demand: 101k tons) gives a sector average of 131 US$/ kg. If the significance of these figures is only small, it is nevertheless still possible to obtain an outline of the market overall. The best cross-industry kilo-price available can therefore only be within a frequency distribution around this average value. Using the data presented in Figure 2.12, the following sector-specific values for the CC market can be determined: Aviation and Aerospace incl. Defence: 307 US$/kg, Wind Energy: 97 US$/kg, Automotive: 87 US$/kg and Sport & Leisure: 91 US$/kg.

The global market for carbon fibres and carbon composites has shown a strong and stable growth since 2009. This progress has continued into 2016 across the individual market sectors and applications, and in doing so, was able to exceed the significant milestone of 100k tons for the CFRP demand volume.

The profitability of the existing business model was further underpinned in the past few years through large planned investment measures of the fibre manufacturers and also through the steady new announcements in 2016.

In general, the carbon fibre reinforced composites are a comparatively new material class. The broad range of potentials is traditionally opposed to a certain degree of market inertia until a broad acceptance is achieved. Especially within the last few years, remarkable progress has been made in all fields of research and development, so that today CFRP is fully recognized as a construction material in many fields of application. Nevertheless, new performance potentials are continuing to be revealed in all areas and the resulting knowledge transferred to ever new fields of applications. In a global perspective, numerous new regional competence centres are being set up and existing structures are being expanded.

Furthermore, the CFRP light-weight segment also benefits from the general growth of other fibre-reinforced composites, such as aramid and glass fibres, due to frequently transferable processing processes and the possibility of hybrid solutions. For example, the aramid segment currently reported strong growth figures, with DuPont investing around US $500 million to increase their aramid fibre production (trade name: Kevlar) by approx. 25% [2.25].

In 2017, the global CFRP-Demand was determined to be 114kt. As compared to the year before this represents a growth of 11.4%, exceeding the previous report´s expectations. The average annual growth rate (CAGR) therefore results in 12.8% since 2010. The worldwide overall turnover with CFRP in 2017 amounts to approx. 14.73bn US$ and a growth of approx. 11.3% compared to the previous year was achieved. This corresponds to an average annual growth of 11.88% since 2013 (CAGR) [2.27].

2.3.3. The European GRP Market in 2017

Fibre reinforced plastics or composites are manufactured using a variety of reinforcing materials, e.g. glass, carbon or natural fibres. Glass fibre reinforced plastics (GRP) dominate the composites market accounting for approx. 95 % of its total volume. In 2017, the GRP market grew – for the fifth consecutive year – by 2 % compared to the previous year in the European countries studied in this report. As in past years, the volume of GRP manufactured in Europe (1.118 million tonnes) reflects the different trends observed in the various market segments. Production of thermoplastics, used primarily in the automobile industry, is generally still growing more strongly than production of most thermosetting materials. However, in 2017, the strongest area of growth in production volume (5 %) was continuous processing – especially the pultrusion process. The majority of these processes use thermosetting materials. In the European region, Germany remains the country with the largest GRP production in absolute terms and the strongest growth. Growth has been consolidating in Southern Europe – Italy, France, Spain and Portugal. Currently, production volume is not contracting in any European country/region [2.25].

The GRP materials considered here include all glass fibre reinforced plastics with a thermoset matrix, glass mat reinforced thermoplastics (GMT) and long fibre reinforced thermoplastics

(LFT) as well as all the quantities of continuous fibre reinforced. Data on European production of short glass fibre reinforced thermoplastics are only available as an overall quantity and therefore stated separately [2.25].

Following the slump in European GRP production during the economic and financial crisis – between 2007 and 2009 – the composites industry is now enjoying its fifth successive year of growth. As in previous years, it is clear that the trend in the first six months of the year is more positive than in the second half. In 2017, the European GRP market is expected to grow by 2 % to an estimated total of 1.118 million tonnes (Figure 2.14).

Figure 2.14 - GRP production volume in Europe since 1999 (kt = kilotonnes, 2017 = estimate) [2.25]

The largest buyers of GRP components are to be found in the transport/mobility and construction sectors. These each consume around one-third of total production and play a major role in national economies. No significant changes have been observed here over recent years. The key role played by these two most important sectors in national economies is one reason why the production of GRP tends to follow the long-term growth trend in GDP. Significant changes in vehicle production in individual countries or a booming construction sector have an immediate knock-on effect for suppliers and thus for the industry. Some GRP components are already firmly established as construction materials. Although there is still excellent potential for new applications, GRP materials are already standard products. As these are in relatively widespread use and production levels are considerable, no dramatic growth in production volume can be expected over the coming years (in contrast to the relatively small CRP segment). Even strong growth in individual segments has a relatively small impact on total production due to the large volumes involved. The diverse nature of the market means that fluctuations in one customer industry are usually “smoothed out” by other applications.

GRP production in Europe continues to grow but is expected to lag behind the global trend. Growth in global production volume is well over 2 %. As a result, Europe’s share of global production continues to fall despite the positive trend in absolute terms. The simple depiction of the total European GRP production is an indicator for the overall trend in the market. As previously mentioned, there are sometimes major differences in the trends for individual countries/regions and applications/manufacturing sectors. It is therefore instructive to look at the individual markets/segments in more detail.

Table 2.5 - GRP production volumes in Europe according to processes/components – current year and the three previous years (kt = kilotonnes, 2017 = estimate) [2.25]

	2014 kt	2015 kt	2016 kt	2017 kt
SMC	190	191	198	202
BMC	74	74	76	78
∑ SMC/BMC	**264**	**265**	**274**	**280**
Hand lay-up	138	139	140	140
Spray-up	94	96	97	98
∑ Open mould	**232**	**235**	**237**	**238**
RTM	**132**	**137**	**141**	**146**
Sheets	84	86	89	93
Pultrusion	48	49	50	53
∑ Continuous processing	**132**	**135**	**139**	**146**
Filament winding	79	80	80	78
Centrifugal casting	66	68	68	67
∑ Pipes and Tanks	**145**	**148**	**148**	**145**
GMT/LFT	**121**	**132**	**140**	**145**
Others	**17**	**17**	**17**	**18**
Sum:	**1.043**	**1.069**	**1.096**	**1.118**

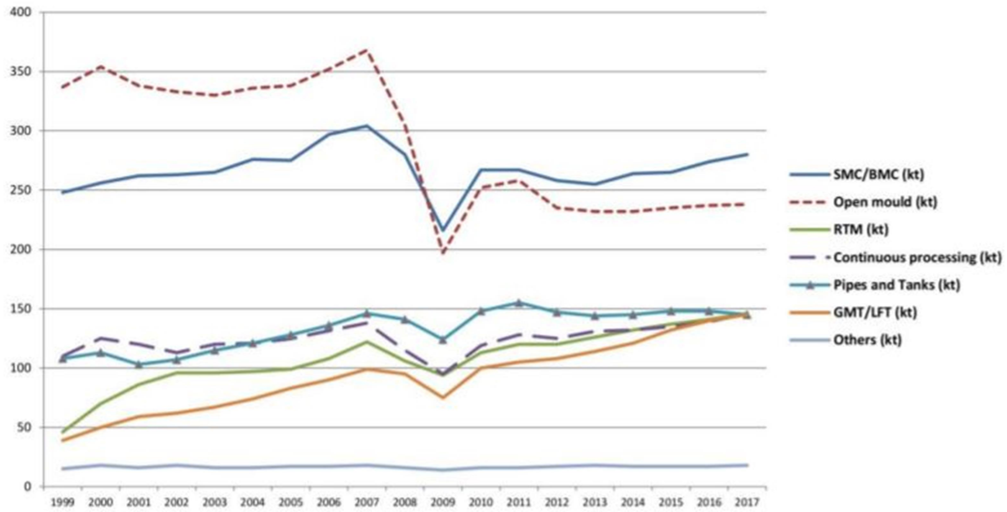


Figure 2.15 - GRP production volumes in Europe according to processes/components – long-term volume trend (kt = kilotonnes, 2017 = estimate) [2.25]

Table 2.5 shows the volume trends for significant processes/components in GRP manufacturing over recent years. However, in addition to these processes, there are many other production processes/technologies which can essentially be classified under one of the areas mentioned. Figure 2.15 shows the long-term trend over the past 19 years. Clearly, SMC/BMC now makes up the largest segment. The next largest continues to be "open processes" – still a segment with a greater emphasis on manual skills and craftsmanship. Growth in the use of SMC/BMC materials has been positive over recent years – in step with the overall market trend – while the open processes of hand lay-up and spray-up have generally declined. Production quantities for all other processes are virtually identical in 2017. In the GRP production considered (not including short fibre reinforced thermoplastics), over 85 % of all GRP components are made from a thermoset matrix based on either a unsaturated polyester, vinylester or epoxy resin. Unsaturated polyester resins are still by far the most commonly used. Glass fibre used for reinforcement generally contributes between 15 % and 70% of the material used in these composites depending the manufacturing process and application. The average proportion of glass used over all segments is around 25-35 %.

The market for GRP pultrusion profiles has the strongest growth rate (6 %) in the European GRP industry and a production volume of 53.000 tonnes. Since the beginning of 2017, the industry has become noticeably more interested in pultrusion, in particular. This is now being reflected in production volume data. Its growth is also in line with forecasts based on other studies which predict the global pultrusion industry is set to grow by just over 5 % this year. The largest applications in the segment, each with an approx. 20 % share of the market for pultrusion components, are the consumer/private sector and the construction industry. Like other composites and GRP market segments, the pultrusion industry is very fragmented. There are probably around 350 pultruders world-wide although the ten largest companies share approx. 40 % of the market. The largest growth area is currently the market for window profiles and reinforcement bars. However, there are also new uses in the transport sector. Typical applications for GRP profiles currently include, e.g. the production of bridge elements, support or cable duct systems, railings, steps in plant construction and certain areas of the transport industry. They are also used in the consumer/private sector in ladders, device sticks or fishing rods. In addition, pultrusion elements can be found in antenna systems, window frames and fences. For a number of years, companies have been increasing their investment in developing techniques to optimise pultrusion processes. In some cases, new opportunities are being hindered by legal regulations. Differences in national approval procedures and a lack of standardisation have slowed the adoption of series produced GRP composites in bridge construction, for example. Although bridges made from GRP are now standard in the Netherlands, they are still a rarity in Germany. The continuous processing segments are characterised by a relatively high level of automation. However, the processes used by the relatively few manufacturers operating in this sector are adapted very specifically to the requirements of the individual companies and are overwhelmingly in-house developments.

GMT, LFT and continuous fibre reinforced thermoplastics are the only thermoplastic materials included in this GRP market report. The material properties, applications and, in some cases, processing methods are similar to those of long and continuous fibre reinforced thermosetting materials so it is reasonable to consider both these areas together. Materials with short glass fibre reinforcement (<2 mm) differ significantly from the materials considered in this report in terms of the influence of reinforcement on material properties and (load-specific) alignment. In 2017, the markets for glass mat reinforced thermoplastics (GMT) and long fibre reinforced thermoplastics (LFT) have continued their above average growth at a rate of 3.6 %, although this is slightly slower than last year. The trend of recent years means that the market share of GMT/LFT products in relation to the total GRP market has risen from 5 % in 2000 to 13 % today (Figure 2.16). The total production of 145,000 tonnes in the segment is split between LFT and GMT in a ratio of around 2:1 with the proportion of LFT rising. These data also include continuous fibre reinforced materials such as organosheets and tapes. The market share of GMT/LFT has been growing steadily for many years. Demand for these thermoplastics has been driven principally by projects in the automobile industry. Thermoplastic materials have a number of special properties in terms of ease of processing/cycle times and recyclability as well as combining well with other materials. This often makes them the material of choice. The pressing and injection moulding techniques for manufacturing/processing components are well-understood in the industry and also used for other materials. In principle they can even be used for large series production of components in the range 100,000+. Typically these include products for underbody protection, bumpers, instrument panels or seat structures. This segment also has great potential due to the possibilities for enhancing and optimising processing methods and materials. For example, a combination of forming and back moulding processes is offering promising results both in terms of material properties and processability.

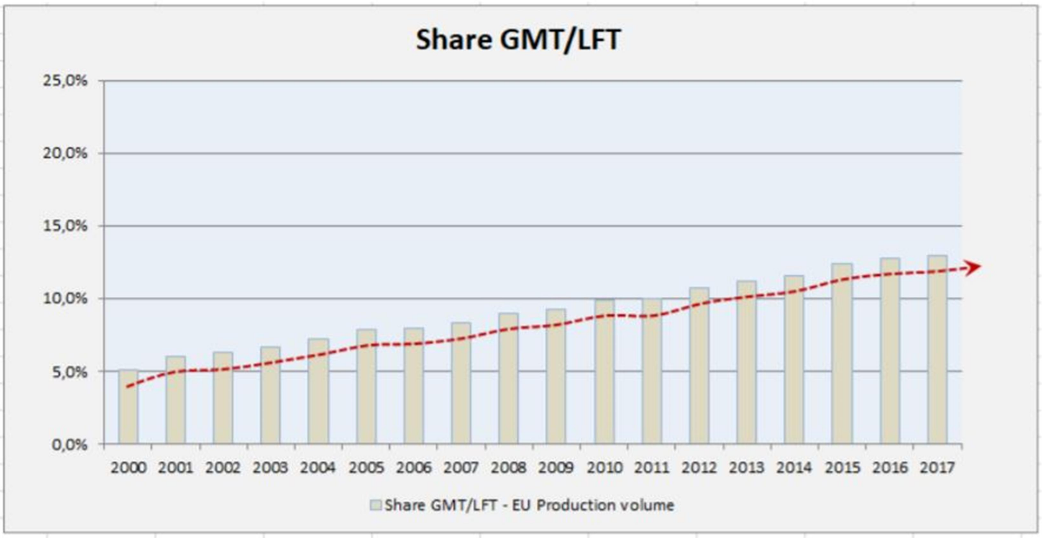


Figure 2.16 - Growth in the market for GMT/LFT as a share of total European GRP production volume [2.25]

Despite the differing trends observed in the markets for the various manufacturing processes, the proportions of GRP used by the major application industries in Europe remain the same as last year. The transport and construction sectors each consume one third of total production. Other application industries include the electro/electronics sector and the sport and leisure segment (Figure 2.17).

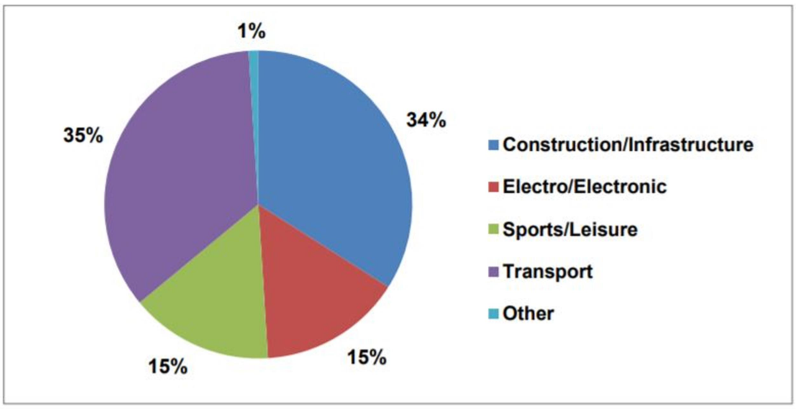


Figure 2.17 - GRP production in Europe by application industry (year: 2017) [2.25]

Growth was recorded in all the European countries included in this report apart from those in Scandinavia where a relatively small production volume stagnated. Growth is relatively similar in most of these countries at approx. 1-3 %. In contrast to the past decade, the European GRP production volume trend now appears to be consolidating. The regional markets are stable and no major declines were reported. Germany remains the largest GRP and composites market in Europe producing a total volume of 226,000 tonnes and recording slightly above-average growth of 3% (Figure 2.18). When other composite materials (short fibre reinforced thermoplastics, carbon fibre and natural fibre reinforced plastics) are included in the data, it becomes clear that Germany is a significantly larger composites producer than any of the other countries considered here.

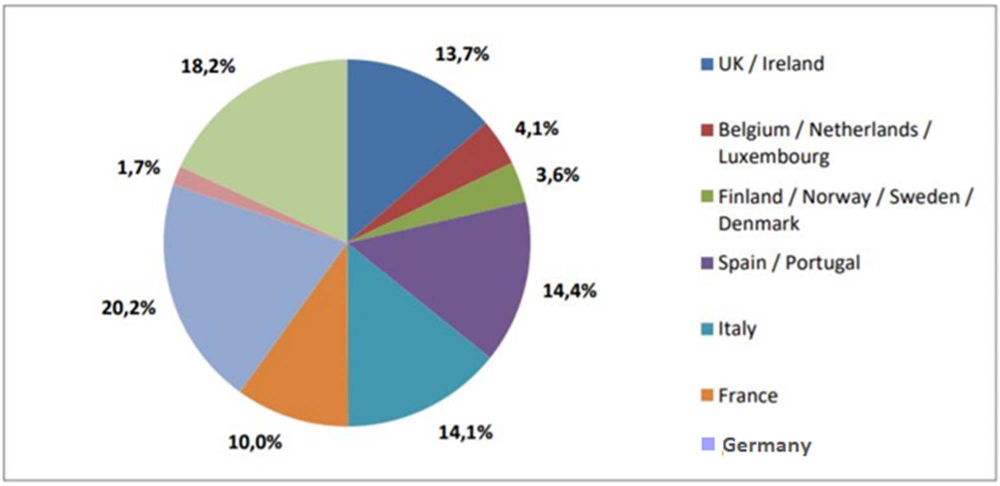


Figure 2.18 - Percentage distribution of European GRP production by country (Date: 2017) [2.25]

Although current media reports and presentations at many conventions and trade fairs may create a different impression, GRP continues to be the largest material group in the composites industry by some distance. Glass fibres are used for reinforcement in over 95% of the total volume of composites (short and long fibres, rovings, woven fabrics, mats …).

Of the over 10 million tonnes of composites manufactured globally in 2016 (Source: JEC Composites), 2.8 million tonnes were glass fibre reinforced plastics produced in Europe (Date: 2016) (Figure 2.19). Of these, the GRP products studied in detail in this report accounted for 1.096 million tonnes and short fibre reinforced thermoplastics for 1.36 million tonnes in 2016. This does not include the quantity of GRP produced using infusion processes which can be assumed to be in the range of approx. 300,000 tonnes. Around half of this quite large amount is used in the construction of wind turbines. The marine sector is also very important to the industry.

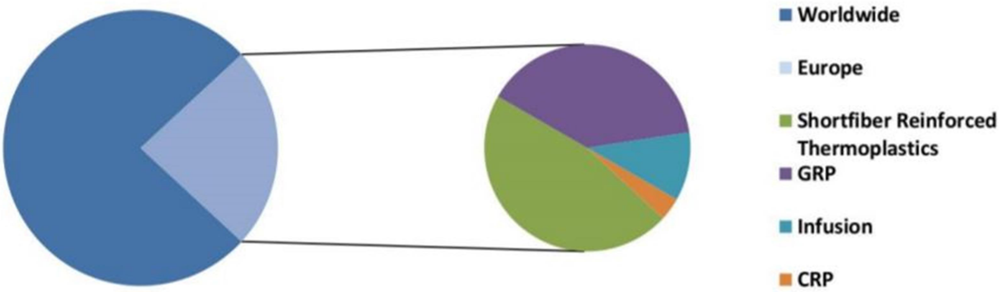


Figure 2.19 - The global and European composites markets (Date: 2017) [2.25]

Often classified as futuristic lightweight materials used primarily in the automotive and aerospace industries, existing applications for composites in existing markets – some of them used for decades – are frequently overlooked. These already include many applications in large scale (automotive) series production – a segment where many observers believe that composites have yet to gain a foothold. Moreover, lightweight design is not the only advantage that composites enjoy over other construction materials. Fibre reinforced plastics have many other useful properties which make them ideal in a number of specific applications. These include outstanding corrosion-resistance, high dimensional stability, low maintenance, long service intervals, excellent durability, load-specific structures and a high level of design freedom. Composites are thus much more than "simply" lightweight materials. In some cases, this potential has already been identified. However, many decision-makers are still unfamiliar with these products. Improving this situation is one of the most important challenges facing the industry as a whole. Often, the full potential of the material is not achieved purely through substitution but by finding new applications. Yet this requires material-dependent planning and design from the outset. In some cases, developers, designers and architects are discovering sometimes completely new possibilities – designed to bring the best out of the material. A large number of architectural projects – including many in the Arab world – showcase the opportunities that composites offer. This is especially true for thermoplastic material systems. These are currently enjoying a period of well above average growth which is expected to continue (combinations of formed continuous fibre-reinforced semi-finished products with over- or back moulding are still a focus of interest). Organosheets are a source of particular excitement in this segment at the moment. Reductions in the costs of continuous fibre reinforced materials/organosheets, fast cycle times and the ability to design optimised, load-specific components should ensure that industry's interest in this type of process technology continues to burn brightly. But even "established" processes such as pultrusion (thermoplastic pultrusion, radius pultrusion or combinations of pultrusion and pressing) and in the SMC sector (carbon fibre SMC and SMC semi-finished products with the addition of continuous fibre structures) are being refined and enhanced. The continuing automation and optimisation of industrial processes – and the associated challenges of Industry 4.0 – thus continue to be important themes. As well as the previously outlined difficulties of establishing composites in the construction/infrastructure sector, changing requirements and developments in the area of mobility present many questions to which the industry must find answers quickly. Composites as materials and the whole industry have enormous potential which, in many cases, has yet to be revealed. The opportunities and capabilities of this still young class of materials are starting to become apparent [2.25].

For the sixth consecutive year, the European glass fibre reinforced plastics market grew in the European countries in 2018. Compared to 2017, the European GRP market is expected to grow again by around 2 % to an estimated total of 1.141 million tonnes. Despite the advances, strong growth, and many innovations in other segments of the fibre reinforced plastics/composites market, GRP still remains the dominant material in the composites market with a market share of over 95 %. As in previous years, the generally positive trend in the European GRP market is more complex than it first appears with very strong regional and applicationor process-specific differences. For example, while so-called open processes (hand lay-up and spray-up) are growing at only 0.4%, the market for thermoplastic systems is increasing by almost 5% in 2018. This year, Southern European countries (e.g. Spain) are enjoying above-average growth while production volumes in most Northern European manufacturing countries are stagnant [2.27].

Pultrusion, the other segment in this area, grew by 3.8 % in 2018. European production of GRP pultrusion products now totals 55,000 tonnes. Interest in this segment grew rapidly in 2017 and is now being reflected in rising market numbers. The trend has continued into 2018. It will be interesting to see whether this is reflected in a further increase in production volume. There have been many new developments and advances in pultrusion in recent months, both in terms of technology and materials. The pultrusion industry considers the construction and infrastructure sectors, in particular, to be major markets of the future. Examples include the public transport sector, bridge construction, window and staircase/ladder profiles, and reinforcement systems. In this area, the specific properties of the materials play a central role in addition to lightweight construction. For example, they should be corrosion resistant, require little or no maintenance, permit load-specific design and be electrical and thermal insulators. The necessary general industrial approvals and norms/standards have not yet been agreed. This lack of “security” increases the reluctance of many architects and decision makers to adopt these materials. Moreover, many decision makers still know too little about the positive properties of GRP compared to other building materials [2.27].

Glass mat reinforced thermoplastics, long fibre reinforced thermoplastics and continuous fibre reinforced thermoplastics are the only thermoplastic materials included in this GRP market report (2018). In 2018, the market for GMT and LFT continues to grow at an above-average rate of 4.8 % having already grown at 3.6 % in 2017. From a long-term perspective, this market segment has almost quadrupled since 1999 – reaching a volume of 152,000 tonnes in 2018. During that period, its share of the total market has risen from 5 % to over 13 %. Projects in the automotive industry, and some in the electronics sector, are the primary growth drivers for thermoplastic materials [2.27].

2.4. Constituent materials

The materials that make up, or constitute, a composite are normally considered including at least the matrix and reinforcement.

2.4.1. Thermosets and thermoplastics matrices

The thermosets resins most commonly used as composite matrices are unsaturated polyesters, epoxies and vinilesteres. Generally, thermosets resins are used for processing as a mixture of two or three components (resin, accelerator and initiator). When the aforementioned components are combined in the appropriate amount, the crosslink or cure reaction happens. The result of the healing reaction is a gigantic three-dimensional molecule that from a macroscopic point of view leads to a transformation of a liquid resin into a rigid solid.

The object of this dissertation is the analysis of the pultrusion process of thermoplastic matrix composites and therefore will devote special attention to the study of this type of constituents.

By the end of the 20th century, the thermoplastic matrix composites were always much less used in structural applications than the traditional thermoset matrix. The main reason was related with the lack of technologies to impregnate conveniently long reinforcement with thermoplastics, leading to obtaining composite materials with low fibre/matrix adhesion and, consequently, lower mechanical properties [2.28]. The problem was also compound by the lack of pre-impregnated materials with sufficient quality to allow manufacture composite structures with reproducible properties [2.29] and with the fibre/thermoplastic most interesting combinations [2.30].

These difficulties in replacing thermoset by thermoplastic matrices in the polymeric composites result from the nature of these two types of matrix. In fact, if is necessary that the matrix was in a viscous liquid state to ensure a convenient fibre wetting, easily notice that the thermoplastics presents, in the molten state, viscosity in the range 50-2000 Pa·s, while the thermosetting resins do not exceed the 50 Pa·s before those begin the cure reaction [2.2].

However, it was verified that the damage tolerance requirements imposed on advanced applications could only be complied with using thermoplastic matrices [2.31], attempts to develop new methods of production and processing composites based on thermoplastic matrices redoubled from the end of the 20th century. Consequently, more appropriate methods of production of pre-impregnated materials with thermoplastic matrix have emerged and new knowledge has been acquired at the level of their transformation [2.2].

The thermoplastic matrix composites, however applied, have been proving to present higher toughness and, consequently, behaviours to the impact and damage rather than the thermoset matrix. As an example, Table 2.6 compares the final properties of two composites widely used in advanced applications, one with a thermoplastic matrix and the other thermoset matrix. Both have the same type of reinforcement and the fibre volume fraction. As can be seen, although the two materials present very similar mechanical properties (basically dominated by reinforcing fibres), the thermoplastic matrix composite presents a very high toughness resistance (represented by the value of G_{Ic}).

Table 2.6 - Comparison of mechanical properties obtained in carbon/PEEK and carbon/epoxy composites (adapted from [2.31])

Property	**Unit**	**Carbon PEEK**	**Carbono Epoxy**
Fibre volume fraction	%	62	62
Tensile strength	GPa	2,44	1,86
Flexure strength	GPa	1,50	1,66
Flexure modulus	GPa	131	131
Compression strength	GPa	1,0	1,3
G_{Ic}	Jm^{-2}	3230	260
Shear strength*	MPa	117	110

* Obtained values with SBT-“Short Beam Test”.

Amorphous thermoplastics have very good surface finish since they not shrink much when they solidify and there is no differential shrinkage from the presence of crystalline regions. The crystallinity also improves high-temperature performance and long-term properties, such as creep. If the crystallinity is too low, these benefits are not seen and if it is too high the material loses toughness and becomes brittle, although gains in stiffness; hence, there is an optimum degree of crystallinity (20 to 35 percent for composite applications). When processing semi-crystalline polymers one thus must consider preferably control the cooling rate. Due to the difference in shrinkage between amorphous and crystalline regions, the surface of semi-crystalline thermoplastics is not a good as for amorphous ones. While, numerous engineering plastics are available, only a few are used as composite matrices, since an engineering plastic with excellent properties is not necessaryly an appropriate composite matrix. [2.5].

Then, the thermoplastics that are most commonly used in structural composites will be introduced [2.5]:

- Polyethylenes (PE) – PE can be both commodity and engineering plastic depending on grade, but is rarely used as composite matrix due to low temperature tolerance and modest mechanical properties. However, PE fibres may be used as composite reinforcement. PE has the highest degree of crystallinity of any polymer due to its simple, regular and flexible molecular structure, thus enabling PE to be used well above its T_g.
- Polypropylenes (PP) – Just like PE, PP is the chemically least complex and cheapest polymer commonly used as composite matrix. One generally talks of homopolymer and copolymer, where the homopolymer version consists of PP units only and the copolymer version is copolymerized with PE units to improve toughness. Homopolymer PP has a glass-transition temperature (T_g) in the range -20 to -10ºC, while crystalline melting temperature (T_m) is in the range 165-175ºC. Obviously the service temperature of composites normally is above PP´s T_g. In structural composite applications PP is usually reinforced with glasses fibres and such composites are often hidden from view since the surface finish tends to be poor. In recent years, PP has become the most common thermoplastic matrix in mass-production structural composite applications, including automobile components. It is widely used due to its low cost, excellent properties of fatigue resistance, electrical insulation and chemical resistance (excellent resistance to a large number of solvents, although it is attacked by strong oxidizing agents) [2.2]. Impact modifiers can be added to PP to further improve impact strength, especially at low-temperature applications.
- Polyamides (PA) – One of the best-known thermoplastic polymer families is the polyamides, often called NYLON®. In the contrast to PE and PP, PA may be used at moderate temperatures, thus greatly improving its usefulness as matrix. PAs are characterized by the presence of amine groups (-CONH-). A number of different PA grades, e.g. PA 6, PA 6.6, PA 6.10, and PA 12, are available, where the numbers indicate the number of carbon atoms in the repeating unit; the properties naturally vary accordingly. The biggest drawback of some of the more common PA grades is that they are hygroscopic, i. e. absorb water. Depending on grade T_gs are in the range 45-80ºC, while T_ms are in the range 180-265ºC. In the composite applications, PAs are normally reinforced with glasses fibres and used in applications similar to glass-reinforced PP, but higher temperature tolerance and improved mechanical properties are required. Where higher performance is required carbon reinforcement may be used.

- Thermoplastic Polyesters – Although perhaps chiefly recognized as thermosets, polyesters also are available in thermoplastics forms, e.g. poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT). The properties of PET and PBT are similar to those PAs (semicrystalline´s), but lacking the hygroscopic disadvantage. PBT´s T_g 60-70ºC while T_m is 225-235ºC; the corresponding transition temperatures of PET are 80ºC and 260-265ºC. In composite applications, thermoplastic polyesters are reinforced with glass fibres and used in in applications similar to glass-reinforced PP and PA.
- Polycarbonates (PC) – the large, complex, aromatic structure of polycarbonate determines the physical and mechanical properties of the molecule. Polycarbonate is amorphous and therefore clear, yet is nearly as strong as highly crystalline PA. The same factors that give strength and stiffness also increase the energy needed to cause melting. In this case, the melting point and the use temperature are much higher than for the competitive PA and thermoplastic polyesters (PC can be used continuously to 135ºC) [2.32].
- Poly(phenylene sulfides) – the most common member of the poly(arylene sulphide) family is poly(phenylene sulfide) (PPS), which has good tolerance to most chemicals and fire. PPS exhibits moderate mechanical properties and temperature tolerance; T_g is 85ºC and T_m 285ºC. In composite applications, PPS is reinforced with glass or carbon fibres and used in high-performance applications.
- Polyketones – Whilst there are numerous aromatic polyketones, including poly(etherketone) (PEK), poly(ether ketone ketone) (PEKK), the most common is poly(ether ether ketone) (PEEK). The polyketones possess high mechanical properties, high temperature tolerance, good solvent resistance, and a high price; T_g of PEEK is 145ºC and T_m 345ºC. In composite applications PEEK is reinforced with glass or carbon fibres and used in critical high-performance applications.
- Polysulfones – Polysulfone (PSU), poly(ether sulfone) (PES), and poly (aryl sulfone) (PAS) are high performance amorphous polymers with good tolerance to high temperatures and fire. These properties come at a high price and the melt viscosities are also very high. Since polysulfones are amorphous, they are not resistant to all solvents although their resistance to many chemicals nevertheless is very good. The T_gs are 190ºC for PSU and 220-230ºC for PES. In composite applications, polysulfones are reinforced with glass or carbon fibres and used in the same type applications as polyketones.
- Thermoplastics Polyimides – The polyimide family includes poly(ether imide) (PEI), polyimide (PI), and (amide imide) (PAI), which are all amorphous. Polyimides have the highest temperature tolerance of the thermoplastic mentioned herein; the T_gs for PEI, PI, and PAI are 215, 255, and 250-290ºC, respectively. Despite being amorphous they are very tolerant to solvents and environmental exposure and offer very good mechanical properties with the disadvantages of very high melt viscosities and high price. In composite applications, the members of the polyimide family are reinforced with glass or carbon fibres and used in the same type of applications as polyketones and polysulfones.

- Poly (para-phenylene) (PPP) - is a crystalline, rigid rod polymer that is insoluble and infusible. Modification of poly (p-phenylene) can result in an amorphous, transparent, and melt-processible polymer. In 2006 Solvay Advanced Polymers offers amorphous p-phenylene copolymers under the PrimoSpire trademark. The structure is based on a string of substituted and unsubstituted benzene rings producing a highly rigid chain structure. The substituted benzene rings have pendant benzoyl groups. These benzoyl-substituted phenylene units along with some m-phenylene units are sufficient to prevent crystallization. The structure is depicted in Figure 2.20.

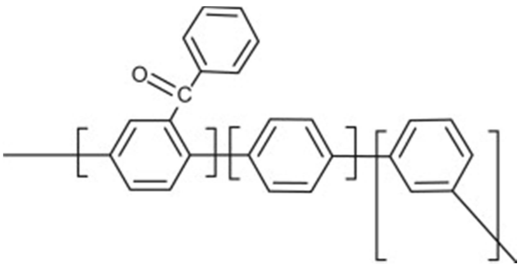


Figure 2.20 - Structure of modified polyphenylene [2.33]

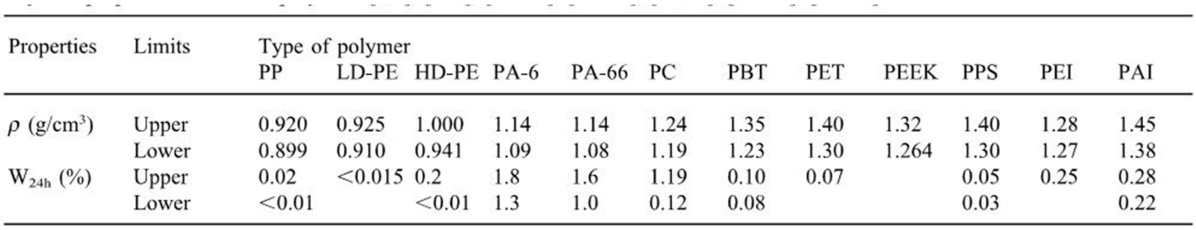
Although the polymer has a good heat resistance, with decomposition temperatures of the order of 400°C can achives a higher value due the presence of substituted benzene rings. The amorphous polymers retain the rigid rod characteristics and are self-reinforcing which results in very high, isotropic mechanical properties. They are the stiffest unreinforced thermoplastics that are commercially available and provide exceptional strength and stiffness without fillers. Depending on the specific side chains present, tensile elastic modulus values range from 5 to 9 GPa and yield strengths vary between 120 to 200 MPa. The glass transition temperature is 165 °C. The highly aromatic polymer is inherently flame-resistant. The high surface hardness results in excellent scratch and wear resistance. Coefficient of friction is very low and compressive strength is more than 690 MPa. PPP has several other favorable properties, which include good thermal stability, biocompatibility and shape-memory properties. For typical PPP processing, temperatures upwards of 320 °C must be employed in fabrication methods such as pressing or injection moulding. The PRIMOSPIRE® is a self-reinforced polyphenylene (SRP) [2.33-2.34].

A much wider range of thermoplastics is, in turn, used in pre-impregnated materials with a thermoplastic matrix. The thermoplastic to be used is much more dependent on the specifications required for the final components that are intended to be manufactured. The cost and thermal and mechanical performances are the characteristics that more determine the choice of polymer to use in each specific application. Whereas low-cost thermoplastic matrix, such as polypropylene (PP), are mainly used in commercial applications, the most expensive and which have better mechanical and thermal properties, such PEEK, are employed in demanding applications [2.35].

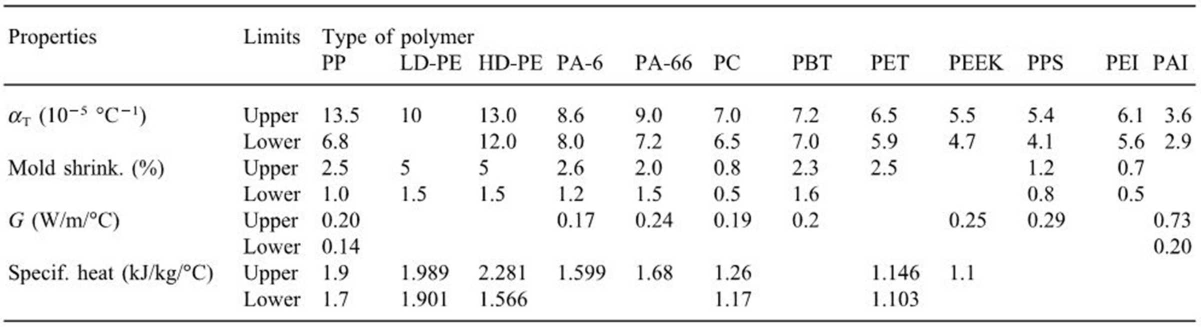
The most commonly used polymers in thermoplastic matrix pre-impregnated materials are the ones that best have penetrated in the high-consumption commercial markets for presenting an attractive "mechanical/cost performance" relationship. In this context, polyamide (PA), polypropylene (PP), thermoplastic polyester (PET) and polycarbonate (PC) are highlighted [2.36].

The thermal properties of the thermoplastic are also often determinant for the selection of the matrix to be used in the pre-impregnated material, given the strong influence they have, not only in the subsequent performance of the composites at the service temperature, but also, at easy that can be processed. Table 2.7 presents the characteristic temperatures and physical, thermal and mechanical properties of thermoplastic used in composites.

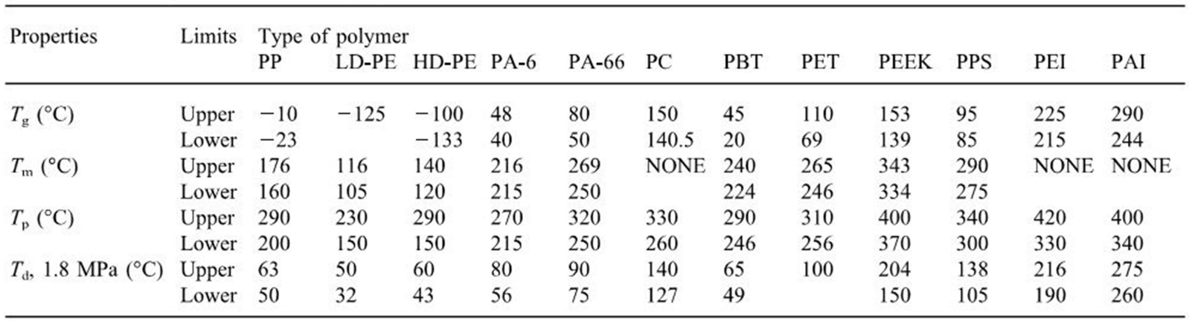
Table 2.7 - Characteristic temperatures and physical, thermal and mechanical properties of thermoplastic used in composites [2.37]



Properties	Limits	Type of polymer											
		PP	LD-PE	HD-PE	PA-6	PA-66	PC	PBT	PET	PEEK	PPS	PEI	PAI
ρ (g/cm^3)	Upper	0.920	0.925	1.000	1.14	1.14	1.24	1.35	1.40	1.32	1.40	1.28	1.45
	Lower	0.899	0.910	0.941	1.09	1.08	1.19	1.23	1.30	1.264	1.30	1.27	1.38
W_{24h} (%)	Upper	0.02	<0.015	0.2	1.8	1.6	1.19	0.10	0.07		0.05	0.25	0.28
	Lower	<0.01		<0.01	1.3	1.0	0.12	0.08			0.03		0.22



Properties	Limits	Type of polymer											
		PP	LD-PE	HD-PE	PA-6	PA-66	PC	PBT	PET	PEEK	PPS	PEI	PAI
α_T (10^{-5} °C^{-1})	Upper	13.5	10	13.0	8.6	9.0	7.0	7.2	6.5	5.5	5.4	6.1	3.6
	Lower	6.8		12.0	8.0	7.2	6.5	7.0	5.9	4.7	4.1	5.6	2.9
Mold shrink. (%)	Upper	2.5	5	5	2.6	2.0	0.8	2.3	2.5		1.2	0.7	
	Lower	1.0	1.5	1.5	1.2	1.5	0.5	1.6			0.8	0.5	
G (W/m/°C)	Upper	0.20			0.17	0.24	0.19	0.2		0.25	0.29		0.73
	Lower	0.14											0.20
Specif. heat (kJ/kg/°C)	Upper	1.9	1.989	2.281	1.599	1.68	1.26		1.146	1.1			
	Lower	1.7	1.901	1.566			1.17		1.103				



Properties	Limits	Type of polymer											
		PP	LD-PE	HD-PE	PA-6	PA-66	PC	PBT	PET	PEEK	PPS	PEI	PAI
T_g (°C)	Upper	−10	−125	−100	48	80	150	45	110	153	95	225	290
	Lower	−23		−133	40	50	140.5	20	69	139	85	215	244
T_m (°C)	Upper	176	116	140	216	269	NONE	240	265	343	290	NONE	NONE
	Lower	160	105	120	215	250		224	246	334	275		
T_p (°C)	Upper	290	230	290	270	320	330	290	310	400	340	420	400
	Lower	200	150	150	215	250	260	246	256	370	300	330	340
T_d, 1.8 MPa (°C)	Upper	63	50	60	80	90	140	65	100	204	138	216	275
	Lower	50	32	43	56	75	127	49		150	105	190	260

Properties	Limits	Type of polymer											
		PP	LD-PE	HD-PE	PA-6	PA-66	PC	PBT	PET	PEEK	PPS	PEI	PAI
σ_{max} (MPa)	Upper	41.4	78.6	38	79	94	72	55.9	70	103.5	90	104.9	192
	Lower	26	4	14.5	43	12.4	53	51.8	50	70	65.6	103.5	90
E (GPa)	Upper	1.776	0.38	1.490	2.9	3.9	3.0	2.37	4.0	3.8	3.9	3.0	4.4
	Lower	0.95	0.055	0.413		2.5	2.3		2.7	3.1	2.6		2.8
σ_f (MPa)	Upper	55.2			117.3	131.1	93.2	96.0	112.3	110.4	151	151.8	240.8
	Lower				69.0	89.7	81.4	82.8	110.4	110	96	144.9	185.6
E_f (GPa)	Upper	1.73		1.07	2.8	3.5	2.38	2.6	2.8	3.9	4.1	3.5	6.6
	Lower	0.83		0.41	1.9	1.1	2.14	1.9		2.8	3.4	3.0	3.6
ε (%)	Upper	700	800	1000	150	>300	125	300	100	50	6	60	12
	Lower	15	90	12	20	35	90	100			1.1	6.0	
Izod, 1/8″	Upper	267		1068	160	854	908	53.4	26.7	50.2	133	133	133
(J/m)	Lower	21.4	>854	26.7	42.7	16.0	534	48.1			10.7	53.4	58.7

2.4.2. Reinforcement fibres

The fibreglass, carbon and aramid fibres are the reinforcements commonly used in all polymer matrix composites.

The major ingredient of glass fibres is silica (SiO_2), which is mixed with varying degrees of other oxides. The mixture is melted and extruded through minute holes in a platinum-alloy plate, or bushing [2.5].

Properties characteristic of glass fibres are advantages such as high strength, very good tolerance to high temperatures and corrosive environments and low price. Among the most important features is the excellent fibre/matrix adhesion, good dielectric properties and weak thermal conductivity, good dimensional stability and an interesting relationship "mechanical performance/cost". Disadvantages include relatively low stiffness, moisture sensibility and abrasiveness [2.5].

Glass reinforcement is mainly used where stiffness is not required and where part cost is a critical factor [2.5].

The definition of Carbon Fibres (CFs) in the past was that of fibres made of at least 92 wt% of carbon and prepared from polymeric precursors [38] or made from carbon allotrope building blocks.

Carbon fibres are produced by controlled oxidation, carbonization and graphitization of rich carbon organic precursors already in the form of fibre resulting in a molecular structure with an orientation along the fibre axis. The most common precursor is the PAN (polyacrylonitrile) because it gives better properties to carbon fibre, but this can be produced from pitch or cellulose. The variation of the graphitization process produces essentially high-strength or high-modulus fibres [2.39].

The PAN fibres normally have good mechanical resistance and high adhesion "fibre/matrix", while pitch fibres present a higher modulus [2.40].

While carbon fibres have the highest strength and stiffness of any composite reinforcement candidate that is accompanied by fairly low strain to failure. Other advantages include tolerance to high temperature and corrosive environments, as well lack of moisture sensibility. The major disadvantage of carbon fibres is their high price, while other includes brittleness and conductivity [2.5].

The low coefficient of thermal expansion and the good electrical and thermal conductivity that carbon fibres presents face to their counterparts, glass and aramid, also makes them often used in the manufacture of structures requiring a high dimensional stability and/or require electricity and/or heat conduction. In addition to its high price, its lower impact resistance and the possibility of galvanic corrosion in contact with metals are the main disadvantages to carbon fibres [2.2, 2.5].

Carbon fibre reinforcement dominates in high-performance applications due to its outstanding mechanical properties combined with low weight. The negative CTE is a most useful property in that permits design of composites with virtually zero effective CTE over several hundred degrees [2.5].

Several organic fibre types have nevertheless been used as composite reinforcement, but the category is dominated by aramid fibres. Kevlar® is often assumed synonymous with aramid, but is in fact just the (Du Pont) trade name of the most common of a few commercially available aramid fibre types. Aramids, short for aromatic polyamides, are members of the Polyamide (PA) family and have a regular structure and aromatic rings in the backbone. Due to high degree of crystallinity and rigid molecular structure, temperature tolerance of aromatic polyamide is very good for an organic material (service temperature up to 250ºC) [2.2, 2.5]. Advantages of aramid fibre are very good mechanical properties, especially toughness and damage tolerance, moderately temperature tolerance and corrosion resistance and good electrical properties. From design point of view it is important to realize that the strength in longitudinal compression is only a fraction of that in tension and that the fibre-matrix compatibility generally is poor (especially in the case of thermoplastics). The outstanding toughness of aramid also creates a problem in that fibres are very difficult to cut and machining of aramid-reinforced composites therefore requires special tools and techniques. Other disadvantages of aramid fibres are high price, moisture sensitivity a low exposure to ultraviolet rays. Aramid fibres have positive transverse CTE, but negative longitudinal CTE [2.2, 2.5].

Aramid fibres are even less used than glass and carbon fibres. The major advantage of aramid fibres lies in their outstanding toughness and damage tolerance which have given rise to energy-absorbing applications, such as in bullet-proof vests woven and helmets. Presenting high specific tensile, abrasion and impact resistance are mainly used in small market niches dedicated to the manufacture of specially demanding parts from the point of view of these properties [2.2, 2.5].

Table 2.8 presents the main properties of the fibres applied to polymeric composites. Table 2.9 compares the above-mentioned reinforcement fibres from the point of view of their most relevant properties.

Table 2.8 – Principal characteristics of the fibres most commonly in polymeric composites [2.4]

Carbon		**Glass**		**Aramid**	
Advantages	***Disadvantages***	***Advantages***	***Disadvantages***	***Advantages***	***Disadvantages***
High elasticity moduli	High cost	High tensile strength	Low elasticity moduli	Moderate elasticity moduli	Low compression strength
High tensile and compressive strength	Low impact resistance	Good compatibility with a number of resins	High hardness (abrasiveness)	High tensile strength	Sensitive to moisture
Low coefficient of thermal expansion	Limited abrasion resistance	Good tolerance to high temperatures and corrosive environments	High density	Excellent vibration damping coefficient	Low compatibilitry between fibre and matrix
Good thermal and electrical conductivity	Sensitive to oxidation (at above 400°C)	Low price	Sensitive to moisture	Low density	Sensitive to ultraviolet radiation
Low density	Risk of galvanic corrosion when in contact with metals	Good dimensional stability		Very good dimensional stability	Difficult to process
Excellent resistance to temperature (in non-oxidising environment) and moisture		Good electrical insulator and low thermal conductivity		Excellent thermal stability	Susceptible to degradation by bases and strong acids
High fatigue strength		Incombustible		Good fatigue strength	High cost
High chemical inertia, resistant to most acids, bases and solvents				Good toughness and impact resistance	
				Excellent dielectric properties	

Table 2.9 - Typical properties of reinforcing fibres [2.40-2.43]

Property	• Unit	• Reinforcement Fibres					
		• Glass			• Carbon		Aramide
		E	S	R	• Pitch	• PAN	Kevlar® 29
Density	-	2.56	2.49	2.58	2.0	1.8	1.44
Specific heat	kJ/kg·K	0.9	0.73	-	-	-	1.1
Tensile Strength*	GPa	3.6	4.5	4.4	1.5	2.8	2.8
Modulus*	GPa	76	86	85	380	270	62
Coefficient of thermal expansion*	10^{-6}/°C	4.9			-1.3	-0.6	-2.0
Coefficient of thermal conductivity*	W/m·K	1.04			7-28	7-10	-
Specific tensile strength*	KNm/kg	1400	1800	1700	750	1555	1944
Specific Modulus*	MNm/kg	29.6	34.5	32.9	190	150	43
Fibres diameter	μm	3-20	8-13	5-24	10-11	7.5	12

* Properties measured in the axial direction of the reinforcing fibres

2.5. Pre-impregnated materials of thermoplastic matrix

The pre-impregnated materials of thermoplastic matrix are classified according to the characteristic length of the reinforcing fibres that they use in three large groups: pre-impregnated with short fibres (SFRT's), long fibres (LFRT's) and continuous fibres (CFRT's) [2.2].

The pre-impregnated materials that will be applied throughout the present study are the CFRT´s and therefore will devote special attention to them.

In the market there is already an interesting variety of pre-impregnated materials of thermoplastic matrix reinforced with continuous fibres. In Table 2.10 the generic properties of some commercially available CFRTs are present.

Table 2.10 - Typical properties of some commercial continuous fibre pre-impregnated materials [2.44]

Propriedade	Unit	PP glass E	PP carbon	Nylon® 6 glass E	Nylon® 6 carbon	PEEK glass S2	PEEK carbon
Fibre volume fraction	%	48	50	51	51	53	53
Polymer mass fraction	%	28	34	30	38	32	40
Specific gravity	gcm^{-3}	1.68	1.34	1.83	1.45	1.94	1.56
Processing temperatue	°C	190-230		250-280		370-390	

The CRFT can be classified according to the flexibility they present in two large categories: i) flexible pre-impregnated or partial impregnation, characterized by not presenting the fully impregnated fibres, and ii) semi-rigid pre-impregnated materials or total impregnation, with less flexibility, which presented the reinforcement completely impregnated. Whereas in the flexible pre-impregnated materials, the total impregnation of the reinforcement is carried out only in the course of its subsequent processing, simultaneously with the consolidation by action of the temperature and pressure, in the second case, presenting the reinforcement already fully impregnated, the transformation is only used to obtain the shape that is intended for the final component, by consolidating a stacking of layers of the pre-impregnated material [2.2].

These are typical examples of pre-impregnated materials with partial impregnation, the bundles of fibres impregnated with drops of thermoplastic powder (usually designated by *towpregs*), the bundles of fibres consisting of thermoplastic filaments and reinforcement arranged in parallel (*commingled fibres*), the mixtures of bundles of reinforcements with thermoplastic powder encapsulated in a thermoplastic sheath (FIT) and also the woven fabrics obtained from these products. The pre-impregnated materials with total impregnation, which as their congeners with a thermosetting matrix are usually designated by *prepregs* in the anglo-saxon language, are commercially in the form of plates, laminated plates, tapes or bands and bars [2.44-2.52].

The *towpregs*, the *commingled fibres* and the *FIT* are normally transformed by pultrusion or filament winding and can use either hot compression as the stamping in the production of components from the flexible woven fabrics obtained from them. The *prepegs* in form of plate and tape are, in turn, usually processed by hot compression, stamping or pultrusion [2.2].

2.6. Production of pre-impregnated thermoplastic matrix reinforced with continuous fibres

The length to be impregnated, pressure to apply, viscosity of the polymer and geometry and spatial disposition of the fibres are the main factors to take into account to ensure a proper and complete impregnation of the reinforcement by a polymer. In fact, the Darcy equation [2.53, 2.54] allows to determinate the impregnation flow velocity (in one direction of impregnation), as (Figure 2.21):

$$u_p = \frac{dx}{dt} = \frac{K}{\eta}\frac{dP}{dx} \tag{2.1}$$

where u_p is the polymer flow rate per unit area, K is the permeability of the fibres, η the viscosity of the polymer and $\frac{dP}{dx}$ the pressure gradient.

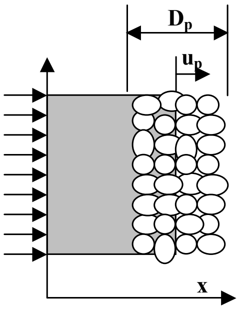


Figure 2.21 – Impregnation of fibres by a thermoplastic, under external pressure action [2.53]

If the pressure gradient is constant, $\frac{P}{x}$, the equation 2.1 can be integrated with the appropriate border conditions, obtaining the necessary time to ensure the full impregnation of the reinforcement, t_{imp}, through:

$$t_{imp} = \frac{\eta D_p^{\,2}}{2KP} \tag{2.2}$$

The previous equation shows that the impregnation length, D_p, is the factor that most affects the phenomenon, increasing the time of impregnation proportionately with the square of its value. This is the main reason why attempts to minimize this distance in most of the techniques of production of pre-impregnated thermoplastic matrix recently have been developed.

This idea is, for example, on the basis of the development of so-called flexible pre-impregnated materials (*towpregs, commingled fibres, FIT*) where polymer and fibres are placed in such intimate contact that it is possible to perform the complete impregnation of the reinforcement, thanks to the short distance that the polymer flow has to go through, during the subsequent transformation of the pre-impregnated materials into final parts. Flexible pre-impregnated materials also have the advantage that they can be woven before their final processing into composites [2.55, 2.56].

As can also be observed by Equation 2.2, the permeability, the viscosity of the polymer and the applied pressure are other factors to take into account during the impregnation of the fibres. The permeability is a property of the reinforcement and one which is determined directly by the fibre architecture and it is a function of the fibre radius, the fibre fraction and a geometric factor k, the Kozeny constant which is a measure of the tortuosity of the flow path (spatial disposition of fibres). Values of this constant are different for the flow parallel and perpendicular to the fibres. A higher permeability value leads to a lesser difficulty of impregnation. It is for this reason that it becomes easier to impregnate the fibre wicks in its longitudinal direction than in the transverse. [2.2, 2.17]

Since the viscosity of the polymer is essentially determined by the temperature of molten polymer, the success of the impregnation is strongly dependent on a aproppriate temperature setting of the process.

It is finally verified that the impregnation time is inversely proportional to the applied pressure. Therefore, the pressure to be applied must also be conveniently chosen in such a way that the impregnation of the reinforcement is carried out at the desired time. As the time available for impregnation is often imposed by the used impregnation method itself, if the impregnation distance, the viscosity of the polymer (or lower is its temperature) and the permeability of the fibres are greater, the pressure to be applied has to be higher.

There are four different techniques for the production of pre-impregnated thermoplastic matrix reinforced with continuous fibres, namely [2.29]: i) use of the thermoplastic in liquid suspension, ii) use of the molten thermoplastic, iii) intimate mixture of thermoplastic and reinforcement fibres, iv) intimate mixture of the polymer powder with the reinforcing fibres.

As liquid suspensions are normally formed by aqueous solutions of thermoplastic powder and may contain additives to improve fibre/polymer adhesion [2.57]. The size of the thermoplastic particles and their concentration in the aqueous suspension are the most important parameters of the process [2.58].

The process (Figure 2.22) begins with the unwinding of the fibre bundles and its passage through an impregnation bath, containing an aqueous suspension of powder polymer stirred mechanically. Then, the fibres bundles already impregnated, after passing through a drying chamber, go through a furnace with controlled temperature to be carried out, in the definitive the adhesion of polymer to the fibres. Finally, the pre-impregnated is wrapped in reels.

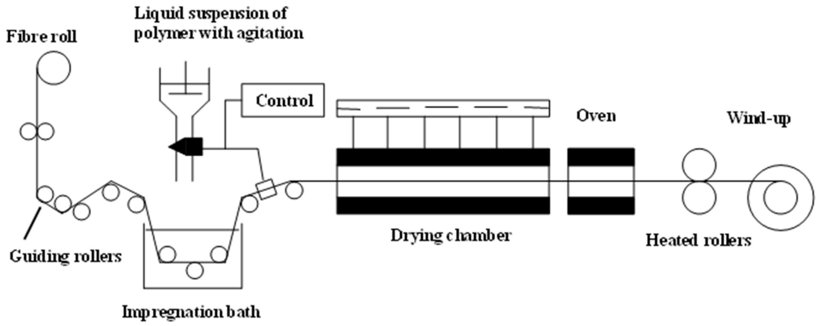


Figure 2.22 - Impregnation of fibres by liquid suspensions (adapted from [2.58])

The resulting continuous pre-impregnated set is called *towpreg* (Figure 2.23), and consists of continuous reinforcement fibres containing thermoplastic powder in its interstices. The proximity between the polymer particles and the fibres allows to reduce considerably the distance (and therefore the time) to go through the thermoplastic flow to achieve a complete impregnation of the material.

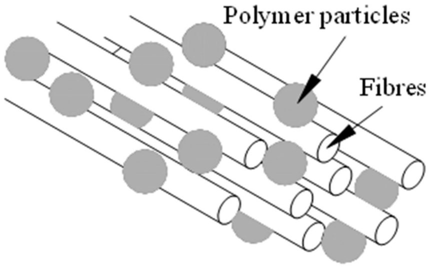


Figure 2.23 - Towpreg pre-impregnated scheme

If the towpreg produced pass by a module consisting of two heated rolls before the final winding operation, it can be produced in a band/tape completely or almost completely pre-impregnated.

Two technologies are normally used to impregnate continuous reinforcement fibres with fused thermoplastics. One of the technologies is the co-extrusion (Figure 2.24), where an extruder is used to inject the thermoplastic into a die where the reinforcing fibres pass through. Total impregnation is achieved by fibre spreading and application of pressure to the trapped molten polymer through the extruder screw. Initially, the process was used only in the manufacture of pre-impregnated short fibres with insufficient impregnation of the fibres that were inside the boundles [2.53, 2.54, 2.59]. A process based on the same principles (DRIFT – Direct ReInforcement Fabrication Technology) [2.60] allows to obtain continuous fibres pre-impregnated materials completely impregnated at high manufacturing speeds (Figure 2.25).

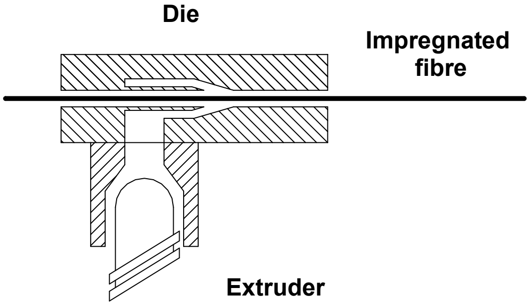


Figure 2.24 - Co-extrusion process

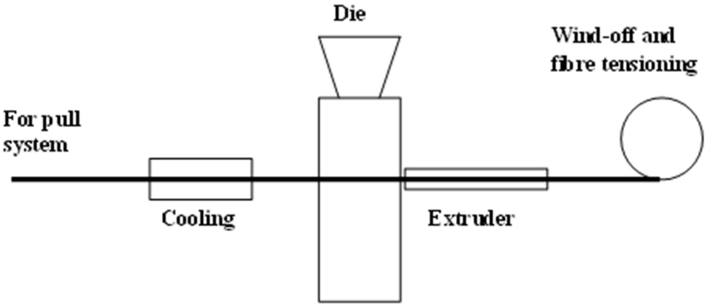


Figure 2.25 - DRIFT process scheme (adapted from [2.60])

On other technology, which by its similarity to pultrusion is designated *pultrusion in continuous*, the fibres bundles are passed through a molten thermoplastic bath. Cylindrical roller assemblies (which can be heated) are used to separate filaments that form the bundles and improve impregnation (Figure 2.26). In the end, the fibres already completely impregnated by thermoplastic undergo a die.

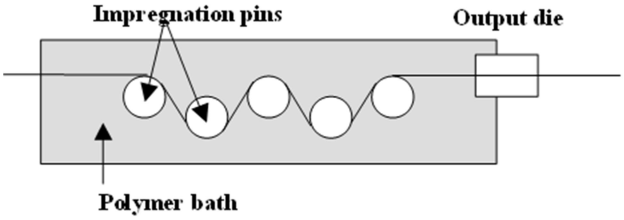


Figure 2.26 - Scheme of the impregnation process by pultrusion in continuous [2.54]

The intimate mixture of thermoplastic and reinforcement fibres is, as said above, another method used in the production of thermoplastic matrix reinforced with continuous fibres. One of these techniques is to mix reinforcement and polymer fibres in order to obtain a product, designated "*commingled fibres*" (Figure 2.27). Normally, the final composite, which results from its transformation, presents more polymer-rich areas than others. However, if the processing variables are selected properly it is possible to manufacture parts that exhibit good mechanical properties [2.61].

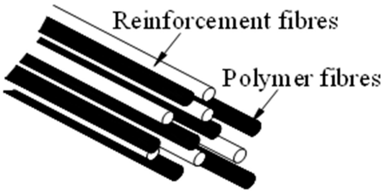


Figure 2.27 - “Commingled fibres” (adapted from [2.61])

The manufacture of complex geometries at low cost represents a field of applications with great potential for this type of flexible pre-impregnated materials, since the times of impregnation of the fibres are very low. High performance composite parts can be manufactured with high fibre levels aligned in a given direction [2.62, 2.63], such as producing fabrics and braids from these bundles [2.62].

Another production technology, based on the dry mixture of the polymer powder with the fibres, was for the first time used by Price [2.64]. The process presents some advantages for other pre-impregnated production processes [2.29, 2.65]:

- Does not depend on the viscosity of the thermoplastic used as a matrix;
- Avoids the use of solvents, water or additives to lower the viscosity, which must be completely removed from the final pré-impregnated due they cause the formation of voids in the composite and, consequently, resulting in the loss of mechanical properties;
- Does not use expensive operations, such as the manufacture of thermoplastic fibres used in the production of “*commingled fibres*”.

Figure 2.28 represents schematically this production technology. The strands of continuous fibres are unwound and made pass through a spreader, where the fibre filaments are separated and scattered with a certain width. The fibres then enter in a deposition chamber where the thermoplastic powder is deposited dry on its surface. Finally, after passing through an oven where it is guaranteed a convenient adhesion of the polymer powder to the fibres, the final product (*towpreg*) is wrapped in reels.

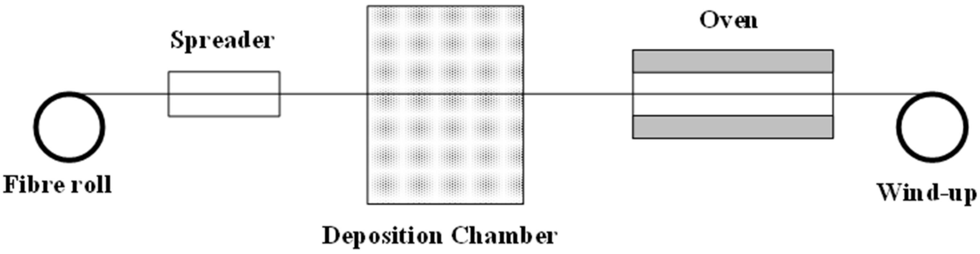


Figure 2.28 - Scheme of the powder polymer deposition on continuous fibres [2.29, 2.66]

Different variants of the *towpregs* production technology from the dry deposition of the polymer powder on the fibres are currently under study [2.67-2.76] and have been the subject of several patents [2.77-2.81]. A reference laboratory system, developed at the University of Clemson – U.S.A., can see if schematically in Figure 2.29.

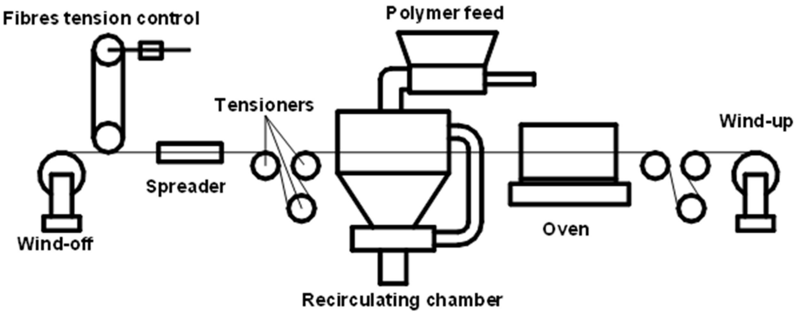


Figure 2.29 - Equipment for the production of towpregs by Clemson [2.70-2.72]

Basically, the machine consists of four parts: two synchronized rotation movements (initial unwinding and final fibre winding) that incorporate a tension control system in the fibres, the fibre spreader, the deposition chamber and the oven that ensures the convenient adhesion of the thermoplastic powder to the fibres. Three of them are considered to be of the greatest relevance to the quality of the product produced: the fibre spreader, the thermoplastic deposition chamber and the oven. In some machines, liquid agents have been used to increase the adhesion of the thermoplastic powder to the fibres [2.82], while in other uses electrostatic loads to deposit the polymeric powder on carbon fibres linked to a lower potential (electric mass) [2.83-2.87].

To manufacture the towpregs of fibreglass reinforced polypropylene (FV/PP), a equipment was developed, designed and built in INEGI in partnership with the Department of Polymer Engineering of Engineering School of University of Minho [2.77-2.78, 2.88-2.104]. The equipment presented substantial improvements in relation to those currently in existence in that time.

A product derived from *towpreg* with great potential application is the FIT – *Fibre Impregnated with Thermoplastic*. It consists of towpregss soaked in a tubular external thermoplastic sheath (Figure 2.30). First, the *towpreg* is produced in a powdered thermoplastic deposition line on the fibres, and then it is made to pass through a extruder where it is wrapped by the thermoplastic sheath [2.61, 2.105].

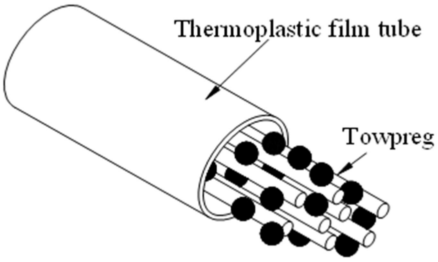


Figure 2.30 - FIT – Fibre Impregnated with Thermoplastic (adapted from [2.61])

Figure 2.31 summarizes the fundamental phenomena, as well as the main drawbacks of the different production techniques of pre-impregnated thermoplastic matrix reinforced with continuous fibres that have been mentioned above.

Whereas, ideally, the production of the pre-impregnated is sought to achieve the total impregnation of its fibres by the thermoplastic matrix, i.e. that the thermoplastic completely fills the interstitial space between the continuous fibres assembly and equally spaced which constitute the bundles (Figure 2.31 a)), it is verified that:

- Techniques using liquid suspensions allow considerably to reduce the viscosity of the thermoplastic and consequently minimise the pressure and temperature to be used during impregnation to ensure adequate penetration and filling the interstitial space of the fibres by the polymer. If there is no need to resort to high-power pressurization and heating equipment, investment costs and consequently the impregnation process become much more economical. However, the main drawbacks are the need to use an extra drying stage for removal by evaporation of the liquids used and the difficulty of obtaining liquids that suit to all applied thermoplastics. In addition, the removal of the liquid solution will result in the formation of voids which must be eliminated, by applying temperature and pressure, during a stage before at the subsequent transformation of the pre-impregnated or, as it happens in the processes that use the dry thermoplastic deposition in its proper processing (Figure 2.31 b));

- The techniques using the molten thermoplastic make use of the classic processes of processing the thermoplastics: heating the thermoplastic above its melting point followed by applying pressure to ensure its disposal and filling the interstitial space of fibres. The equipment necessary for the heating of the polymer and the application of the pressures required by the high viscosity of the fused thermoplastics, make the cost of the process much higher and only profitable for large volumes of production. The filling of the fibres interstices is slow, making it difficult to guarantee the absence of voids and a good impregnation of the fibres inside the tow without recourse to sophisticated equipment (Figure 2.31 c));

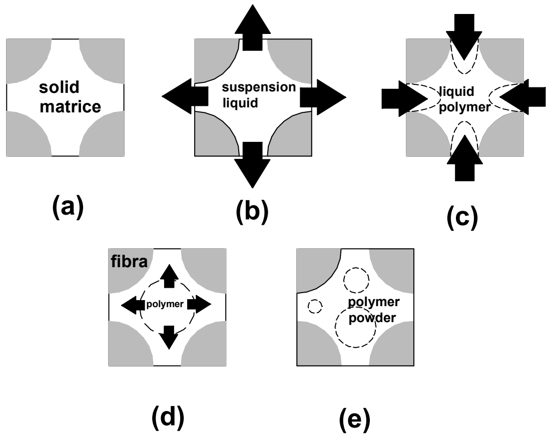


Figure 2.31 - Differences in the consolidation of pre-impregnated materials (adapted from [2.106])

- Techniques using the intimate mixture of thermoplastic and reinforcement fibres (Figure 2.31 d)) allow to minimise the impregnation time. They do not guarantee the full impregnation of the reinforcing fibres which are only actually carried out during the final processing of the pre-impregnated. The great flexibility of the prepregs produced allows the use of looms for fabric manufacture. However, the costs inherent in the manufacture of thermoplastic fibres cause this process to have higher costs than those based on the intimate mixture of the reinforcement fibres with thermoplastic powder. During the final transformation, the complete impregnation of the reinforcement is also hampered by much of the flow of the thermoplastic to occur across the reinforcing fibres;
- As in the previous case, the impregnation time is minimised in the techniques using the intimate mixture of the thermoplastic powder with the reinforcing fibres (Figure 2.31 e)). The total impregnation of the reinforcement is also carried out only during

> the subsequent processing of the pre-impregnated materials. In recent years, the interest in the application and the study of these techniques has been increasing due to the low cost associated with them and the fact that the impregnation of the reinforcement during the transformation becomes easier due to flow of the thermoplastic carry out essentially in the direction of the fibres. The difficulty in obtaining some thermoplastics powder and the fact that the size of the thermoplastic particles can affect the conditions of deposition and impregnation of the fibres are the biggest problems pointed to this technique.

In recent years, a new line of deposition thermoplastic dry powder in continuous fibres to produce *towpregs* has been design and built by the Institute for Polymers and Composites (IPC) - Minho University and allows to develop the studies already performed previously [2.88-2.104].

The dry powder coating equipment is schematically shown in Figure 2.32 [2.107-2.117]. It consists of six main parts: wind-off system, fibre spreader unit, heating section, coating section, consolidation unit and a wind-up section. Initially, the reinforcing fibres are wound-off and pulled through a pneumatic spreader and then coated with polymer by heating in a convection oven and made to pass into a polymer powder vibrating bath. A gravity system allows maintaining the amount of polymer powder constant. The consolidation unit oven allows softening the polymer powder, promoting its adhesion to the fibre surface. Finally, the thermoplastic matrix towpreg is cooled down and wound-up on a spool.

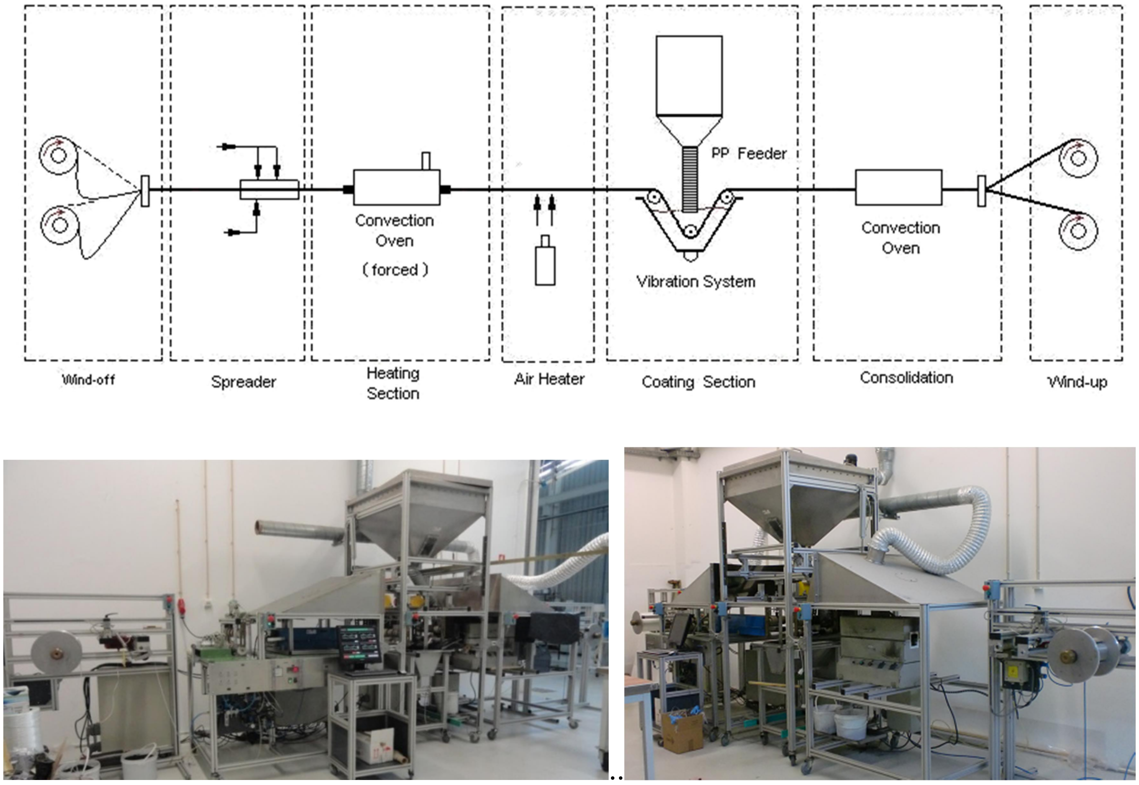


Figure 2.32 - Powder coating line setup

2.7. Processing of thermoplastic matrix pre-impregnated materials

Thermosets clearly dominate in composite applications and that thermoplastics are relative newcomers to the filed. In fact, it is only in injection and compression moulding and to some degree in prepreg layup that thermoplastics-based composites are currently of any commercial significance. However, since thermoplastics pre-impregnated materials became readily avaible there has been an immense interest in this material family. The main overall reasons for the interest are related to potencial improvements in composite properties. From a manufacturing point of view, the main attraction of thermoplastics lies in possibility of achieving very short demoulding times since no chemical reaction needs to take place for composite to solidify. Although the interest in thermoplastics composites has not resulted in any great number of commercially important manufacturing techniques, the large research and development efforts in industry and academia through-out the world have proven the technical - if not always the economical - feasibility of a number of more or less innovative processing routes.

Most manufacturing techniques that have been tried with thermoplastics are heavly inspired by the commercially successful techniques used with thermosets. Other techiniques have been borrowed from sheet-metal forming; these include compression moulding and rollforming (although the former obviously via thermoset composite manufacturing).

The quality, performance and commercial success of a final component in thermoplastic matrix composite material depends largely on a discerning choice of the binomial manufacturing process and operative variables (applied pressure, temperature and processing time) to be used in the transformation of the thermoplastic matrix pre-impregnated material.

The optimization of the variables to be used in the transformation of the pre-impregnated material depends both on the equipment used (e.g., mold temperatures or pressures that can be reached) as well as the specific properties of the thermoplastic matrix used. In fact, the degradation and the rheological characteristics of the thermoplastic are factors that also condition strongly the values to be selected for the transformation variables. Chosen, for example, a given processing temperature, the degradation of the thermoplastic will limit the maximum processing time to be used. The choice of a too low processing temperature will lead, on the other hand, to a very high matrix viscosity and, consequently, to a time of processing so long that the process becomes commercially unfeasible.

Selected the process to be used in the transformation of a given type of thermoplastic matrix pré-impregnated material, it is important to define its "processing window", that is, the range of possible combinations of the processing variables that allow to obtain final pieces with commercially acceptable quality and performance. This concept is schematically synthesized in Figure 2.33.

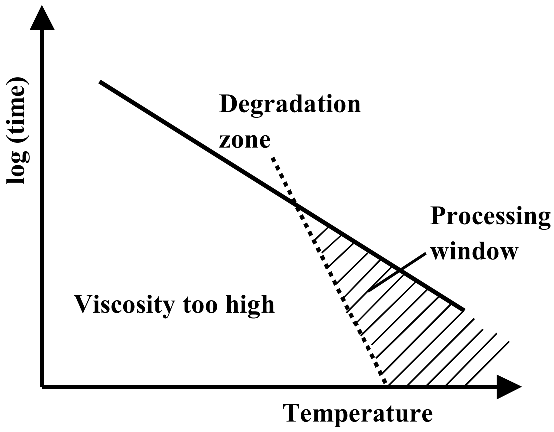


Figure 2.33 - Time and temperature corresponding to the "processing window" of a thermoplastic matrix pre-impregnated material [2.53]

The main processes of transformation of reinforced thermoplastics are the injection, the hot compression, the thermoforming, the pultrusion and the fibre placement techniques, where it includes the filament winding as the most used technology.

Many of the equipment used in the transformation of thermoplastic matrix pre-impregnated materials result from adaptations of the commonly employed in the processing of thermosetting matrix composites. In the absence of low-cost technologies suitable for its transformation, some large companies have also opted for the development of their own manufacturing technologies [2.118].

2.8. Pultrusion of thermoplastic matrix pre-impregnated materials

Pultrusion is a continuous manufacturing technique that allows produce constant section profiles in composite material with a high degree of automation, allowing reduction of the production costs. The most used equipment in the pultrusion of thermoplastic reinforced profiles results from the convenient adaptation of conventional machines used in the manufacture thermoset reinforced profiles. It is usually necessary to introduce an oven to pre-heat the thermoplastics reinforced rovings and use two dies, one heated and one that is cooled to ensure the final profile solidification (Figure 2.34) [2.119-2.137].

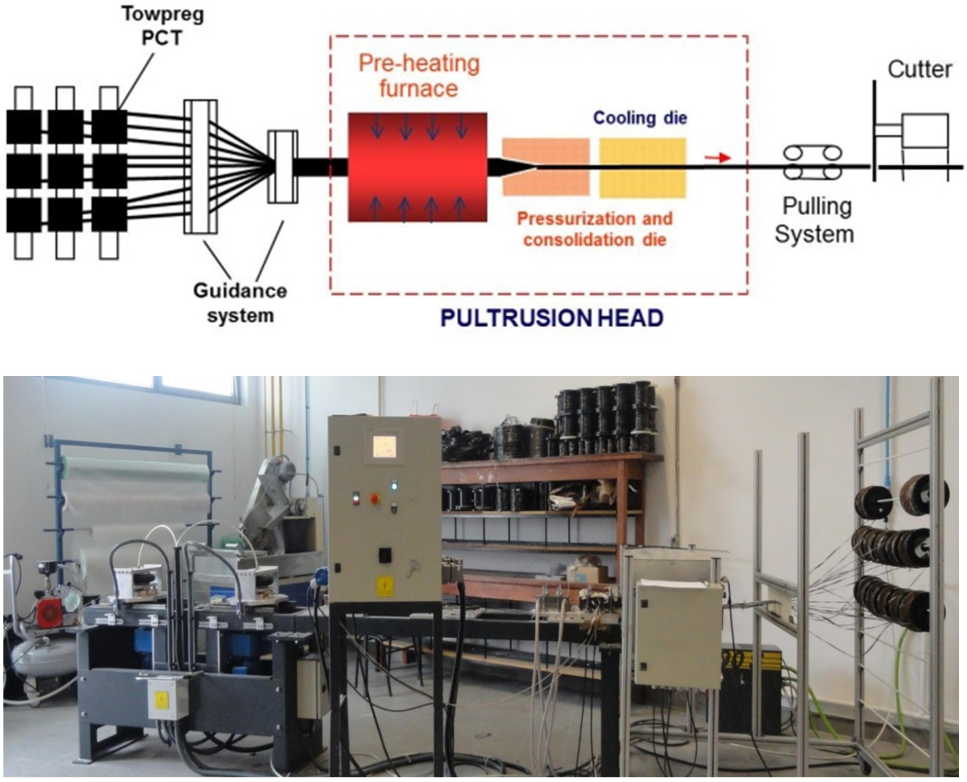


Figure 2.34 - Schematic diagram and image of the pultrusion line

To produce the composite profiles, the pre-impregnated materials are guided into the pre-heating furnace to be heated up to the required temperature. Then, they enter in the pultrusion die to be heated up and consolidated to the required size in its first zone and, after cooled down in order to solidify. The pultruded material is then cut into specified lengths. In this work, a die was designed and manufactured to allow producing a 20×2 mm^2 tape-shaped profile. The pre-heating furnace may reach a temperature of 1000 ºC and was designed to allow processing almost every type of fibre/thermoplastic-based pre-impregnated materials.

The pultrusion process allows the use of a large combination of types of reinforcements and thermosetting or thermoplastic polymer matrices. In the pultrusion with thermoplastic matrices is used a wide range of polymeric materials, such as PP, PET, PC, ABS, PA 6, PA 12, PBT, PMMA, PPS, PEEK, PEI and PAI.

The reinforcements most common are glass fibres, but also can be use carbon fibres and aramid fibres. The continuous fibres (roving) are the most commonly used reinforcement because they provide an excellent longitudinal strength.

Typically, within the limits of project, pultruded profiles are produced with a higher fibre mass fraction and that can achieve de value of 70%.

In the pultrusion of thermoplastic matrix composites there is no chemical reaction during the consolidation, but only the application of heat and pressure to consolidate the impregnated reinforcement. Thus, while in pultrusion with thermosetting matrices the die system is typically composed by a heated die, with thermoplastic matrices are required at least two dies, the last being necessarily for the cooling of the consolidated profile. Also notes that the heated die for thermoplastic matrices tends to be shorter, with the convergent section, for material pressurization, covering a much larger portion of the total length [2.138, 2.139].

A *typical process of thermoplastic matrix composites pultrusion* encompasses the following stages [2.140]:

1 - Output and pre-impregnated material guide sistem;

2 – Pre-heating;

3 - Pressurization and consolidation;

4 - Cooling of the consolidated profile;

5 - Profile cutting.

Phases 2, 3 and 4 develop a set of elements which designate a head of pultrusion.

The process begins with a number of pre-impregnated materials (tows) needed to make the production of profile, which are rolled out from their coils.

For a given cross section of the desired profile with a final fibre mass fraction, w_f, the number of towpregs/commingled fibres/PCT´s/tapes required, Nreq., is given by:

$$N_{req.} = \frac{\rho_c \text{ x } A_t}{d_{lin.pe}} \tag{2.3}$$

where,

ρ_c – is the density of composite [Mg/m^3];
$d_{lin.pe}$ – is the linear weight per unit length of pre-impregnated material [TEX (g/km)]
A_t – is the cross-sectional area of the profile [m^2].

The density of the composite is obtained using the Rule of Mixtures:

$$\rho_c = \rho_f \nu_f + \rho_p \nu_p \tag{2.4}$$

where,

ν_f is a fibre volume fraction,
ν_p is the polymer mass fraction,
ρ_f and ρ_p are the densities of the fibres and matrix, respectively.

The pre-impregnated materials are guided towards pre-heating oven by steel or plastic (e.g. HDPE) drilled plates.

To favor the impregnation of the matrix into the fibres by pressure of pre-impregnated materials in convergent zone of pressurization and consolidation die, the viscosity of the thermoplastic matrix must be the lowest possible. Since viscosity varies inversely with temperature, it is necessary pre-heating the matrix before pre-impregnated materials entering in the die.

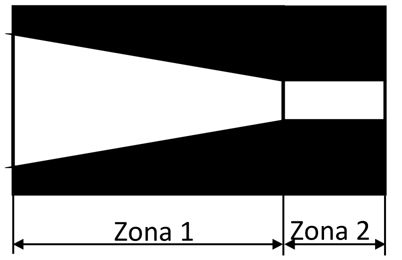
Pre-heating of the pre-impregnated materials is made up to a temperature between the glass transition temperature and melting temperature of matrix [2.141]. The softening of the matrix also promotes the adherence of pre-impregnated materials, stacked on top of each other.

Due heat conduction be low for a normal direction to the fibres, one of the biggest problems in the pre-heating is a quick fusion of matrix without running the risk of degrading the surface. This problem can be overcome by subjecting the material to a long warm-up period, so that the intensity of surface heating can be reduced. The temperature profile during the processing depends on the speed of the process, the size, the temperature of the heating elements, etc., as well as by the properties of the material [2.141].

The exit of the oven should be close to the entrance of the die pressurization and consolidation to be no significant cooling during this transition [2.142].

After pre-heating, the pre-impregnated materials enter in a heated die to be pressurised and consolidated until to the final form of profile. This die has, at the entrance, a convergence zone that pressurizes the pre-impregnated materials to eliminate gaps, ensuring even the necessary fibre impregnation by the flow of the molten polymer powder, involving the fibres. The increased pressure along the convergence zone is due to the flow matrix relatively to the fibres, caused by translation of the fibres in the convergence zone and by thermal expansion of composite in that area [2.138, 2.139, 2.143]. In this section of the die, it is important that the temperature along the cross-section of profile be as uniform as possible in order to obtain a uniform matrix flow and consequently a regular distribution of fibres in final product.

A typical geometry of heated die is shown in Figure 2.35.



Zone 1 – Pressurizing and consolidation zone

Zone 2 – Shaping zone

Figure 2.35 - Typical geometry of the pressurization and consolidation die [2.143]

On the other hand, it is also important the length of the die is sufficient to heat the pre-impregnated materials set up a uniform temperature along the cross-section. Heating is generally promoted by the electrical cartridges arranged regularly through the die. For the process control, it is advisable to incorporate temperature sensors. These sensors provide monitoring and the temperature control of the die works in different areas, ensuring thus a heating profile [2.138, 2.142].

To reduce loss of heat to the environment, the external walls of the die must be lined with insulating boards.

After pressurizing and consolidation zone is the zone of shaping with the profile form.

The entry and exit areas of the die must have radii of curvature generous, so that transitions suffered by material in these areas are the smoothest possible [2.144].

The moulding areas of the die, as well as the entry and exit areas may be, in certain cases, polished and protected with a final coating of chromium from at least 25 µm. This protection, which prolongs the life of the die, is due to the abrasive nature of the reinforcements used, mainly fibreglass [2.144].

A controller installed in the pultrusion machine carries out the temperature control of the pressurization and consolidation die. Two PT 100 sensors are set in two zones (at the bottom and top of the die).

Composite profile, which comes out consolidated of the pressurization and consolidation die, enters into the cooling die, contrived with the cross-section of the profile. This die must have sufficient length to promote cooling, ensuring that, outside of the die, the temperature is lower than the distortion temperature of the thermoplastic used.

The two dies (pressurization and consolidation die and cooling die) should be isolated from each other by ceramic [2.142] plates or simply by the existence of a small air spacing [2.138, 2.139].

In the cooling die, the profile is cooled to a temperature, which ensures stability of its shape at the exit of the die. The cross section of the die is closed to the final shape of the composite profile and is constant over its entire length.The cooling of the thermoplastic matrix can be assured by different methods, depending on the processing speed range used and surface quality required. Cooling by natural convection is sufficient for low speeds and when processing the surface quality of the profile is not a product specification. On the other hand, if processing speeds are used and required a good surface quality of the profile, the cooling must be done by a water bath, forced convection or by contact. In addition, comparing the different cooling systems, are clearly highlighted by the highest cooling rates obtained, based on the use of water as a refrigerant [2.142].

Temperature control of the cooling die is carried out by a Regloplas Model 90S / 6 / TP20 / 1K / RT22 water thermoregulator.

Most of the past efforts have been directed towards modeling of thermosets and thermoplastic pultrusion [2.145]. The first authors who have shown an interest in thermoplastic pultrusion modeling are Lee and Springer [2.146], Larock et al. [2.147] and Aström and Pipes [2.148]. Neverthless, Lee et al. [2.149] and Aström and Pipes [2.139] were the first to develop a model coupling heat transfer, flow and pulling resistance of thermoplastic process. Aström and Pipes [2.139] have proposed a one-dimensional model with an analytical solution using Kozeny-Carman permeability expression coupled to a heat transfer model. Later, only focusing on the flow modeling, Raper et al. [2.150] have developed a two-dimensional model with an analytical transverse expression of the permeability of tows (Gebart [2.151]). And even three dimensional models have been developed recently to simulate the resin flow [2.152]. Moreover thermoplastic pultrusion with prepreg products such commingled yarns [2.153] or powder –impregnated bundles [2.154, 2.155] have already been studied. All these approaches model the polymer flow at a macroscopic scale without considering any microscopic effect.

An understanding of the effects of processing parameters and geometry of the pultrusion process dies can require the development of mathematical models to minimize the number of necessary experiences, thus saving time and money on process optimization [2.138, 2.139].

The temperature and pressure are the most important parameters in processing thermoplastic matrix composites [2.138, 2.139, 2.156]. Models were developed to predict the temperature and pressure along a line of pultrusion with thermoplastic matrices. The pull force, which depends on the temperature and pressure distributions on the composite, is a parameter that is easy to measure continuously during processing.

The models of pressure and pull force assume that the key to understand the process of pultrusion with thermoplastic matrices is the matrix flow in relation to fibres, which occurs in the convergent section of pressurization and consolidation die. In the pultrusion with pre-impregnated materials, it is assumed that the flow occurs in a longitudinal direction to the fibres. The movement of the fibres induces a reflux of the matrix opposite to the pressure gradient in the axial direction at the converging section of the die [2.155].

The pressure developed depends on the die cross section, the contact length of the composite in the die, the viscosity of the matrix, the volumetric ratios and thermal expansion coefficients of the fibre and the matrix, and the contraction of composite material in the solid state.

An important parameter in the pultrusion process with thermoplastic matrices is the fibre volume fraction. With high fibre volume fractions, the fibres are closer to each other, and the matrix is forced to flow through a narrower space. This results in a considerable increase in pressure in the spinning area [2.143].

The model of the distribution of temperatures considers the composite into the pressurization and consolidation die and cooling die, separated by a small air space. The model predicts the composite temperature depending on the distance to the neutral line composite and the position in pultrusion line. In these models, it is assumed that the preheating temperature rises strengthening impregnated at a uniform temperature before the entry on die pressurization and consolidation [2.138, 2.139, 2.156].

From the pultrusion process analysis, it is possible to establish some relationships between the most significant process parameters, the dies characteristics and the properties of the composite and its constituents [2.140, 2.143, 2.156, 2.157].

In pultrusion, the time above a certain temperature is increased by decreasing the pulling speed and by increasing the lengths and the temperatures of preheater and the heated die. The cooling rate is increased by increasing the pulling speed and by decreasing the temperatures of the air in the gap and the cooled die. Processing will, in principle, be more reliable with lower pull speeds, as in these cases the temperature profile at the exit of the dies is more homogeneous; the homogeneity of the temperature is more important in the pressurization and consolidation die, to obtain a uniform matrix flow and consequently a regular distribution of the fibres in the consolidated profile.

Another critical factor in the consolidation of thermoplastic-matrix composites is the time at or above a certain moulding pressure. Therefore, methods to increase the time under pressure include increasing taper length and decreasing the pulling speed. The pressure increases progressively with the advancing of the pre-impregnated material in the pultrusion die, with a sharp rise in the pressure value at the end of die converging zone and falls off at a similar rate in constant cross-section. As would be expected, it is also observed that for higher pulling speed, the pressure increases. Pressure increases with decreasing die temperature because viscosity variation is inversely proportional to temperature. The pressure distribution is also influenced by the geometry of pressurization and consolidation die converging zone, as different angles provide different lengths and residence times of the material in the convergence zone and change the pressure values.

With given die and material systems, the two principal ways to alter the pulling force are to change the pulling speed and to change the temperature of material. Hence, to decrease the pulling force one can decrease the pulling speed, increase the preheater and heated die temperatures, minimize the over-filling of the heated die and decrease the length of the constant cross-section portion of heated die. Since the pressure in the taper contributes to the pulling force, there is a trade off between creating the necessary consolidation pressure for the desire duration and keeping the pulling force low.

Material characteristics also affect the compression of pre-impregnated materials in the convergence zone of the pressurization and consolidation die, as well as the final fibre volume fraction in the composite and the polymer particle dimension (for towpregs). High fibre volume fractions cause significant pressure increase as the fibres are closer to each other, and the polymer is forced to flow through a thinner gap. The values of the pressures are very dependent on the size of the polymer particles, corresponding to a larger particle radius, higher pressures in the composite. In addition to increasing consolidation pressure, a larger polymer particle size also increases the likelihood of voids in the composite.

2.9. Heated compression moulding of pultruded profiles

Several pultruded profiles and pre-impregnated materials (GF/PP PCT and weaved prepreg tape) were subjected to the process of compression for better consolidation, during which the different layers of the pre-impregnated materials or own pultruded profiles interpenetrate across in order to adhere to each other [2.119, 2.124, 2.127, 2.135]. Previous studies and the development of several models related to the compression process of prepreg materials have already been carried out as indicated in the references [1.3, 1.5, 1.38-1.65] of chapter 1. The process can also facilitate and improve impregnation of materials used in compression, if the fibres are not yet completely impregnated (in this case, a thermoplastic matrix flow between the filaments of fibre). Thus, during the process the materials to compress are first heated and then cooled and is necessary control carefully the levels and the times of temperature and pressure applications in order to ensure the attainment of the desired properties in the final piece. During the heating phase the mould plates only transfer heat to the material, but in the cooling cycle, the pressure is the same as the phase of consolidation in order to maintain their dimensional stability. The resin penetration into the reinforcing fibrous preforms can be improved by applying high consolidation pressure but, at the same time, high consolidation pressure de-aligns the reinforcing fibres, apart from increasing the power consumption [2.158].

The pultruded profiles or pre-impregnated materials (GF/PP PCT and weaved prepreg tape) after having been cut were introduced, in one direction, in a mold cavity placed between the heated platen of a hot press. After a selected time delay at press platen temperature higher than polymer melt temperature, the press was closed until reaching the maximum compression force (the pressure value is chosen to obtain full impregnation of the fibres). Sometime after reaching the maximum force necessary to full impregnation and not to let the polymer degrade, the press platen were cooled down maintaining constant the press closing force. When the room temperature is reached, the press platen was opened and the final unidirectional or woven (from weaved prepreg tape) composite plate is removed from the mold.

The processing conditions were planned in order to compare the mechanical properties of the final plates with the pultruded profiles used as raw material. In this sense, the process variables were similar to those used in pultrusion process.

The possibility of producing a plate from pultruded profiles may allow various combinations of materials and fibres orientations of several layers that are forming a laminate.

The advantage of using pultruded profiles in relation to pre-impregnated materials is that these are already practically impregnated and the orientation of the fibres is very well defined, but the flexibility of pre-impregnated materials may also be an advantage for complex geometry parts.

In the heated compression process must be aware of the factors which influence significantly the flow of thermoplastic polymer on fibres and that determine the level of impregnation that can achieve (see subchapter 2.6). The pressure applied, the viscosity of the polymer (depending on the chosen temperature) and the permeability of the fibres are variables to control and determine the processing time.

For the compression of materials in which it is necessary to apply very high temperatures the choice of appropriate release agents is critical to the success of the operation.

2.10. Objectives of the work

From what has been previously exposed, it can be noted that the expansion of the market of thermoplastics reinforced with continuous fibres in commercial applications is strongly dependent on the development of technologies that allow producing thermoplastic matrix pre-impregnated materials with lower costs.

It is also noted that the vast majority of the technologies used in the transformation of these pre-impregnated materials are still in the experimental stage. It is therefore still not possible to safely predict and keep controlled the properties of composites produced, which is an absolutely necessary condition for their passage to the industrial stage.

The main objective of the PhD thesis is to develop a Pultrusion processing solutions for systems of thermoplastic matrix composites using the following pre-impregnated materials:

- towpregs/commingled yarns/PCT of polypropylene reinforced with glass and carbon fibre for consumer markets.
- towpregs of PRIMOSPIRE® reinforced with carbon fibres for high perform applications.

Thus, the main tasks of this work are:

- Elaborate the State of the Art about the thermoplastic pultrusion composites and the most relevant connected issues.
- Characterize the raw materials, in particular the constituents of pre-impregnated materials and the pre-impregnated materials themselves.
- Study and evaluate the techniques for the production of pre-impregnated materials.
- Develop towpregs production prototype equipment.
- Produce pre-impregnated materials (towpregs) for manufacture pultruded profiles.
- Develop towpregs production equipment.
- Produce profiles from three different pre-impregnated raw materials: comingled system, powder coated towpregs and PCT´s, using a prototype pultrusion equipment.
- Establish processing windows for the studied systems and optimize the process parameters using the Design of Experiments (DOE) methodology.
- Study the influence of compatibilizing agents on the mechanical performance of pultruded profiles.
- Process the pultrusion profiles by heated compression moulding into composite plates.
- Analyse the different composite produced under Optical and SEM microscope and assess their mechanical behaviour through the determination of fibre content and tensile, flexural and ILSS properties and by DMA.
- Compare the mechanical test results with theoretical ones that can be predicted by using the mechanics of composites concepts (Classical Laminate Theory, Macro and Micromechanics).
- Determine the fibre volume fraction of a composite with a high melting temperature thermoplastic polymer used as matrix, comparing the results of thermogravimetric analysis (TGA) with calcination tests and image processing.
- Analyse and discuss the results and estabilish suggestions for future work.

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Chapter 3

THEORY

3.1. Introduction

In this chapter, the main theoretical concepts to be used in the development of certain subjects of this thesis will be addressed, notably in the study of the production of thermoplastic matrix pre-impregnated materials, its subsequent processing by pultrusion and heated compression and in the prediction of the mechanical properties obtained in the final composites.

This chapter is structured in two sub-chapters: i) Classic laminate theory, which exposes the basic principles of this theory used in predicting the elastic properties and mechanical resistance of composites produced in this work [3.1] ii) Design of Experiments and the Taguchi Method to determine the combination of process parameters that would best maximize simultaneously some properties of the pre-impregnated materials and the pultruded profiles.

3.2. The Classical Laminate Theory

The Classical Laminate Theory (CLT) is a commonly used predictive tool, which evolved in the 1960s and made possible to analyze complex coupling effects that may occur in composite laminates. It is able to predict strains, displacements and curvatures that develop in a laminate under mechanically and hygrothermal loads. CTL is the more generally accepted theory to study the mechanical behavior of composite structures. It was developed based on Kirchhoff Plate Theory for isotropic materials, with the main difference appearing in the lamina stress-strain relationships, that establishes relationships between plate curvatures and bending and torsional internal moments, which are usually generated by concentrated or distributed transverse loads [3.2-3.8].

According to this theory, a composite laminate consists of a stack of orthotropic layers, perfectly linked structurally each other. Are defined two coordinate axes systems: the system of main axes (1, 2, 3) which the direction of 1 axis coincides with the direction of the fibres and the axes of the system requests (x, y, z), as can be seen from Figure 3.1. The angle between the x axis and the 1 axis, measured counterclockwise and at plan of layer is identified by the letter θ.

As with any analytical technique, some assumptions must be considered in order to make the problem solvable:

i) each layer presents a linear elastic behavior (Hooke's law);

ii) although the properties are anisotropic (vary with the direction) are constant at all points of the same layer;

iii) the laminate is subjected to a plane stress;

iv) the strain distribution is linear throughout the thickness of the laminate and,

v) displacements u and v are assumed to be linear functions of the thickness coordinate z (no warping);

vi) the normal and shear stresses and strains transverse to the plane of the laminate are negligible.

Assumptions iii), iv) v) and vi) together define the Kirchhoff hypothesis.

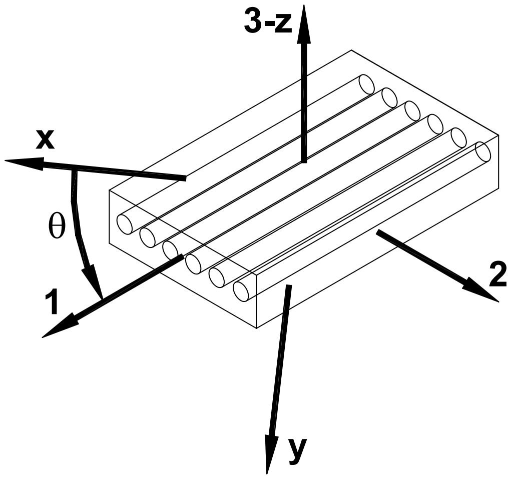

Figure 3.1 – Main axes systems (1, 2, 3) and in direction of the request (x, y, z) of a orthotropic layer [3.1]

3.2.1. Properties of composite laminates

Considering the external loads applied (forces and moments) per unit of width in the global coordinate system, X, Y, Z, (Figure 3.2), the general expressions of the stress-strain relation for a generic laminate are given by[3.1]:

$$\{\varepsilon^o\}_{xy} = [a^*]\{\sigma^o\}_{xy} + \frac{[b^*]}{3}\{\sigma^f\}_{xy} \tag{3.1}$$

and

$$\{\varepsilon^f\}_{xy} = [b^*]^T\{\sigma^o\}_{xy} + [d^*]\{\sigma^f\}_{xy} \tag{3.2}$$

where:

$[a^*] = h[a]$, $[b^*] = \dfrac{h^2}{3}[b]$ and $[d^*] = \dfrac{h^3}{12}[d]$ are the normalized compliance matrices and h is the total thickness of the laminate.

$\{\kappa\}_{xy}$ is the matrix of laminate curvatures,

$\{\varepsilon^o\}_{xy}$, $\{\varepsilon^f\}_{xy} = \dfrac{h}{2}\{\kappa\}_{xy}$ are the middle plane strains (membrane strains) and the outer layer (bending strains) of the laminate, respectively,

$\{\sigma^o\}_{xy}$ and $\{\sigma^f\}_{xy}$ are the normalized membrane and bending stresses, respectively,

$[a]$, $[b]$ and $[d]$ are the compliance matrices and the index, T, indicates that the matrix is transposed.

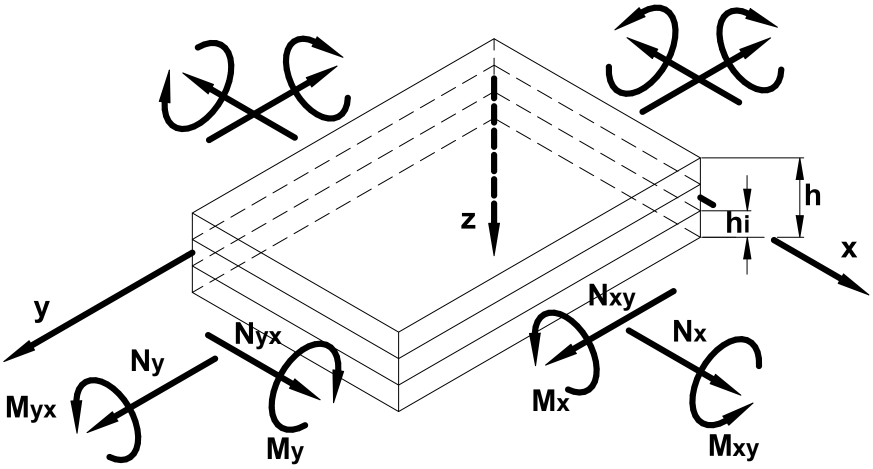

Figure 3.2 – Global coordinate system and external loads per unit width on a laminate [3.8]

The displacements of laminate *u*, *v* e *w*, respectively, in the x, y, e z directions, can be generically defined as:

$$u = u^o(x,y) + zF_1(x,y) \tag{3.3}$$

$$v = v^o(x,y) + zF_2(x,y) \tag{3.4}$$

$$w = w^o(x,y) \tag{3.5}$$

where,

u^0 is the displacement in the middle plane of the laminate in the x-axis direction,

v^0 is the displacement in the middle plane of the laminate in the y-axis direction, and

w^0 is the displacement in the middle plane of the laminate in the z-axis direction.

The F1 and F2 functions can be defined from the expressions that annul the shear strains according to the z axis, such as:

$$\varepsilon_{xz} = \frac{\partial u}{\partial z} + \frac{\partial w}{\partial x} = F_1(x,y) + \frac{\partial w}{\partial x} = 0 \tag{3.6}$$

and

$$\varepsilon_{yz} = \frac{\partial v}{\partial z} + \frac{\partial w}{\partial y} = F_2(x,y) + \frac{\partial w}{\partial y} = 0 \tag{3.7}$$

In matrix notation the total strains of the laminate can then be defined as:

$$\{\varepsilon\}_{xy} = \begin{Bmatrix} \varepsilon_x \\ \varepsilon_y \\ \varepsilon_{xy} \end{Bmatrix} = \begin{Bmatrix} \varepsilon_x^o \\ \varepsilon_y^o \\ \varepsilon_{xy}^o \end{Bmatrix} + z \begin{Bmatrix} \kappa_x \\ \kappa_y \\ \kappa_{xy} \end{Bmatrix} \tag{3.8}$$

Where, the membrane strain (gradient of the displacement) matrix of the middle plane of the laminate is given by:

$$\{\varepsilon^o\}_{xy} = \begin{Bmatrix} \varepsilon_x^o \\ \varepsilon_y^o \\ \varepsilon_{xy}^o \end{Bmatrix} = \begin{Bmatrix} \dfrac{\partial u^o}{\partial x} \\ \dfrac{\partial v^o}{\partial y} \\ \dfrac{1}{2}\left[\dfrac{\partial u^o}{\partial y} + \dfrac{\partial v^o}{\partial x}\right] \end{Bmatrix} \tag{3.9}$$

and the curvatures (second derivatives of the displacement) matrix by:

$$\{\kappa\}_{xy} = \begin{Bmatrix} \kappa_x \\ \kappa_y \\ \kappa_{xy} \end{Bmatrix} = \begin{Bmatrix} -\dfrac{\partial^2 \omega^o}{\partial x^2} \\ -\dfrac{\partial^2 \omega^o}{\partial y^2} \\ -2\dfrac{\partial^2 \omega^o}{\partial x \partial y} \end{Bmatrix} \tag{3.10}$$

Therefore, the bending strain matrix should be defined as:

$$\left\{\varepsilon^{f}\right\}_{xy}=z\left\{\kappa\right\}_{xy}=z\begin{Bmatrix}\kappa_{x}\\ \kappa_{y}\\ \kappa_{xy}\end{Bmatrix} \tag{3.11}$$

On the other hand, the normallized membrane stresses matrix of laminate as well as the bending stresses can be defined by:

$$\left\{\sigma^{0}\right\}_{xy}=\begin{Bmatrix}\sigma_{x}^{0}\\ \sigma_{y}^{0}\\ \sigma_{xy}^{0}\end{Bmatrix}=\frac{1}{h}\left\{N\right\}_{xy}=\frac{1}{h}\begin{Bmatrix}N_{x}\\ N_{y}\\ N_{xy}\end{Bmatrix} \tag{3.12}$$

and

$$\left\{\sigma^{f}\right\}_{xy}=\begin{Bmatrix}\sigma_{x}^{f}\\ \sigma_{y}^{f}\\ \sigma_{xy}^{f}\end{Bmatrix}=\frac{6}{h^{2}}\left\{M\right\}_{xy}=\frac{6}{h^{2}}\begin{Bmatrix}M_{x}\\ M_{y}\\ M_{xy}\end{Bmatrix} \tag{3.13}$$

Being able to clarify in relation to stresses the stress-strain relations for a laminate in the global coordinate system, by reversal of the EQS. 3.1 and 3.2, like:

$$\left\{\sigma^{o}\right\}_{xy}=\left[A^{*}\right]\left\{\varepsilon^{o}\right\}_{xy}+\left[B^{*}\right]\left\{\varepsilon^{f}\right\}_{xy} \tag{3.14}$$

and

$$\left\{\sigma^{f}\right\}_{xy}=3\left[B^{*}\right]^{T}\left\{\varepsilon^{o}\right\}_{xy}+\left[D^{*}\right]\left\{\varepsilon^{f}\right\}_{xy} \tag{3.15}$$

where,

$$\left[A^{*}\right]=\frac{1}{h}\left[A\right] \tag{3.16}$$

$$\left[B^{*}\right]=\frac{2}{h^{2}}\left[B\right] \tag{3.17}$$

and

$$\left[D^{*}\right]=\frac{12}{h^{3}}\left[D\right] \tag{3.18}$$

are the normalized stiffness matrices of the laminate.

The terms of the compliance matrix of the laminate can be determined from their values of the engineering constants, i. e.:

$$E_x = \frac{1}{a^*_{11}} \tag{3.19}$$

$$E_y = \frac{1}{a^*_{22}} \tag{3.20}$$

$$G_{xy} = \frac{1}{a^*_{66}} \tag{3.21}$$

$$E_x^f = \frac{1}{d^*_{11}} \tag{3.22}$$

$$E_y^f = \frac{1}{d^*_{22}} \tag{3.23}$$

$$\nu_{xy} = -\frac{a^*_{12}}{a^*_{11}} \tag{3.24}$$

$$\nu_{yx} = -\frac{a^*_{12}}{a^*_{22}} \tag{3.25}$$

In the previous expressions, E_x^f and E_y^f represent the bending stiffness.

Is also possible determine the stiffness matrices of laminate in the global coordinate system (x, y, z) from the weighted sum of stiffness matrices of each layer given by the following expressions:

$$[A] = \sum_{i=1}^{n_c} \left[\overline{Q}\right]_i h_i \tag{3.26}$$

$$[B] = \frac{1}{2}\sum_{i=1}^{n_c} \left[\overline{Q}\right]_i (z_i^2 - z_{i-1}^2) \tag{3.27}$$

$$[D] = \frac{1}{3}\sum_{i=1}^{n_c} \left[\overline{Q}\right]_i (z_i^3 - z_{i-1}^3) \tag{3.28}$$

where,

n_c is the number of layers of the laminate,

$[A]$, $[B]$, e $[D]$ are the matrices of membrane stiffness, membrane-bending coupling stiffness and bending stiffness of laminate, respectively and,

$[\overline{Q}]_i$ is the stiffness matrix of layer i in the global coordinate system (x, y, z), h_i is the thickness of the layer i and z_i is the coordinate in the z axis of the outer surface of the layer i.

Compliance matrices ([a], [b] and [d]) of the laminate can be determined from the stiffness matrices using the following transformations:

$$[a]=[A]^{-1}+[A]^{-1}[B]\left([D]-[B][A]^{-1}[B]\right)^{-1}[B][A]^{-1} \tag{3.29}$$

$$[b]=[A]^{-1}[B][B]\left([D]-[B][A]^{-1}[B]\right)^{-1} \tag{3.30}$$

$$[d]=\left([D]-[B][A]^{-1}[B]\right)^{-1} \tag{3.31}$$

The stiffness matrix, $[\overline{Q}]_i$, of each layer, i, can be calculated to the global coordinate system x, y, z, by:

$$[\overline{Q}]_i=[T]^{-1}[Q]_i\left([T]^T\right)^{-1} \tag{3.32}$$

where the transformation matrix of the coordinated system, [T], is defined by:

$$[T]=\begin{bmatrix} \cos^2\theta & sen^2\theta & 2\cos\theta sen\theta \\ sen^2\theta & \cos^2\theta & -2\cos\theta sen\theta \\ -sen\theta\cos\theta & sen\theta\cos\theta & \cos^2\theta-sen^2\theta \end{bmatrix} \tag{3.33}$$

where $[Q]_i$ is the stiffness matrix of each layer in the main coordinate system (1, 2, 3), given by:

$$[Q]_i=\begin{bmatrix} \dfrac{E_1}{1-\nu_{12}\nu_{21}} & \dfrac{\nu_{12}E_2}{1-\nu_{12}\nu_{21}} & 0 \\ \dfrac{\nu_{12}E_2}{1-\nu_{12}\nu_{21}} & \dfrac{E_2}{1-\nu_{12}\nu_{21}} & 0 \\ 0 & 0 & G_{12} \end{bmatrix} \tag{3.34}$$

The values of the elastic properties of the layer can be calculated from the elastic constants of fibres reinforcement and matrix as well as the respective volume fractions.

The following expression allows calculating the fibres volume fraction from their mass fraction:

$$v_f = \frac{w_f \rho_p (1 - v_v)}{\rho_f + w_f (\rho_p - \rho_f)} \tag{3.35}$$

where,

v_f is a fibre volume fraction,

w_f is the fibre mass fraction,

ρ_f and ρ_p are the densities of the fibres and matrix, respectively and,

v_v represents the voids content.

The polymer mass fraction, w_p, can be obtained by the expression $w_p = (1\text{-}w_f)$. If the voids content is not significant the previous expression can be simplified, considering $v_v = 0$.

3.2.2. Layer Properties

The composites generally have a laminated structure, which consist, in general, of several stacked layers with all the fibres aligned in the same directions. The layer is therefore an elementary block whose mechanical behavior is critical to characterize. The *Macromechanics* study the stress-strain relations of the unidirectional layer in continuous fibres composites and each layer is treated as a homogeneous solid. The constitutive laws of the layer are generally valid for pultrusion unidirectional composites, although these do not have a laminated structure. There is a great interest to have models capable of predicting the properties of the layer function of the content and properties of the constituents (*Micromechanics*).

The reinforcing fibres influence significantly the mechanical behavior of composites increasing stiffness and mechanical strength of the polymer matrix. The simplest theoretical treatment of this effect is obtained by application of the Rule of Mixtures (ROM) [3.9-3.15]. Thus, considering null the voids volume fraction:

$$E_1 = E_f v_f + E_p (1 - v_f) \tag{3.36}$$

where,

E_1 is the elastic modulus of the layer in the direction of fibres,

E_f is the fibre elastic modulus,

E_p is the matrix elastic modulus and

v_f is the fibre volume fraction.

Similarly, for the mechanical tensile strength:

$$X = X_f v_f + X_p(1 - v_f) \tag{3.37}$$

where,
X is the mechanical strength of the layer in the direction of the fibres,
X_f is the fibre strength,
X_p is the matrix stress at a strain equal to fibre strength,
v_f is the fibre volume fraction.

The expression 3.37 should be considered only valid for fibres volume fractions greater than 5% (critical fibre volume fraction) and when the failure strain is less in fibres than in the matrix (which happens in most practical cases and, in particular, to the fibres and matrix used in this work).

In practice and for the materials used in this work, the values of the modulus and the mechanical strength of the matrix are much smaller than the corresponding values for the fibres and 3.36 e 3.37 expressions can be simplified to:

$$E_1 \approx E_f v_f \tag{3.38}$$

and

$$X \approx X_f v_f \tag{3.39}$$

On the other hand, the greater Poisson coefficient than can be estimated on the basis of the Rule of Mixtures [3.11, 3.12], being given by:

$$\nu_{12} = \nu_f v_f + \nu_p(1 - v_f) \tag{3.40}$$

where,
ν_{12} is the major Poisson coefficient,
ν_f is the Poisson coefficient of fibres and
ν_p is the Poisson coefficient of the matrix.

The experimental results showed that it is difficult to obtain the properties of composites in the transverse direction at reinforcing fibres, being these, in practice, often estimated from knowledge of the properties of the fibres and the matrices. The simplest equations that allow calculating these properties are inverse of the Rule of Mixtures. It is assumed that the same stress state develops in the fibres and matrix, in transversal direction. Thus, the following expression represents the elastic modulus in transversal direction to the fibres, E_2:

$$E_2 = \frac{E_f E_p}{E_f(1-v_f)+E_p v_f} \tag{3.41}$$

Similarly, the shear modulus, G_{12}, can be estimated by:

$$G_{12} = \frac{G_f G_p}{G_f(1-v_f)+G_p v_f} \tag{3.42}$$

where, G_p and G_f are the shear moduli of matrix and fibres, respectively.

Assuming that the fibres and matrix are isotropic materials, we have the following relations for the calculation of their shear moduli:

$$G_f = \frac{E_f}{2(1+\nu_f)} \tag{3.43}$$

and

$$G_p = \frac{E_p}{2(1+\nu_p)} \tag{3.44}$$

Finally, the minor Poisson coefficient (ν_{21}) can be calculated by considering the relationship between the coefficients of Poisson and the Young moduli, for the case of an elastic material [3.16]:

$$\nu_{21} = \nu_{12}\frac{E_2}{E_1} \tag{3.45}$$

If the main axis system (1, 2, 3) does not match with the external loads applied axis system (x, y, z), it may be useful to calculate the elastic constants in this last axis system. The following equations allow performing this calculation:

$$\frac{1}{E_x} = \frac{\cos^4\theta}{E_1}+\frac{\sin^4\theta}{E_2}+\frac{1}{4}\left(\frac{1}{G_{12}}-\frac{2\nu_{12}}{E_1}\right)\sin^2(2\theta) \tag{3.46}$$

$$\frac{1}{E_y} = \frac{\sin^4\theta}{E_1}+\frac{\cos^4\theta}{E_2}+\frac{1}{4}\left(\frac{1}{G_{12}}-\frac{2\nu_{12}}{E_1}\right)\sin^2(2\theta) \tag{3.47}$$

$$\frac{1}{G_{xy}} = \frac{1}{E_1}+\frac{2\nu_{12}}{E_1}+\frac{1}{E_2}-\left(\frac{1}{E_1}+\frac{2\nu_{12}}{E_1}+\frac{1}{E_2}-\frac{1}{G_{12}}\right)\cos^2(2\theta) \tag{3.48}$$

$$\nu_{xy} = E_1\left[\frac{\nu_{12}}{E_1} - \frac{1}{4}\left(\frac{1}{E_1} + \frac{2\nu_{12}}{E_1} + \frac{1}{E_2} - \frac{1}{G_{12}}\right)\sin^2(2\theta)\right] \tag{3.49}$$

$$\nu_{yx} = \nu_{xy}\frac{E_y}{E_x} \tag{3.50}$$

where,

E_x is the elastic modulus in the direction of the x axis,
E_y is the elastic modulus in the direction of the y axis,
G_{xy} is the shear modulus in plane of the (x-y) layer and,
ν_{yx} is the minor Poisson coefficient in the (x-y) plane.

3.2.3. Composite laminate failure

The analysis of the failure of a composite laminate is more difficult than the establishment of their elastic behaviour. In fact, being practically composite resistance determined by the strength of the fibres, it is very dependent on the direction of them. Thus, the resistance of the layer in the direction of the fibres is much larger than in the transverse direction. Additionally, the compressive strength in these directions can be quite different from the corresponding tensile strength.

The failure of a composite is normally predicted by comparing the stresses or strains that each layer can support at the main directions with the resulting from the application of external efforts through one of the following criteria: i) maximum stress criterion ii) maximum strain criterion, or following quadratic criteria: iii) the Tsai-Hill criterion, iv) the Tsai-Wu criterion and v) the Hoffman criterion [3.11, 3.17]. Finally, the composite failure is usually determined using the principle “First Ply Failure - (FPF)” which associates total failure of laminate to failure of a weak layer.

In practice the failure criteria most used is Tsai-Hill. This criterion predicts that the failure occurs in the weakest layer, when the following expression occurs:

$$\left(\frac{\sigma_1}{X}\right)^2 - \frac{\sigma_1\sigma_2}{X^2} + \left(\frac{\sigma_2}{Y}\right)^2 + \left(\frac{\tau_{12}}{S}\right)^2 = 1 \tag{3.51}$$

where σ_1, σ_2 and τ_{12} are the normal and shear stresses developed in the main directions (1-axis, 2-axis and plane 1-2, respectively) and X, Y, and S are normal (longitudinal and transverse, respectively) and shear strengths of the layer.

3.3. Design of Experiments (DOE) – Taguchi Method

The use of statistical techniques to optimize the processes under study allows you to decrease the time and resources required to achieve the best solutions. In this work and where that is considered appropriate, it will applied the statistical tool DOE (Design of Experiments) and the Taguchi method. The production of towpregs and the pultrusion process will likely be the preferred targets for application of this tool.

The DOE technique helps us to study many factors (variables) simultaneously and most economically. By studying the effects of individual factor on results, the best factor combinations can be determined. When applied to product or process design, the technique helps to seek out the best design among many alternatives. The technique can also be used to solve scientifically problems whose solution lies in the proper combinations of ingredients (factor or variables) rather than innovations or a single identifiable cause. Taguchi´s approach is a form of DOE with special application principles [3.18-3.24].

Taguchi method is a technique for designing and performing experiments to investigate processes where the output depends on many factors (variables, inputs) without having tediously and uneconomically run of the process using all possible combinations of values. Thanks to systematically chosen certain combinations of variables it is possible to separate their individual effects.

The DOE consists of a system analysis (process or product), by performing a test or a series of tests in which they deliberately change the input variables of the system so that they can observe and identify the reasons that caused the changes obtained in output variables (Figure 3.3) [3.19, 3.20].

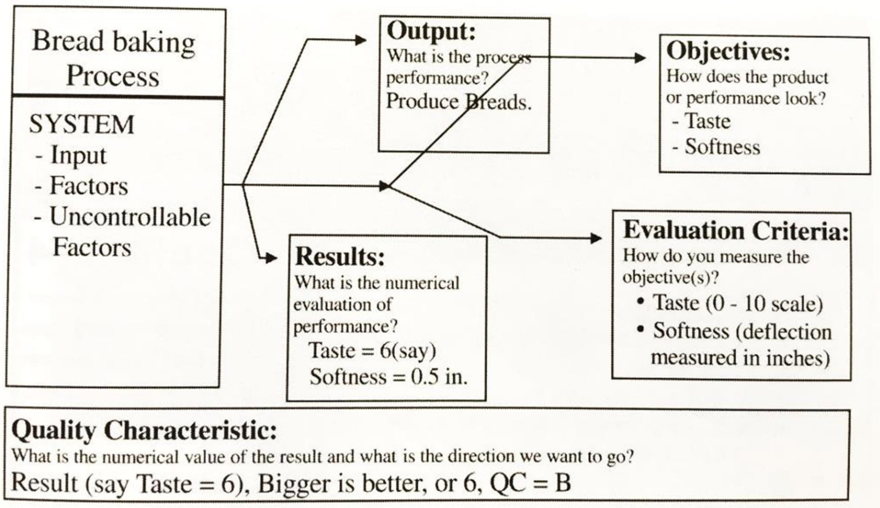

Figure 3.3 – Relationships among output measuring terms [3.18]

Contrary to what happens in the design of conventional experiments proposed by Fisher, known for factorial plan, in which all possible combinations are tried, resulting in a large number of tests and, consequently, an expenditure of time and money, Taguchi uses fractional factorials plans, composed of experiences that correspond to certain points of the factorial plan, which reduces number of experiments needed to estimate the system model [3.19]

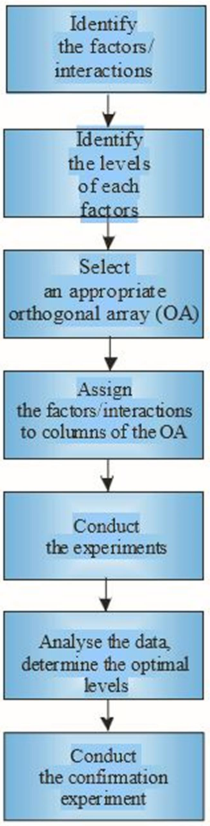

Figure 3.4 – Scheme of the major steps of implementing the Taguchi method [3.21, 3.22]

The Taguchi method (Figure 3.4) begins with a determination of study objective. The next step is to determine output of process. The output is the parameter which dramatically has a significant effect on final quality of product. Then, it is necessary chose a quality feature that better adapts to the study.

There are three types of quality feature: bigger is better, smaller is better and nominal is best. In the case of nominal-best feature is intended to achieve a value previously set. With a smaller-better feature is intended to achieve the lowest possible value. When select a characteristic bigger-better is to achieve the greatest possible value.

Select a quality feature, is necessary identify the factors which can have a significant effect on the output variable. The factors should be classified in noise factors and control factors. After defined, set the number of levels of the factors.

The next step is choice of the matrix. A methodology developed by Taguchi is based on orthogonal matrices. As orthogonal arrays allow collecting a small sample of data and obtain significant information from those. The use of this type of matrix is more efficient in economic terms, it is not necessary to test all combinations of factors.

Selected the orthogonal matrix, in order to be as small as possible, but with the necessary information. The choice of the matrix is always dependent on the number of factors and interactions between them, as well as the number of levels associated with each factor.

After performing the tests, analyses the results of the same. Taguchi suggests using a statistical measure called the signal-to-noise (S/N), to evaluate the experimental results. If the criterion chosen for the analysis of the results of multiple samples of an experimental condition is the average of the same, this does not cover the variation of results around the average (mean). The use of signal-to-noise ratio allows identify the factors affecting variation. Various expressions have been developed that allow you to transform the data in a signal-to-noise ratio, depending on the type of quality feature.

Analysis in DOE refers to the things that are done with results after experiments are carried out and test samples are evaluated. All calculations using the results are carried out support the observations, conclusions and recommendations made from the experiments. Depending on the complexities of the calculations involved, the analysis can be performed in two parts [3.18].

Part I: **Simple Analysis**

This part of the analysis is performed to produce a *grand average* of results and the *average effects* of factors and help to make observations and conclusions in the following areas:

- Factor influence or main *effects*;
- *Optimum condition* for a desired quality feature;
- Performance expected at the *optimum condition*.

Part II: **Analysis of variance**

The analysis of variance (ANOVA) calculation is something that would need begin to look for items beyond the three obtained from the simple analysis. Generally, ANOVA will support calculations, tests, and observations of the following nature:

- Relative influence of factor and interaction to the variation of results;

- Test of significance of factor and interactions assigned to the columns;
- Confidence interval (C.I.)on optimum performance;
- Confidence interval on main effect of factors
- Error factor/term, which includes the influence of all factors not included in the experiments and effects of experimental error.

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Chapter 4

PRODUCTION OF TOWPREGS AND PCT´S

4.1. Introduction

Continuous fibre reinforced thermoplastic matrix composites have been successfully employed in the aircraft, military and aerospace industries due to the excellent properties. In these and many other commercial engineering applications, they can replace other materials, such as thermosetting matrix composites. However, the high cost of the impregnation of continuous fibre thermoplastic composites, arising from the melting of the polymer or the use of solvents, still restricts their use in commercial applications. Hence, cost reduction largely depends on developing more efficient methods for impregnating fibres with high-viscosity thermoplastics and for processing final composite parts [4.1-4.25].

Two major technologies are used to allow impregnation of reinforcing fibres with thermoplastic polymers [4.1-4.16]: i) the direct melting of the polymer and, ii) the intimate fibre/matrix contact prior to final composite fabrication. Continuous fibre reinforced thermoplastic matrix pre-impregnated tapes are, for example, produced by direct melting processes. Alternatively, intimate contact processes allow producing cheap and promising pre-impregnated materials, such as, commingled fibres, co-woven fabrics and towpregs.

This chapter describes the production of towpregs and PCT´s based on different fibres and thermoplastic matrices and analyses the main effects of the process parameters into the quality of the pre-impregnated materials obtained. The aim of *paper 1* is to optimize the production of new continuous carbon fibres reinforced polypropylene matrix pre-impregnated materials (towpregs) continuously processed by dry deposition of polypropylene (PP) powder. The method of Taguchi/DOE (Design of Experiments) was used to achieve this goal allowing improved choices of processing windows. Towpregs were characterized by scanning electron microscopy (SEM), visual analysis and their polymer mass contents were also determined. In *paper 2*, continuous fibre reinforced thermoplastic matrix towpregs were produced for commercial markets and advanced markets. The former based on glass fibre reinforced polypropylene matrix (GF/PP) and the latter on carbon fibre PRIMOSPIRE® matrix (CF/P). Both towpregs were processed into composite parts by different technologies. The mechanical properties determined on the final composites were compared with the theoretical predictions and have shown to be acceptable for the targeted markets.

In *paper* 3, the aim has been to produce and optimize the processing of carbon fibres thermoplastic matrix pre-impregnated materials (towpregs and PCT´s) using the dry powder coating equipment from our own laboratories. The optimization of the pultrusion process was made by studying the influence of the most relevant processing parameters in the final properties of the produced carbon fibres thermoplastic matrix pre-impregnated materials and composites. The composite relevant mechanical properties were determined and studied. The final composites were also submitted to Scanning Electron Microscopy (SEM), optical microscopy and calcination tests. The determination of the fibre volume fraction of a composite with a high melting temperature thermoplastic polymer used as matrix was obtained comparing the results of thermogravimetric analysis (TGA) with the calcination tests.

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4.2. Paper 1

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OPTIMIZING THE PRODUCTION AND PROCESSING OF FIBRE REINFORCED THERMOPLASTIC PRE-IMPREGNATED MATERIALS

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Abstract

The aim of this work is to optimize the production of new continuous carbon fibres reinforced polypropylene matrix pre-impregnated materials (towpregs) continuously processed by dry deposition of polypropylene (PP) powder. The processing of the produced towpregs by pultrusion using a prototype equipment was also optimized.

The method of Taguchi/DOE (Design of Experiments) was used to achieve this goal allowing improved choices of processing windows.

Towpregs were characterized by scanning electron microscopy (SEM), visual analysis and their polymer mass contents were also determined. The final pultruded composite profiles were also submitted to tensile, interlaminar, flexural, calcination and optical microscopy tests.

1. Introduction

During the last decades, composites have successfully replaced traditional materials in many engineering applications due to its excellent properties, mainly their excellent specific mechanical properties [1,2].

Pultrusion is a continuous manufacturing process used to shape polymeric composite materials into parts with constant cross section. The reinforcement fibres in the form of continuous strands or mats are pulled through a guide plate and impregnated passing by a thermosetting resin bath.

So far, almost all applications of pultrusion manufacturing technologies use thermosetting resins due to inherent difficulties associated with the use of thermoplastic matrices in this process. However, with recent developments, the use of preforms to facilitate impregnation, such as pre-consolidated tapes, commingled yarns and towpregs, allowed the thermoplastic pultrusion to gain a great interest [3].

Composites with thermoplastic matrices offers increased fracture toughness, higher impact tolerance, short processing cycle time and excellent environmental stability. They are recyclable, post-formable and can be joined by welding. The use of long/continuous fibre reinforced thermoplastic matrix composites involves, however, great technological and scientific challenges since thermoplastics present much higher viscosity than thermosettings, which makes much difficult and complex the impregnation of reinforcements and consolidation tasks [2,4-9].

Today, two major technologies are being used to allow wet reinforcing fibres with thermoplastic polymers [6-9]: i) the direct melting of the polymer and, ii) the intimate fibre/matrix contact prior to final composite fabrication. Continuous fibre reinforced thermoplastic matrix pre-impregnated tapes

(PCT´s) are, for example, produced by direct melting processes. Alternatively, intimate contact processes allow the production of cheap and promising pre-impregnated materials, such as, commingled fibres, co-woven fabrics and powder coated towpregs.
Sometimes, thermoplastic compatibilizers were added to the matrices to improve their adhesion and facilitate impregnation to reinforcements [10].

2. Experimental

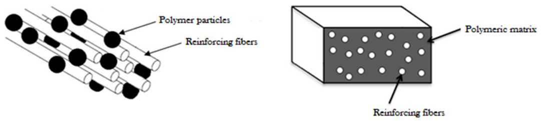
2.1 Raw materials

The following raw materials were used to produce CF/PP pre-impregnated materials for this work: i) a PP powder ICORENE 9184B P$^{®}$ and carbon fibre roving M30 SC$^{®}$ from the ICO Polymers and TORAY, respectively, were used to produce the CF/PP towpregs (Fig. 1a), ii) PP powder Moplen RP348U$^{®}$ from Basell and the carbon fibre roving already mentioned were used to manufacture the CF/PP tapes (Fig. 1b). Table 1 present the properties of these raw-materials.
Some batches of CF/PP towpregs were also produced using PP powder (ICORENE 9184B P$^{®}$) with 1% in mass content of maleic anhydride additive, S 47 29608 707$^{®}$ from Merck Schuchardt OHG, in order to assess the possible enhancement of fibre/matrix adhesion [10-14].

Property	**PP powder** (ICORENE 9184B P$^{®}$)		**PP granules** (MOPLEN RP348U $^{®}$)	**Carbon fibre** (TORAY M30 SC$^{®}$)	
	Manufacturer datasheet	Experimental	Manufacturer datasheet	Manufacturer datasheet	Typical values
Linear density (Tex)	-	-	-	760	-
Specific gravity (Mg/m^3)	0.91	0.91	900	1.73	1.75
Tensile strength (MPa)	30[1]	19[1]	301	5490	2600
Young Modulus (GPa)	1.3	0.98	1.1	294	170
Poisson´s ratio	-	0.21	-	-	-
Average powder size (μm)	440	163	-	-	-

[1] Yield Strength

Table 1. Properties of carbon fibre and polypropylene raw-materials



a) towpregs b) Pre-consolidated tapes (PCT´s)

Fig. 1. CF/PP pre-impregnated products under study

2.2 Production of Thermoplastic Matrix Pre-Impregnated Products

2.2.1 Production of towpregs

The CF/PP towpregs were produced in a dry powder coating equipment schematically shown in Fig. 2 [14, 15]. It consists of six main parts: wind-off system, fibre spreader unit, heating section, coating section, consolidation unit and a wind-up section. Initially, the reinforcing fibres are wound-off and pulled through a pneumatic spreader and then coated with polymer by heating in a convection oven and made to pass into a polymer powder vibrating bath. A gravity system allows maintaining the amount of polymer powder constant. The consolidation unit oven allows softening the polymer powder, promoting its adhesion to the fibre surface. Finally, the thermoplastic matrix towpreg is cooled down and wound-up on a spool.

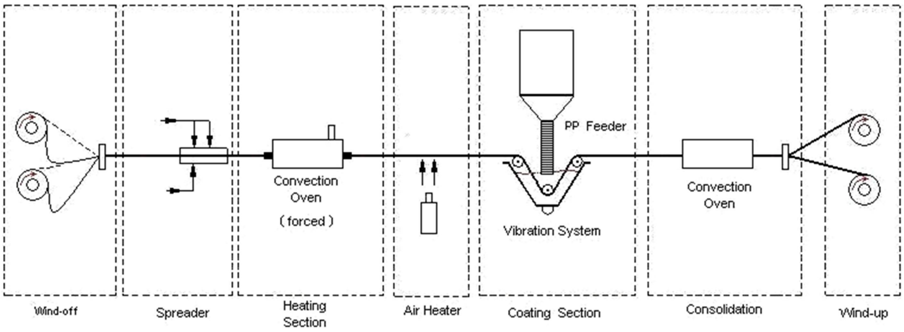


Fig. 2. Powder coating line setup

2.2.2 Towpreg production optimization

In order to optimize the production of CF/PP powder coated towpregs, different processing variables combinations were experimented and the number of trials optimized using the Taguchi approach. The studied operational parameters were:

- heating oven temperature (600, 650 and 700 ºC);
- consolidation oven temperature (350, 400 and 450 ºC);
- linear pull speed (4, 6 and 8 m/min).

The Taguchi approach was applied to the towpregs production process in order to obtain the condition that maximizes polymer powder content. The polymer mass fraction in the towpregs was determined by weighting towpreg strips produced in those different conditions.

Table 2 shows the used processing conditions and obtained results, according to the established design of experiments.

	Processing variables			**Results:**
Experiments	**Heating oven temperature (ºC)**	**Consolidation furnace temperature (ºC)**	**Linear pulling speed (m/min)**	**Polymer mass fraction (%)**
1	600	350	4	32.2
2	600	400	6	31.4
3	600	420	8	20.6
4	650	350	8	27.9
5	650	400	4	39.9
6	650	420	6	40.7
7	700	350	6	35.6
8	700	400	8	40.6
9	700	420	4	40.4
			Average	34.5

Table 2. Taguchi approach applied to towpregs manufacturing process

The mains effects of the processing variables on the results can be seen from Fig. 3. The optimal condition obtained from Taguchi method application led to the following operating parameters selection: heating oven temperature and consolidation oven temperatures of 700 ºC and 400ºC respectively, and a linear pulling speed of 4 m/min. Using this optimal operative condition, the amount of polymer should increase up to 45.6%. However, the operative condition that has chosen as optimal had a line pull speed of 6 m/min allowing a high rate of production, lower processing problems and sufficiently levels of polymer content (40%, enough for the of use of towpregs in the pultrusion process). Also, the addition of 1% of maleic anhydride to the PP polymer had no influence on the towpreg polymer mass fraction.

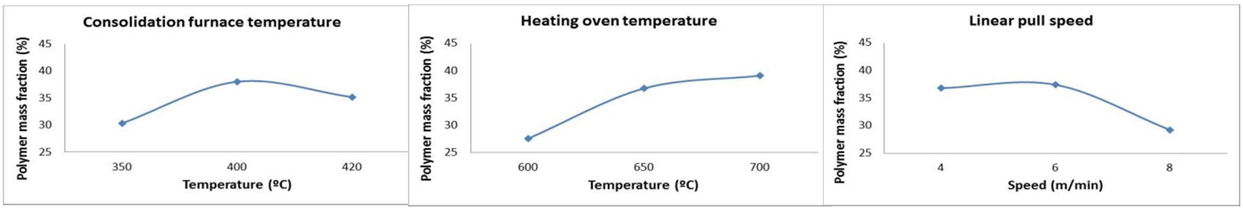


Fig. 3. Variation of towpreg polymer content with processing parameters

2.2.3 Production of pre-consolidate tapes (PCT)

The CF/PP PCT used in this work was produced in a cross-head extrusion equipment existing in our laboratories (see Fig. 4). The core of this technology is an impregnation unit where the carbon fibres are introduced, spread and impregnated by the polymer melt. Impregnation is achieved by pressurizing the molten polymer trapped between the unit's spreading elements and the fibre rovings.

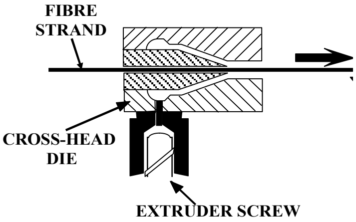


Fig. 4. Cross-head extrusion die

The apparatus consists of a creel holding system for fibre rovings, a guidance unit allowing an adequate transport of fibre into the impregnation section, an extruder to melt and feed the molten polymer into the impregnation unit, the impregnation unit itself and, subsequently, a cooling unit, a puller, and a take-up device where the composite tape is collected [17]. Main properties of the PCTs produced by this way are given in Table 3.

Property	Description
Fiber type	Carbon, 760 Tex
Filament diameter	5 µm
Fiber content	45 wt.%
Matrix type	Polypropylene (PP)
Tape width	25 mm
Tape linear density	14000 Tex

Table 3. Overview of the main properties of the produced pre-consolidated tapes (PCT´s)

2.3 Processing of the pre-impregnated materials

The CF/PP pre-impregnated materials (towpregs and PCT's) were processed into composite bar profiles using a prototype pultrusion line [17, 18]. Our developed 10 kN pultrusion equipment, schematic depicted in Fig. 5, consists in five main parts: i) an initial towpreg bobbins holding cabinet; ii) guiding system; iii) pultrusion head, that includes a pre-heating furnace and the pressurization/consolidation and cooling dies; iv) pulling system and, v) the final profile cutting system.

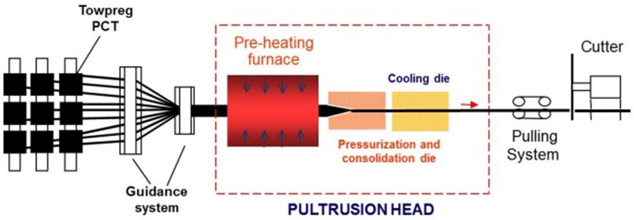


Fig. 5. Schematic diagram of the pultrusion line

To produce composite profiles, the pre-impregnated materials are guided into the pre-heating furnace to be heated up to the required temperature. Then, they enter in the pultrusion die to be heated up and consolidated to the required size in its first zone and, after cooled down in order to solidify. The pultruded material is then cut into specified lengths. A die with a cavity of 20 ×2 (mm) was used to produce a composite rectangular shaped bar.

2.3.1 Towpreg processing and optimization

Bar profiles were manufactured by pultrusion from different towpregs, using operating conditions in order to optimize the processing. The studied processing variables were:

-Furnace temperature (160 and 180 ºC);
-Heating die temperature (240 and 260 ºC);
-Cooling die temperature (25 ºC);
-Linear pull-speed (0.2 and 0.3 m/min).

Results have shown that was not possible to produce in steady conditions pultruded profiles from towpregs at pultrusion speeds and consolidation die temperatures higher than 0.4 m/min and 260 ºC, respectively. By using higher values in these two parameters the process became unsteady mainly due to reflux and accumulation of the thermoplastic polymer at the entrances of the consolidation and cooling dies, respectively. Table 4 summarizes the flexural test results obtained with the studied processing conditions.

	Processing variables			**Flexural properties**	
Exper.	**Furnace temperature (ºC)**	**Heating die temperature (ºC)**	**Linear pulling speed (m/min)**	**Flexural modulus (GPa)**	**Flexural strength (MPa)**
1	160	240	0.2	86.7 ± 1.3	229.0 ± 7.3
2	180	240	0.2	79.5 ± 2.0	212.4 ± 12.6
3	160	260	0.2	91.0 ± 0.4	241.2 ± 1.6
4	180	260	0.2	85.1 ± 1.7	218.2 ± 9.1
5	160	240	0.3	82.1 ± 2.8	241.7 ± 13.1
6	180	240	0.3	87.5 ± 1.9	239.6 ± 13.3
7	160	260	0.3	85.0 ± 4.4	234.5 ± 11.5
8	180	260	0.3	83.7 ± 2.8	221.3 ± 7.1

Table 4. Flexural testing results from towpregs

The variation of the flexural modulus and strength with the selected processing parameters can be seen in Figures 6 and 7. The optimal condition concerning flexural stiffness maximization obtained led to the following operating parameters selection: furnace and heated die oven temperatures of 160 ºC and 260ºC respectively, and a linear pulling speed of 0.2 m/min. For optimizing the flexural strength the obtained parameters combination was: furnace and heated die oven temperatures of 160 ºC and 240ºC respectively, and a linear pulling speed of 0.3 m/min. It is possible to observe that the furnace temperature of 160ºC leads to better results. That could be explained by the lower polymer reflux on the entrance of the heated die. The optimal operating conditions to maximize both flexural properties (modulus and strength) were: furnace and heated die oven temperatures of 160 ºC and 260ºC respectively, and a linear pulling speed of 0.2 m/min.

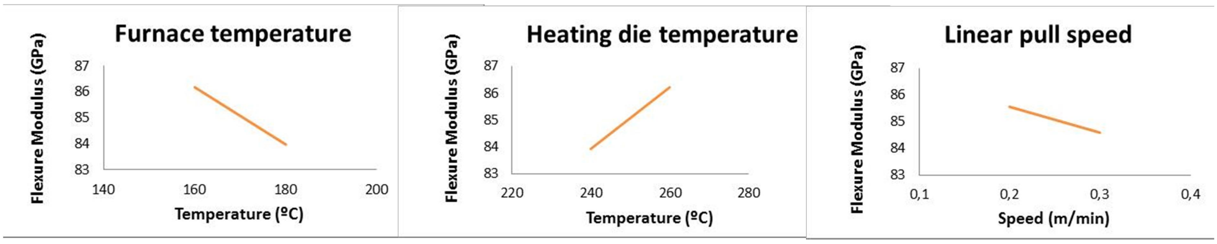


Fig. 6. Variation of the flexural modulus with the selected processing parameters

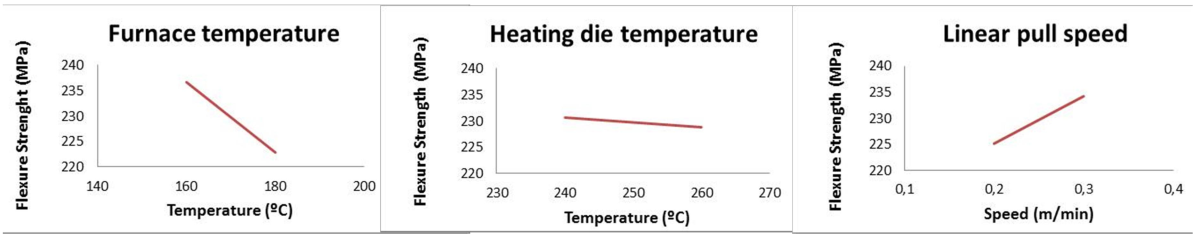


Fig. 7. Variation of the flexural strength with the selected processing parameters

Finally, towpregs with additive were also pultruded into bars using the condition that optimizes both flexural properties and two more conditions (see Table 5).

Exper.	**Processing variables**			**Flexural properties**	
	Furnace temperature (ºC)	**Heating die temperature (ºC)**	**Linear pulling speed (m/min)**	**Flexural modulus (GPa)**	**Flexural strength (GPa)**
1	160	260	0,2	229.0 ± 7.3	87.6± 1,3
2	160	240	0,2	191.7 ± 7.8	70.4 ± 2.8
3	160	240	0,3	237.4 ± 11.8	80.5 ± 2.6

Table 5. Flexural properties of towpregs with additive processed by pultrusion

Table 6 shows the obtained results from flexural tests using towpreg pultruded bars with and without additive of maleic anhydride. It is possible to conclude that use of additive had no significant influence on the flexural properties.

Processing parameters		**Flexural modulus (GPa)**		**Flexural strenght (GPa)**	
		Without additive	**With additive**	**Without additive**	**With additive**
Furnace temperature (ºC)	160	90.1 ± 0.4	87.6 ± 1.3	241.2 ±1.6	229.0 ± 7.3
Heating die temperature (ºC)	260				
Linear pulling speed (m/min)	0,2				

Table 6. Flexural test results on towpreg bars with and without additive

2.3.2 Pre-consolidate tapes processing

CF/PP PCT were processed into composite bar profiles using the already mentioned pultrusion equipment die and the following typical operating conditions:

-Furnace temperature (160 ºC);
-Heating die temperature (260 ºC);
-Cooling die temperature (50 ºC);
-Linear pull-speed (0.2 m/min).

2.4 Testing

2.4.1 Towpreg testing

Towpregs were characterized by scanning electron microscopy (SEM) and visual analysis. Several CF/PP produced towpreg samples were analysed under a Nova NanoSEM 200 Scanning Electron Microscope to evaluate the adhesion of the polymer powder to the fibres and its distribution. Figure 8 show SEM micrographs of towpreg samples. As may be seen, a reasonable degree of adhesion between the carbon fibres and the polymer powder particles was obtained. Also, the polymer particles distribution on the fibres can be considered sufficient and eventually improved.

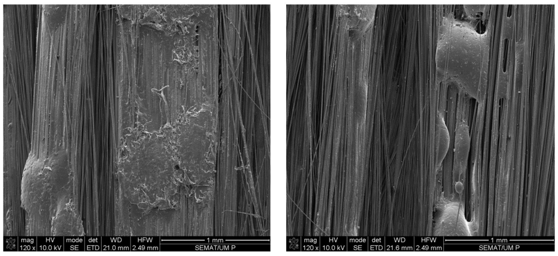


Fig. 8. Typical towpreg SEM micrographs (magnification of 120×)

2.4.2 Composites testing

Samples of pultruded bars were submitted to flexural, tensile, interlaminar and calcination tests according to the ISO standards 14125, 527, 14130 and 1172, respectively, and had their cross-sections studied under optical Microscopy (see Fig. 9). PCT's were also submitted to the same tests.

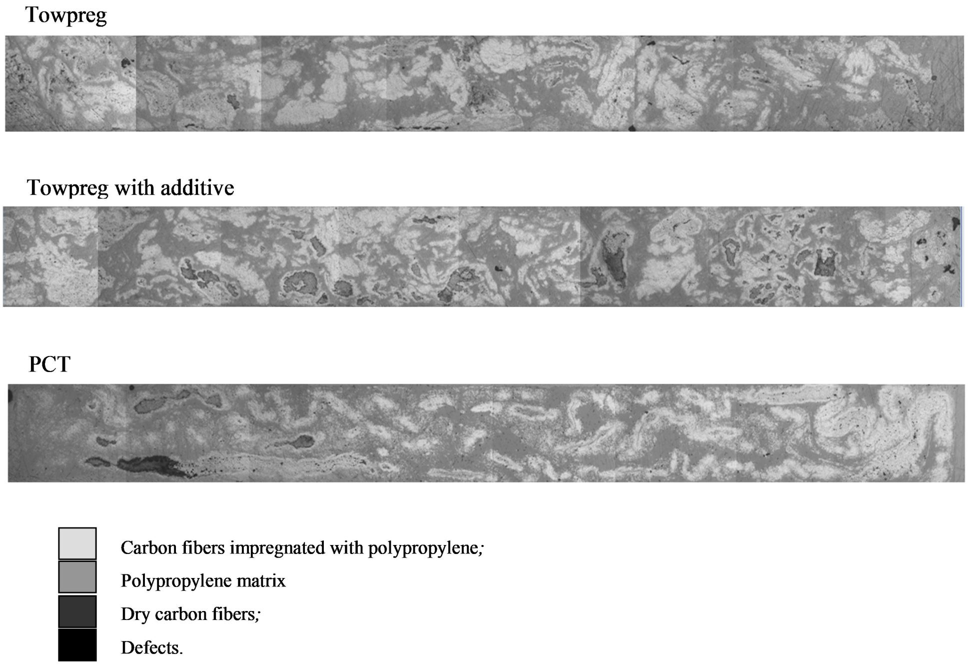


Fig. 9. Optical micrographs of the pultruded profiles cross-section (magnification of 8.75×)

2.4.3 Test results

Table 7 summarizes all experimentally obtained test results.

Test Type	**Property**	***Pultrusion***		
		Towpreg	***Towpreg with additive***	***PCT***
Flexural	Flexure Modulus (GPa)	90.1±0.4	87.6±1.3	37.7±2.2
	Flexure Modulus / Fibre volume fraction (GPa)	178.1±0.8	173.5±2.6	118.2±6.9
	Flexure Strength (MPa)	241.2±1.6	229.0±7.3	158.7±4.2
	Flexure Strength / Fibre volume fraction (MPa)	476.7±3.2	453.5±14.5	497.5±13.2
Tensile	Tensile Modulus (GPa)	110.6±5.9	106.1±6.3	63.5±4.3
	Tensile Modulus / Fibre volume fraction (GPa)	218.6±11.7	210.1±12.5	199.1±13.5
	Tensile Strength (MPa)	1068.8	-	-
	Tensile Strength / Fibre volume fraction (GPa)	2112.3	-	-
Inter-laminar Shear	Interlaminar Shear Strength (MPa)	12.3±0.3	13.0±0.4	14.0±0.2
Fibre volume fraction (%)		50.6	50.5	31.9

Table 7. Composite mechanical test results

In table 8, different common engineering materials are compared concerning flexural mechanical properties.

Material	**Density**	**Flexural Properties**			
	(kg/m^3)	**Strength (MPa)**	**Specific strength (kN*m^3/Kg)**	**Modulus (GPa)**	**Specific modulus (MN*m^3/Kg)**
CF/PP [35%] (without additive)	1320	241.2	182.7	90.9	68.9
CF/PP [35%] (with additive)	1320	228.9	173.4	86.6	65.6
CF/Epoxy [40%]	1410	1800	1276.6	120	85.1
Stainless steel	7850	980	124.8	185	25.4
Aluminium	2700	90	33.3	70	25.9
Aluminium alloy	2810	500	177.9	71	25.2
Nylon 66 (PA)	1060	85	80.6	2.8	2.6
Polyester	1200	90	75.0	2.3	1.9
Polypropylene	905	40	44.2	1.5	1.6
PEEK	1380	-	-	3.8	2.7

Table 8. Comparison of flexural properties of different engineering materials

Conclusions

Obtained results allow the conclusion that all the pre-impregnated products studied in this work presented enough good properties to be employed in the major commercial engineering structural applications. Composites processed from the PCTs demonstrated to have better mechanical strength than those produced from towpregs. As can be seen from the Fig. 9, all profiles have a reasonable distribution of the reinforcing fibres over the cross-sections. However, large differences in impregnation quality occur between the different samples that are likely to be related, directly, to the impregnation state of the semi-finished used on pultrusion. The samples of towpreg with additive show a higher quantity of dry zones than the ones without additive. It also may be noted that any of the composites made from the towpregs and PCTs reached failure in the interlaminar shear tests. This fact reveals the high degree of ductility exhibited by these materials which may be relevant for many applications. Thus, the interlaminar shear strength results shown in Table 7 correspond to maximum force applied in the test. The tests made using a proprietary pultrusion equipment already allow the conclusion to be possible to produce in good conditions profiles from almost all commercial available thermoplastic matrix pre-impregnated raw-materials using pull speeds of 0.3 m/min. It was possible to optimize the production of pultruded profiles and towpregs, through the use of Taguchi method, achieving optimal conditions. The addition of the compatibilizing agent (1% maleic anhydride) did not improve the polymer mass content in towpregs and the mechanical properties on the final composites.

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4.3. Paper 2

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PRODUCTION AND PROCESSING OF THERMOPLASTIC BASED TOWPREGS FOR COMMERCIAL AND ADVANCED MARKETS

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Keywords: Thermoplastic matrix composites, Towpregs, Processing, Mechanical properties
In this work continuous fibre reinforced thermoplastic matrix towpregs were produced for commercial markets and advanced markets. The former based on glass fibre reinforced polypropylene matrix (GF/PP) and the latter on carbon fibre Primospire® matrix (CF/P). Primospire® is an amorphous highly aromatic material specifically developed by Solvay Advanced Polymers for application in advanced markets.

Both towpregs were processed into composite parts by different technologies. The mechanical properties determined on the final composites were compared with the theoretical predictions and have shown to be acceptable for the targeted markets.

1. Introduction

Continuous fibre reinforced thermoplastic matrix composites have been successfully employed in the aircraft, military and aerospace industries due to the excellent properties. In these and many other commercial engineering applications, they can replace other materials, such as thermosetting matrix composites. However, the high cost of the impregnation of continuous fibre thermoplastic composites, arising from the melting of the polymer or the use of solvents, still restricts their use in commercial applications. Hence, cost reduction largely depends on developing more efficient methods for impregnating fibres with high-viscosity thermoplastics and for processing final composite parts [1-3].

Two major technologies are used to allow wet reinforcing fibres with thermoplastic polymers [2, 3]: i) the direct melting of the polymer and, ii) the intimate fibre/matrix contact prior to final composite fabrication. Continuous fibre reinforced thermoplastic matrix pre-impregnated tapes are, for example, produced by direct melting processes. Alternatively, intimate contact processes allow producing cheap and promising pre-impregnated materials, such as, commingled fibres, co-woven fabrics and towpregs.

In this work, towpregs based on different fibres and thermoplastic matrices were produced and processed into composites for highly demanding and more commercial applications. Heated compression moulding and pultrusion were the processing methods used to obtain final composite parts. The processing parameters used both to produce the towpregs in our own developed coating line equipment [4, 5] as well as to process them, at industrial compatible production rates, into final parts composite having adequate properties were studied. Thus, the efficient processing windows allowing producing continuously the thermoplastic matrix towpregs, by dry deposition the thermoplastic matrix on the reinforcing fibres, and also transform them into composites were established. Two different raw-materials were used in the production of the thermoplastic matrix towpregs, those to be used in parts for highly demanding markets were based on carbon fibres and Primospire® [6] and those for more commercial composites on glass fibre and polypropylene.

2. Experimental

2.1. Raw materials

The PP powder ICORENE 9184B P® from ICO Polymers and type E glass fiber direct rovings 305E-TYPE 30® from Owens Corning were, respectively, the raw materials used to produce the glass fibres reinforced polypropylene matrix towpregs studied in this work and intended for being used in more common composites for commercial markets. Table 1 shows the main properties of those materials.

Property	Units	Glass fibres	Polypropylene
Density	Mg/m^3	2.56	0.91
Tensile strength	MPa	3500	30
Tensile modulus	GPa	76	1.3
Average powder particle size	µm	-	440
Melting temperature	ºC	-	166
Linear roving weight	Tex	2400	-

Table 1. Properties of raw materials used in towpregs for common applications.

On other hand, composite parts for highly demanding advanced markets were processed from towpregs manufactured by using a highly aromatic amorphous thermoplastic polymer in powder form, the PRIMOSPIRE® PR 120 from Solvay Advanced Polymers, and 760 Tex M30SC carbon fibre tows TORAYCA. Table 2 presents the most relevant properties determined on both these raw materials.

Property	Units	Carbon fibres	Primospire®
Density	Mg/m^3	1.73	1.21
Tensile strength	MPa	2833	104.3
Tensile modulus	GPa	200	8.0
Average powder particle size	µm	-	139.4
Glass transition temperature (T_g)	ºC	-	158
Linear roving weight	Tex	760	-

Table 2. - Properties of raw materials used in towpregs for advanced applications

2.2. Production of the towpregs

The towpregs were produced in a developed dry powder coating equipment schematically shown in Figure 1 and illustrated in the photo of Figure 2 [4, 7]. It consists of six main parts: i) wind-off system, ii) fiber spreader unit, iii) heating section, iv) polymer coating section, v) consolidation unit and vi) a wind-up section. Initially, the reinforcing fibers are wound-off and pulled through a pneumatic spreader and then coated with polymer by heating in a convection oven and made to pass into a polymer powder vibrating bath. A gravity system allows maintaining the amount of polymer powder constant. The consolidation unit oven allows softening the polymer powder, promoting its adhesion to the fiber surface. Finally, the thermoplastic matrix towpreg is cooled down and wound-up on a spool.

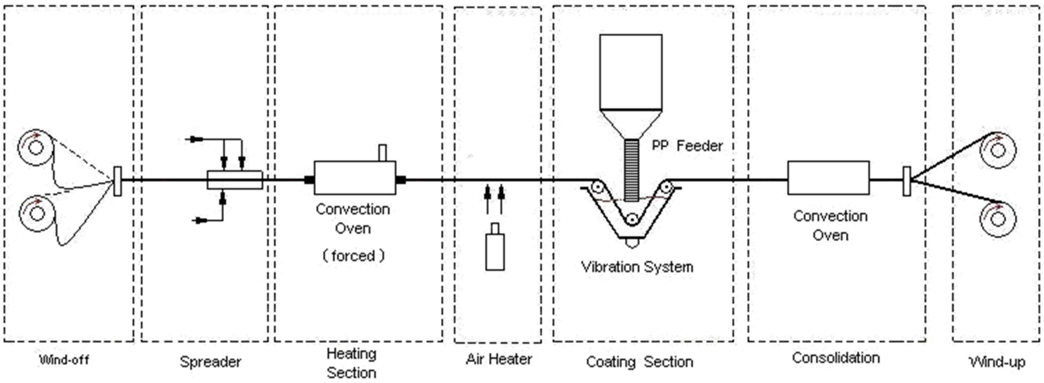

Figure 1. Schematic drawing of the powder coating line

Figure 2. Powder coating line equipment used to produce towpregs

In order to optimise the conditions to produce towpregs, the powder coating equipment was operated at different woven temperatures and fibre linear pull speeds. From such work the best values of the operational variables depicted in Table 3, which allow simultaneously producing towpregs in good and stable circumstances and having the maximum polymer powder content were determined.

Variable	Units	Values	
		GF/PP towpregs	CF/Primospire® towpregs
Convective oven temperature	ºC	700	700
Consolidation furnace temperature	ºC	400	650
Coating line pulling speed	m/min	4	5

Table 3. Best conditions to produce towpregs used in composites for commercial and advanced markets.

2.3. Processing composites by compression moulding

A technique described elsewhere [8] was used to produce unidirectional fibre reinforced laminate plates with 100×100×4 mm directly from the towpregs. First, the towpreg were wound over a plate with appropriate dimensions and the resultant pre-form then conveniently placed in the cavity of a heated mould. A 400 kN SATIM hot platen press was used to obtain the desired consolidation pressure. After heating the cavity, pressure was applied and, finally, the mould was cooled down to room temperature and the final composite laminate plate removed.

Table 4 shows the compression moulding conditions used to process composites by using the two kinds of towpregs produced in the present work

Variable	Units	Values	
		GF/PP towpregs	CF/Primospire® towpregs
Platen temperature	ºC	250	320
Compression pressure	MPa	20	20
Compression time	min	15	20
Final cooling temperature (at press opening)	ºC	30	30

Table 4. Conditions used to process composites by compression moulding by using the towpregs

2.4. Flexural properties of the composite plates obtained by compression moulding

The flexural properties in fibre direction were determined in the composite plates obtained by compression moulding, using three-point bending tests accordingly to ISO 178 standard. The tests were made in an universal INSTRON 4505 testing machine on five 100 × 15 × 4 (mm) specimens cut from the processed composite plates and by using a cross-head speed of and a distance between supports of 2 mm/min and 80 mm, respectively. The fibre mass fraction was also determined according to EN 60. Table 5 summarizes the experimental results obtained on the two different studied composites.

As may be seen, flexural properties compatible with the applications envisaged for the composites processed from the produced towpregs were obtained in this work. Better properties may be certainly obtained through the improvement of fibre/matrix adhesion, polymer powder distribution and fibre alignment.

Property	Units	GF/PP	CF/Primospire®
Flexural strength	MPa	66.3±9.4	124.3±15.0
Flexural modulus	GPa	24.7±2.6	30.0±5.0
Fibre mass fraction	%	85.6±1.6	59.7±0.3

Table 4. Properties of composite plates made from the towpregs

2.5. Processing composites by pultrusion

A 10 kN pultrusion equipment [9] was purposely designed and built to allow producing of continuous profiles made from thermoplastic matrix towpregs. Such equipment, schematically shown in Figure 3 and illustrated in Figure 4, includes three main parts: a pre-heating furnace, a pressurisation and consolidation die and a cooling die.

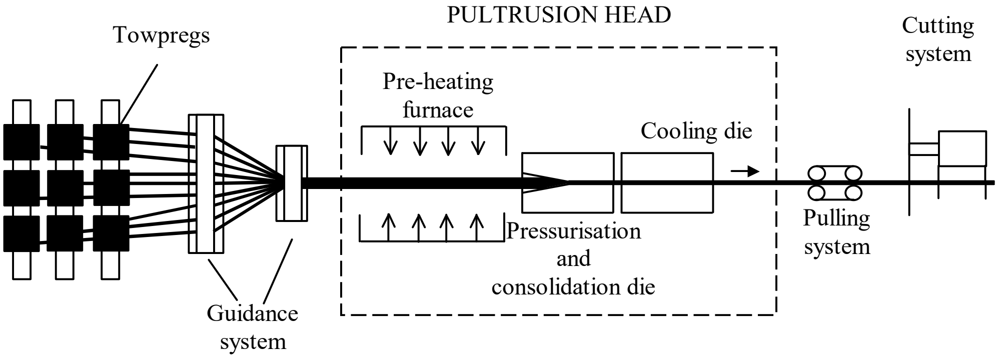

Figure 3. Schematic diagram of the developed pultrusion line

The towpregs are guided into the pre-heating furnace where the material is heated up to the required temperature. In the entering zone of the pultrusion die, the material is heated up and consolidated, and then cooled down to achieve the desired shape. After reaching the solid state the material is cut into specified lengths.

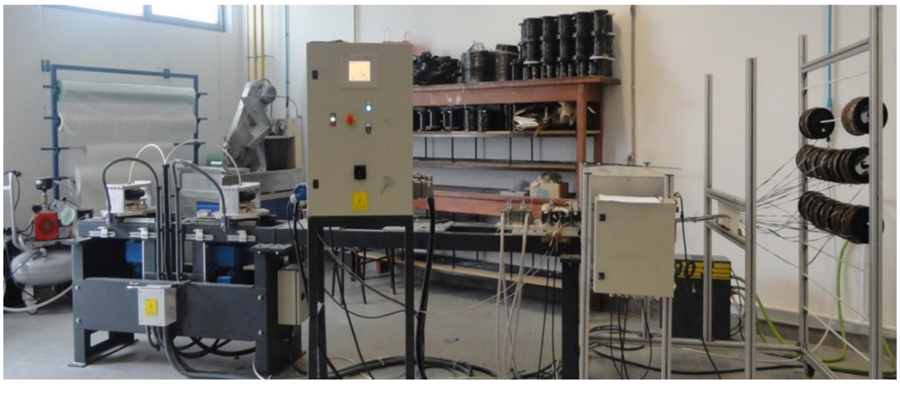

Figure 4. Developed prototype pultrusion line

Two 20 × 2 (mm) rectangular cross-section bars were pultruded from both types of towpregs produced in this work in operational conditions presented in Table 5.

Variable	Units	Values	
		GF/PP towpregs	**CF/Primospire® towpregs**
Pultrusion pull speed	m/min	0.2	0.2
Pre-heating furnace temperature	ºC	160	400
Pressurisation/consolidation die temperature	ºC	260	475
Cooling die temperature	ºC	20	20

Table 5. Conditions used to process the pultruded composite bars from the towpregs

As it may be seen and as expected, the CF/Primospire® towpregs required the use of much higher temperatures than the GF/PP ones in pre-heating furnace and pressurization/consolidation die. Due to such higher temperatures, tests still continue being done to optimise the operational conditions to be used in the pultrusion of the CF/Primospire® towpregs. We expect to be able to present the final results obtained from those tests in the conference.

Table 6 presents the mechanical properties obtained on the already pultruded profiles. As it was previously mentioned tests still are being made on pultruded profiles processed from the CF/ Primospire® towpregs we expect to present in the conference.

Property	Units	Value
Flexural strength	MPa	241.2±1.6
Flexural modulus	GPa	90.1±0.4
Fibre mass fraction	%	85.6±1.6

Table 6. Flexural test results on the pultruded composite profiles processed from the GF/PP towpregs

As results from above Table 6 show, composites pultruded from GF/PP towpregs presented much higher mechanical properties than those obtained on the compression moulding ones. This seems to be related with the much better consolidation and fibre alignment that pultrusion allows achieving.

3. Conclusions

Two different types of thermoplastic matrix towpregs were studied and produced in this work: one intended to be used in common commercial markets, made from glass-fibre reinforced polypropylene (GF/PP), and the other one using a carbon fibre reinforced Primospire® (CF/ Primospire®) for more high demanding advanced markets.

The production of both towpregs was optimised in order to maximise the polymer powder deposition and operating stable conditions.

The processing of both produced thermoplastic matrix towpregs into composite parts by compression moulding and pultrusion was also studied. The mechanical properties of the processed composites were determined and evaluated. From obtained results it was possible to conclude that the mechanical properties were compatible with the requirements of the envisaged applications. As expected, composites processed by compression moulding from the CF/ Primospire® towpregs presented higher mechanical properties than those obtained from the GF/PP towpregs.

It was also possible to conclude that the pultruded profiles processed from the GF/PP towpregs presented much higher mechanical properties than those ones determined on compression moulding plates made with the same material. This seems to be mainly related with the better consolidation and more accurate fibre alignment that the pultrusion processing allows achieving.

In case of pultrusion, work still is ongoing in order to optimise the processing and determine the mechanical properties on pultruded profiles made from CF/ Primospire® towpregs.

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4.4. Paper 3

21st International Conference on Composite Materials
Xi'an, 20-25th August 2017

PROCESSING OF CARBON REINFORCED THERMOPLASTIC COMPOSITES

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Keywords: carbon fibre; thermoplastic; towpreg; composites; composites processing

ABSTRACT

The aim of this work is to produce and optimize the processing of carbon fibres thermoplastic matrix pre-impregnated materials (towpregs and PCT´s) using the dry powder coating equipment from our own laboratories. Pultrusion was the selected manufacturing method for processing all carbon fibres thermoplastic matrix pre-impregnated materials into composite parts.

The optimization of the pultrusion process was made by studying the influence of the most relevant processing parameters in the final properties of the produced carbon fibres thermoplastic matrix pre-impregnated materials and composites.

The composite relevant mechanical properties were determined and studied. The final composites were also submitted to Scanning Electron Microscopy (SEM), optical microscopy and calcination tests.

The determination of the fibre volume fraction of a composite with a high melting temperature thermoplastic polymer used as matrix was obtained comparing the results of thermogravimetric analysis (TGA) with the calcination tests.

1. Introduction

Composites with thermoplastic matrices offer increased fracture toughness, higher damage tolerance, short processing cycle times and excellent environmental stability. They are recyclable, post-formable and can be joined by welding. The use of long/continuous fibre reinforced thermoplastic matrix composites involves, however, great technological and scientific challenges since thermoplastics present much higher viscosity than thermosettings, which makes much difficult and complex the impregnation of reinforcements and consolidation tasks [1-4].

Today, two major technologies are being used to allow wet reinforcing fibres with thermoplastic polymers [1-2]: i) the direct melting of the polymer and, ii) the intimate fibre/matrix contact prior to final composite fabrication. Continuous fibre reinforced thermoplastic matrix pre-impregnated tapes (PCT´s) are, for example, produced by direct melting processes. Alternatively, intimate contact processes allow producing cheap and promising pre-impregnated materials, such as, commingled fibres and powder coated towpregs.

Pultrusion was the selected manufacturing method for processing all these pre-impregnated materials into composite parts. It is a versatile continuous high speed production technology, allowing the production of fibre reinforced complex profiles. The optimization of the pultrusion process was made by studying the influence of the most relevant processing parameters in the final properties of the produced pre-impregnated materials and composites [5-10]. The method of Taguchi/DOE (Design of Experiments) was used to achieve this aim.

The possibility of using maleic anhydride as compatibilizer of carbon and glass fibre reinforced polypropylene composites was also analysed in the present work.

The final composite parts were also submitted to tensile, interlaminar and flexural tests, as well as calcination, optical microscopy and SEM. The experimental results were compared with theoretical ones that can be predicted by using the ROM (Rule Of Mixtures).

2. Experimental

2.1. Raw Materials

The following raw materials were used to produce CF/PP pre-impregnated materials for this work: i) a PP powder ICORENE 9184B P® and carbon fibre roving M30 SC® from the ICO Polymers and TORAY, respectively, were used to produce the CF/PP towpregs, ii) PP powder Moplen RP348U® from Basell and the carbon fibre roving already mentioned were used to manufacture the CF/PP PCT tapes. On other hand, composite parts for highly demanding advanced markets were processed from towpregs manufactured by using a highly aromatic amorphous thermoplastic polymer in powder form, the Primospire® PR 120 from Solvay Advanced Polymers, and 760 Tex M30SC carbon fibre tows TORAY.

Tables 1 and 2 summarise relevant properties of the polypropylene, Primospire® and carbon fibres used in present work to produce pre-impregnated raw materials (towpregs and PCT´s).

Property	**PP powder** (ICORENE 9184B P®)		**Primospire®**		**PP granules** (Moplen RP348U ®)
	Manufacturer datasheet	Experimental	Manufacturer datasheet	Experimental	Manufacturer datasheet
Specific gravity (Mg/m^3)	0.91	0.91	1.21	-	0.90
Tensile strength (MPa)	Yield Strength 30	Yield Strength 19	207	104	Yield Strength 30
Young Modulus (GPa)	1.3	0.98	8.3	8.0	1.1
Poisson´s ratio	-	0.21	-		-
Average powder particle size (μm)	440	163	-	139	-
Glass transition temperature (T$_g$)	Typical value 0-20	-	158	156	Typical value 0-20
Melting temperature (T$_m$)	Typical value 170	166	-	-	Typical value 170

Table 1. Properties of Towpregs and PCT powders raw-materials

Property	**Carbon fibre** (TORAY M30 SC®)	
	Manufacturer datasheet	Experimental
Linear density (Tex)	760	-
Specific gravity (Mg/m^3)	1.73	-
Tensile strength (MPa)	5490	2731
Young Modulus (GPa)	294	194.5
Average fibre diameter	5	7.37

Table 2. Properties of Towpregs and PCT fibre raw-materials

2.2 Production of Thermoplastic Matrix Pre-Impregnated Products

The dry powder coating equipment used to produce fibre reinforced towpregs is schematically depicted in Figure 1 [7-10].

The pre-consolidated tapes (PCT´s) used in this work were produced in a cross-head extrusion equipment (see Figure 2) from our own laboratories [10].

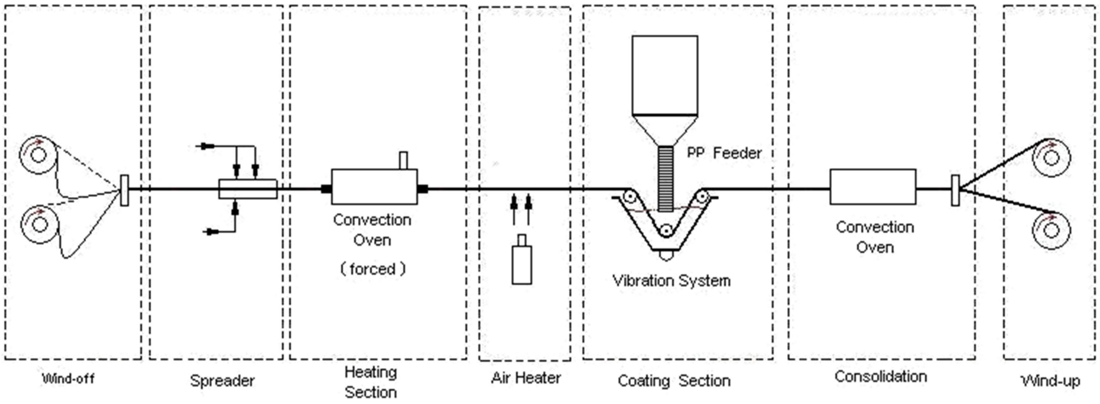

Figure 1. Powder coating line setup

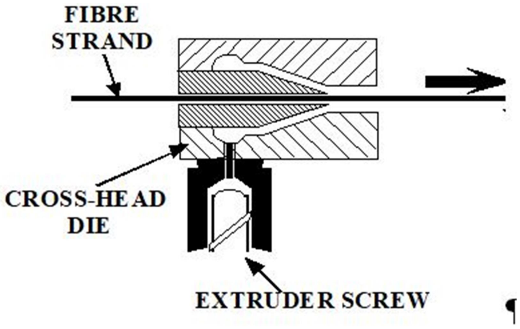

Figure 2. Cross-head extrusion die

2.2.1. CF/PP and CF/Primospire® towpregs production

In order to optimize the production of CF/PP powder coated towpregs, different processing variables combinations were experimented and the number of trials optimized using the Taguchi approach. The studied operational parameters were:

- heating oven temperature (600, 650 and 700 ºC); consolidation oven temperature (350, 400 and 450 ºC); linear pull speed (4, 6 and 8 m/min).

The Taguchi approach was applied to the towpregs production process in order to obtain the condition that maximizes polymer powder content.

The polymer mass fraction in the towpregs was determined by weighting towpreg strips produced in those different conditions.

The optimal condition obtained from Taguchi method application led to the following operating parameters selection: heating oven temperature and consolidation oven temperatures of 700 ºC and 400ºC respectively, and a linear pulling speed of 6 m/min. Using this optimal operative condition, the amount of polymer should increase up to 45.6%. However, it was found that the average polymer content in continuous towpreg production was only 40.0%.

In order to produce CF/Primospire® towpregs, the powder coating equipment was operated at different following woven temperatures and fibre linear pull speeds:

- heating oven temperature (700 ºC); consolidation oven temperature (500 - 550 ºC); linear pull speed (4 and 6 m/min). From such work the best values of the operational variables, which allow simultaneously producing towpregs in good and stable circumstances and having the maximum polymer powder content were:
- heating oven temperature - 700 ºC; consolidation oven temperature - 525 ºC and linear pull speed - 6 m/min. Using those conditions towpregs with a polymer mass content of approx. 40% were produced.

2.3 Pultrusion of pre-impregnated materials

The towpregs and PCT’s were processed into composite bar profiles using the laboratorial pultrusion line, Figure 3 [7-10].

To produce composite profiles, the pre-impregnated materials are guided into the pre-heating furnace to be heated up to the required temperature. Then, they enter in the pultrusion heated die to be heated and consolidated to the required size and, after cooled down in the cooling die to solidify.

In this work, it was designed and manufactured a die to allow producing a 20×2 mm2 bar-shaped profile.

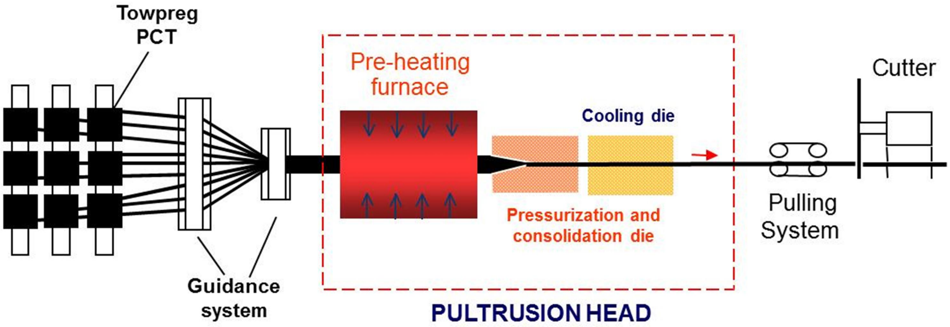

Figure 3. Schematic diagram of the pultrusion line

Those profiles were manufactured from different pre-impregnated materials, using operating conditions in order to optimize the processing.

2.3.1 Towpreg processing

CF/PP towpregs were manufactured by pultrusion into composite bar profiles using the most relevant operating conditions. The Taguchi´s/DOE method was applied, maintaining the cooling die at 25 ºC, in order to optimize the processing parameters:

i) furnace temperature (160 or180 ºC); ii) heating die temperature (240 or 260 ºC); iii) linear pull-speed (0.2 or 0.3 m/min).

Results have shown that was not possible to produce, in steady, conditions pultruded profiles from towpregs at pultrusion speeds and consolidation die temperatures higher than 0.4 m/min and 260 ºC, respectively. By using higher values of these two parameters, the process became unsteady, mainly due to reflux and accumulation of the thermoplastic polymer at the entrances of the consolidation and cooling dies.

The found optimal operating conditions that maximize mechanical properties were: furnace and heated die oven temperatures of 160 ºC and 260ºC respectively, and a linear pulling speed of 0.2 m/min.

The CF/Primospire® pultruded bars were produced in this work with the following operational conditions: i) furnace temperature (380 - 400 ºC); ii) heating die temperature (420 - 475 ºC); iii) linear pull-speed of 0.2 m/min.

2.3.2 Pre-consolidate tapes (PCT´s) processing

PCT´s were processed into rectangular 20×2 (mm2) bar using the already mentioned pultrusion equipment being operating conditions shown in Table 3.

Raw-material	Heated die temperature (ºC)	Cooled die temperature (ºC)	Furnace temperature (ºC)	Pulling speed (m/min)
CF/PP PCT	230	50	160	0.2

Table 3. Pultrusion processing parameters for PCT´s

2.4 Testing

2.4.1 Microscopy analysis

To determine the impregnation quality and to evaluate the fibre distribution and fibre/matrix adhesion of the thermoplastic composites, their cross-sections were studied under optical microscopy (CF/PP) and under by SEM-scanning electron microscopy (CF/Primospire®).

2.4.2 Mechanical testing

Bar samples were submitted to flexural, tensile and interlaminar testing according to the ISO standards 14125, 527 and 14130, respectively.

The mechanical properties were compared to the theoretical ones predicted by using the Rule of Mixtures (ROM).

Tensile tests were conducted, according to ISO 527, in a 100 kN universal testing machine at the crosshead speed of 2 mm/min using 180×20×2 mm^3 rectangular samples obtained from pultrusion.

The tensile modulus was determined from the slope of the initial linear portion of the experimental stress/strain curve. A SG Shimadzu® 50 mm length strain-gauge was used up to 0.3% strain, for accurate determination of the tensile modulus.

Three-point flexural tests were also conducted on five $100 \times 20 \times 2$ mm^3 pultruded profiles specimens and $100 \times 15 \times 4$ mm^3 for the compression moulded samples, using 100 kN universal testing machine and a distance between supports of 80 mm, according to ISO 14125, at a crosshead speed of 1 mm/min.

Samples with dimensions of 20 × 20 × 2 (mm3), cut from composites processed from each pre-impregnated raw material, were submitted to interlaminar shear tests according to ISO 14130. The tests were conducted in a 50 kN universal testing machine by using an initial pre-load of 1 N at the crosshead speed of 1 mm/min and a 10 mm span between supports.

2.4.3 TGA tests

The determination of mass fractions of composites made from carbon fibre and polymer with high temperature resistance like Primospire® is difficult and usually assessed by image processing techniques. Standard calcination tests are the mostly used with glass-reinforced plastics composites.

In this work we intend to use calcination tests for the evaluation of fibre mass fraction on carbon fibre and Primospire® composites, but since there's only a partial degradation of reinforcement and matrix, this method cannot be applied directly as in the case of glass-reinforced plastics composites.

In order to obtain carbon fibre and Primospire® temperature degradation behaviour TGA test were carried out using a thermo-gravimetric balance TA Q500 under different atmospheres (inert, oxidative and air).

In tests made under inert (N_2), oxidative (O_2) and air atmospheres, carbon fibres and polymer samples were heated from 30/40/60ºC until 900ºC using a 10ºC/min constant heating rate.

Being Air the atmosphere in the muffle furnace for calcination, TGA tests were also carried out under the same condition.

Polypropylene polymer matrix was also submitted to TGA tests with air as atmosphere to evaluate its degradation behaviour which is a relevant parameter to the determination of the processing conditions of composites that uses this polymer.

To avoid weight loss due to air flow, this was not used in all TGA tests performed with air atmosphere.

2.4.4 Calcination testing

Calcination tests were carried on the CF/Primospire® composites using results obtained from the TGA tests since this polymer matrix exhibits high temperature resistance and so is not fully eliminated on conventional calcination tests.

Initially, matrix (Primospire®) and reinforcement (CF) mass loss curves as a function of time resulting from the TGA tests were evaluated. This analysis concluded that the temperature 700 ºC was a good compromise between the end of Primospire® high degradation rate and the beginning of significant carbon fibre mass loss.

In order to simulate TGA behaviour calcination tests were performed on the constituents of the studied composite using the same thermal cycle (10° C/min) until the temperature of 700 ºC was reached. The initial mass of the samples, placed in a ceramic crucible, was approximately 2 g in accordance with the conventional standard.

CF/PP composites fibre mass content was determined by using calcination tests according to the EN ISO 1172. Composite samples, weighting approximately 2 g, were submitted to calcination inside a crucible in a muffle furnace during 10 min at 625º C.

3. Results and Discussion

The cross-sections of the pultruded composites were studied under optical Microscopy and SEM. As can be seen from Figures 4 and 5, all CF/PP and CF/Primospire® composite profiles from towpregs (with and without additive) and PCT´s have a reasonable distribution of the reinforcing fibres over the cross-sections. However, large differences in impregnation quality occur between the different samples that are likely to be related, directly, to the impregnation state of pre-impregnated materials used in pultrusion. It may be seen that the impregnation quality of the PCT composite samples is good, presenting almost all fibres completely surrounded ('wet-out') by the polymer. Only a few large dry spots were observed. This is most likely due to the good degree of impregnation already achieved in the PCT raw-material tape prior to the pultrusion step. In the case of PCT tape based composites, its outside layers exhibited richer polymer regions.

The samples from CF/PP towpreg with additive show a higher quantity of dry zones than the ones without additive. This could be due to some lack of compatibility between the fibre sizing and the used maleic anhydride coupling agent.

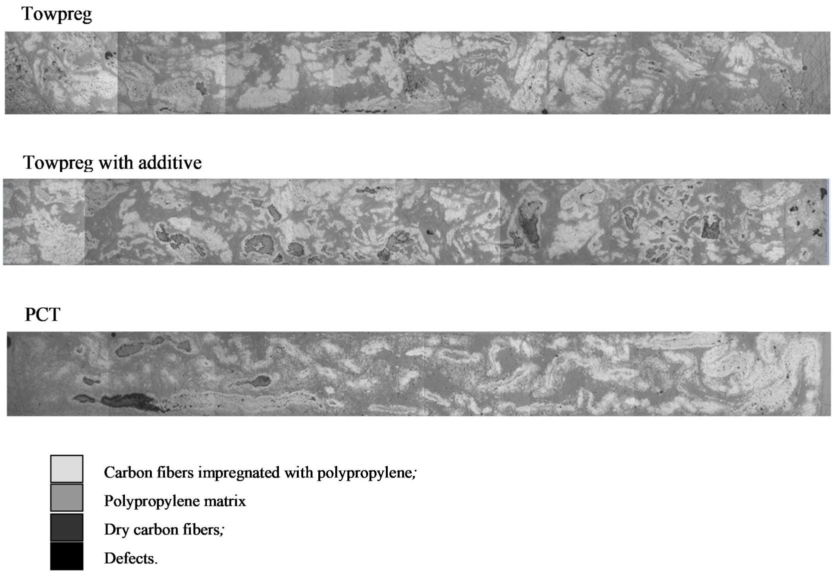

Figure 4. Optical micrographs of pultruded profiles cross-section (magnification of 8.75×)

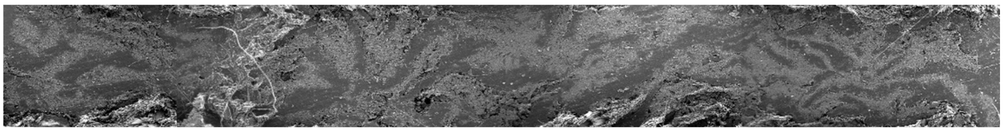

Figure 5. SEM image of CF/Primospire® pultruded profile cross-section sample (magnification of 40×)

Figure 6 show the results obtained in TGA test samples that were tested under inert and oxidative atmospheres. As can be seen, the polymer only shows the first degradation effects at temperatures above 450 ºC. It is also possible to conclude that, under inert atmosphere and until 900 ºC, only about 25% of the polymer mass is really lost. In the case of oxidative atmosphere almost all the polymer mass was completely lost at the final maximum temperature of 700 ºC.

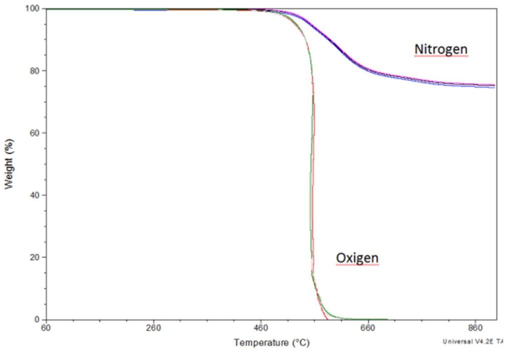

Figure 6. Comparison between the TGA results carried out on Primospire® under inert (N_2) and oxidative (O_2) atmospheres

The results obtained for carbon fibre and Primospire® TGA tests under air atmosphere (Figure 7) show that the degradation behaviour is between the one found for inert and oxidative atmospheres.

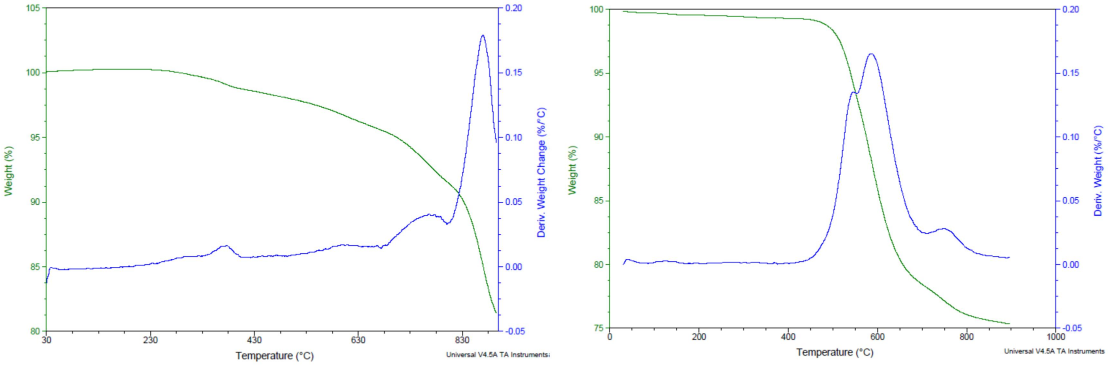

Figure 7. TGA results carried out on carbon fibres (left) and Primospire® (right) under air atmosphere

The results obtained in the calcination (Table 4) were similar to those of the TGA tests. The calcinations of Primospire® and carbon fibres at 700 ºC allowed establishing 25.9% and 7.2% as average mass losses, respectively, and as a consequence, the proportion of the remaining mass was 74.1% (*wp*) and 92.8% (*wf*). In TGA tests, the average mass loss of carbon fibre and Primospire® was 21.55% and 5.97%, respectively. Then, it was applied to the composite the same calcination parameters that were used for the testing of their constitutive materials.

Experiments	**Loss mass** (%)	
	Primospire®	Carbon Fibre
1	25.9	6.1
2	26.4	7.5
3	26.1	7.2
4	25.3	7.8
Average	**25.9**	**7.2**
SD	0.5	0.7
Remaining mass fraction (w)	**74.1**	**92.8**

Table 4. Primospire® and carbon fibre calcination results

After calcining the composite sample, the carbon fibre mass fraction, wfc, was obtained by:

$$wfc = 1 - \frac{mc_f - wf \cdot mc_i}{mc_i \cdot (wp - wf)} \qquad (1)$$

where mc_i and mc_f are the measured composite sample initial and final weights, respectively. Also, wf and wp are the carbon fibre and Primospire® remaining mass fractions, respectively.

Furthermore, by knowing the fibre and polymer densities, ρ_f and ρ_p, respectively, the fibre mass fraction (wfc) may be converted in fibre volume fraction (vf) by:

$$vf = \frac{\frac{wfc}{\rho f}}{\frac{wfc}{\rho f} + \frac{(1 - wfc)}{\rho p}} \qquad (2)$$

Table 5 summarizes the composite calcination test obtained results. As can be seen, the composite had a fibre mass fraction of 54.1% corresponding to a fibre volume fraction of 45.2%.

Experiments	**Loss mass** (%)	**Fibre mass fraction** (wfc)	**Fibre volume fraction** (*vf*)
1	16.6	49.9	41.1
2	16.8	48.8	40.0
3	15.8	54.2	45.2
4	16.4	50.8	41.9
5	14.7	59.9	51.1
6	14.5	60.9	52.1
Average	**15.8**	**54.1**	**45.2**
SD	1.0	5.2	5.3

Table 5. Composite calcination test results

Concerning polypropylene TGA tests, it was found that the degradation temperature was about 270 ºC (Figure 8).

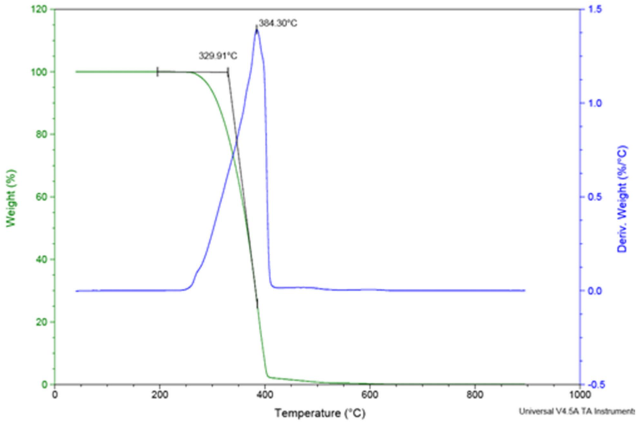

Figure 8. TGA results carried out on polypropylene under air atmosphere.

Tables 6 and 7 summarize all experimentally results obtained from the CF/PP and CF/Primospire® composites processed by pultrusion from the pre-impregnated products under study. To better evaluate and compare the mechanical properties obtained on the composites processed from the different pre-impregnated products studied. The tables also present theoretical expected values and relative values of specific properties.

As can be seen from Table 6 the experimental moduli obtained from de CF/PP composites are in good agreement with the predicted theoretical ones. Some experimental values are even higher than the theoretical expected ones. This can be explained considering that the fibre volume fraction content of some samples can be higher than the determined by the calcination tests.

Analysing Table 6, one can conclude that composites processed from the CF/PP PCT´s demonstrated to have better flexural and interlaminar shear strengths than those produced from CF/PP towpregs. Concerning the interlaminar shear tests, the CF/Primospire® composites shown a much higher value than CF/PP probably due to the better mechanical properties that the Primospire® matrix exhibits. As it may be seen and expected, the CF/Primospire® towpregs required the use of much higher temperatures than the CF/PP ones in pre-heating furnace and pressurization/consolidation die. Due to such higher temperatures, tests still continue being done to optimise the operational conditions and, consequently, the obtained mechanical properties.

Finally, it may be noted that any of composites made from pre-impregnated materials under study reached failure in the interlaminar shear tests. This fact reveals the high degree of ductility exhibited by these materials which may be relevant for many applications. Thus, the interlaminar shear strength results shown in Tables 6 and 7 correspond to maximum force applied in the test.

Test Type	**Property**		***Pultrusion***	
			Towpreg	***PCT***
Flexural	Flexure Modulus (GPa)	Experimental	90.1±0.4	37.7±2.2
		Theoretical	98.9	62.7
	Flexure Modulus / Fibre volume fraction (GPa)		178.1±0.8	118.2±6.9
	Flexure Strength (MPa)	Experimental	241.2±1.6	158.7±4.2
	Flexure Strength / Fibre volume fraction (MPa)		476.7±3.2	497.5±13.2
Tensile	Tensile Modulus (GPa)	Experimental	110.6±5.9	63.5±4.3
		Theoretical	98.9	62.7
	Tensile Modulus / Fibre volume fraction (GPa)		218.6±11.7	199.1±13.5
	Tensile Strength (MPa)	Experimental	1060.8±43.1	636.9±38.4
	Tensile Strength / Fibre volume fraction (MPa)		2096.4±85.2	1996.6±120.4
Inter-laminar Shear	Interlaminar Shear Strength (MPa)		12.3±0.3	14.0±0.2
Fibre volume fraction (%)			50.6	31.9

Table 6. CF/PP composite mechanical test results

Test Type	**Property**	**Pultrusion**
		CF/Primospire® towpreg
Flexural	Flexure Modulus (GPa)	56.1±2.9
	Flexure Strength (MPa)	253.6±16.1
Tensile	Tensile Modulus (GPa)	92.2±5.6
	Tensile Strength (MPa)	839.2±28.7
Inter-laminar Shear	Interlaminar Shear Strength (MPa)	25.4±2.1

Table 7. Test results on the processed CF/Primospire® composites

The theoretical values of moduli, E, were directly obtained from the rule of mixtures using the raw-material properties presented in Tables 1 and 2, following the Eq. 3:

$$E = E_f \cdot vf + E_p \cdot (1 - vf) \qquad (3)$$

where, Ef, Ep and vf are the fibre modulus, polymer modulus and fibre volume fraction, respectively.

In the case of CF/Primospire® composites, using expression 3 and the experimental tensile moduli, it was possible to estimate the fibre volume fraction as approximately 45%. This result is in good agreement whit the one obtained from calcination test (45.2±5.3).

4. Conclusions

The tests made using a proprietary pultrusion equipment already allow to conclude that is possible to produce, in good conditions, profiles from almost all available thermoplastic matrix pre-impregnated raw-materials using pull speeds of 0.3 m/min.

Existing powder-coating equipment was shown to be suitable to produce CF/PP and CF/Primospire® towpregs that could be adequately processed into pultruded profiles. From the tests made, the towpregs can be easily and continuously produced at industrial production speeds between 2 a 8 m/min.

It was possible to optimize the production of CF/PP pultruded profiles and CF/PP towpregs, through the use of Taguchi/DOE method, achieving optimal conditions.

In particular, for CF/PP pultruded profiles, very good agreement was found between the experimental moduli values of all composites produced and the theoretical ones.

More research must be done in order to increase the processing speeds of CF/PP and CF/Primospire® towpregs as well as PCT's and to improve the impregnation, uniformity and dispersion of raw-materials in the composites.

CF/Primospire® composites obtained by pultrusion showed a higher value for the interlaminar strength than all other ones. Due to higher processing temperatures, further tests should be done to optimise the operational conditions and further improve the obtained composite mechanical properties.

The mechanical properties obtained in all pultruded composites allow predicting their adequate use either in general or structural engineering applications.

The calcination tests based on the results obtained from TGA tests reveal to be a very interesting method to experimentally determine composite mass fractions in the case of temperature resistant materials used as matrix and reinforcement.

Primospire® TGA tests showed that this material exhibits an excellent temperature resistance and, therefore, is a good candidate for high-demanding applications.

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4.5. Conclusions

Existing powder-coating equipment was shown to be suitable to produce GF/PP, CF/PP and CF/PRIMOSPIRE® towpregs that could be adequately processed into pultruded profiles. From the tests made, the towpregs can be easily and continuously produced at industrial production speeds between 2 a 8 m/min.

It was possible to optimize the production of CF/PP towpregs, through the use of Taguchi/DOE method, achieving optimal conditions.

Relatively good agreement was found between the experimental moduli values of all composites produced and the theoretical ones.

More research must be done in order to increase the processing speeds of GF/PP, CF/PP and CF/PRIMOSPIRE® towpregs as well as PCT's and to improve the impregnation, uniformity and dispersion of raw-materials in the composites.

The calcination tests based on the results obtained from TGA tests reveal to be a very interesting method to experimentally determine composite mass fractions in the case of temperature resistant materials used as matrix and reinforcement.

PRIMOSPIRE® TGA tests showed that this material exhibits an excellent temperature resistance and, therefore, is a good candidate for high-demanding applications.

Chapter 5

PULTRUSION OF THERMOPLASTIC COMPOSITES

5.1. Introduction

Pultrusion is a versatile continuous high speed production technology allowing the production of fibre reinforced complex profiles. Thermosetting resins are normally used as matrices in the production of structural constant cross section profiles. In contrast, the use of thermoplastic matrices, that can allow higher production speeds and present higher toughness, chemical resistance, damping and are more ecological, are still in an early stage [5.1-5.14].

Nevertheless, only recently new technologies allowed the production of low-cost continuous fibre reinforced pre-impregnated thermoplastic raw-materials. With these technologies it is possible to replace the former expensive thermoplastic matrix prepregs (obtained by melting and solvent based processes) by cheap dry commingled fibres [5.15-5.17] and powder coated pre-impregnated materials (towpregs) [5.5, 5.18, 5.19]. Work is currently in progress to consolidate and process these new promising materials into final composite parts by using existing high throughput technologies, such as heated compression moulding, filament winding and pultrusion [5.6, 5.20-5.28].

Firstly, the pultrusion machine used in the present work and the dies will be presented (sub-chapter 5.2). The improvements made in that equipment and project change suggestions will be described.

In *paper 1*, it is described the design and manufacture of a low-cost full scale pultrusion prototype equipment and discussed the production and mechanical properties of polypropylene/glass (GF/PP) reinforced composite bars fabricated by using the prototype equipment. Three different GF/PP pre-impregnated raw-materials, a commercial GF/PP comingled system from Vetrotex, a GF/PP powder coated towpreg and a GF/PP pre-consolidated tape (PCT) produced in our laboratories, were used in the production of composite bars processed in a laboratorial pultrusion equipment developed for such purpose

[5.29]. In *paper 2*, it has been studied the influence of the towpregger fibre pull-speed and furnace temperature on the final towpreg polymer's content was determined. The towpregs' quality was also assessed using optical microscopy and SEM. Then they were pultruded into composite profiles and the influence of the pull-speed and dies temperatures on their mechanical and other relevant physical properties studied. Finally, the best processing window and the optimisation of the final composite profiles are discussed. The aim of *paper 3* has been to optimize the production of new continuous carbon fibres reinforced polypropylene matrix pre-impregnated materials (towpregs) continuously processed by dry deposition of polypropylene (PP) powder. The processing of the produced towpregs by pultrusion, using a prototype equipment, was also optimized. The optimization of both processes was made by studying the influence of the most relevant processing parameters in the final properties of the produced towpregs and composites. The possibility of using maleic anhydride as compatibilizer for polypropylene reinforced carbon fibre composites (CF/PP) was also analyzed. A pre-consolidated tape was produced by the melting cross-head extrusion process and its properties compared with those of towpregs. The polymer mass contents were determined and the final pultruded composite profiles were also submitted to tensile, interlaminar, flexural, calcination and optical microscopy tests. *Paper 4* aims to further optimize the production of new continuous carbon fibres reinforced thermoplastic matrix pre-impregnated materials (towpregs) continuously processed by dry deposition of polymer powders. Two different thermoplastic matrices were studied: one for commercial applications (polypropylene) and another for advanced markets (PRIMOSPIRE$^{®}$).

The optimization was made by studying the influence of the most relevant processing parameters in the final properties of the produced towpregs and composites. The final pultruded composite profiles were submitted to mechanical tests in order to obtain relevant properties. To improve the temperature distribution profile in heating die, different modifications were performed and are presented in *paper 5*.

In order to optimize both processes, towpregs production and pultruded composites profiles were analysed to determine the influence of the most relevant processing parameters in the final properties. The final pultruded composite profiles were submitted to mechanical tests and the relevant properties are discussed.

In *paper 6*, towpregs were characterized by scanning electron microscopy (SEM), visual analysis and their polymer mass contents were determined. The final composite parts obtained by pultrusion were also submitted to tensile, interlaminar and flexural tests, as well as calcination and optical microscopy tests and the results were compared with theoretical ones that can be predicted by using the ROM (Rule Of Mixtures) and other engineering traditional materials.

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5.2. Development of a pultrusion manufacturing equipment

The equipment used in the pultrusion manufacturing process can be seen in the assembly drawing shown in Figure 5.1.

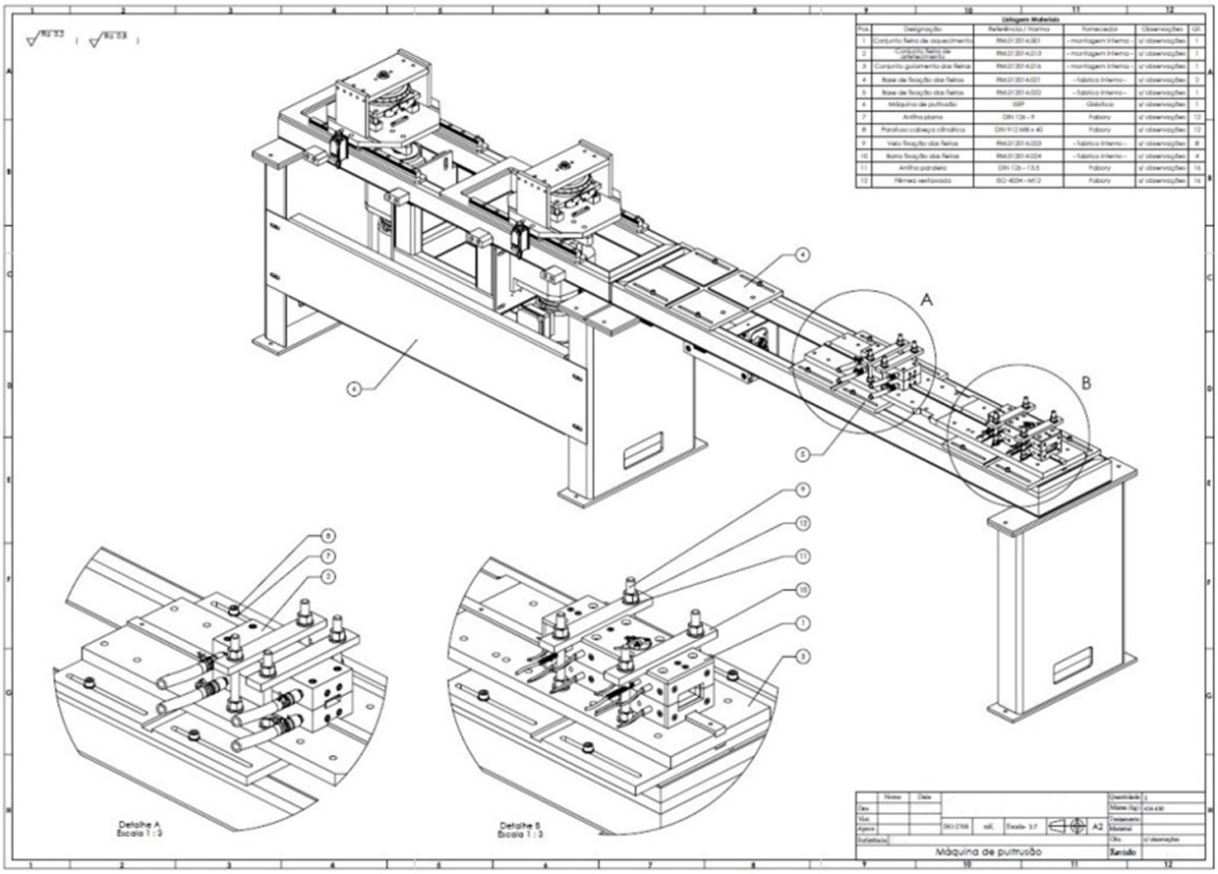
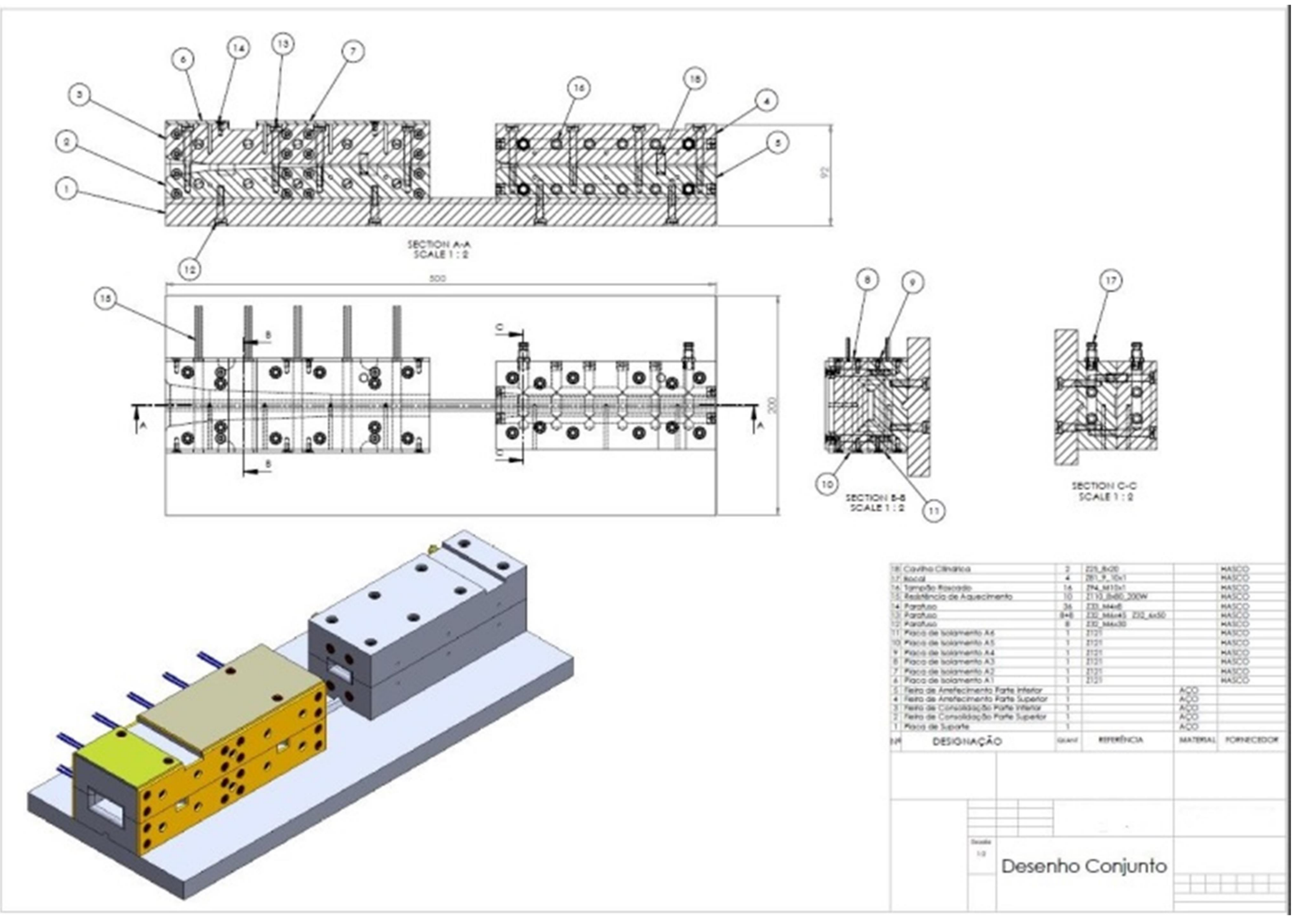


Figure 5.1 – Pultrusion equipment.

The machine works with two dies, a heated one for pressurizing and consolidating and the other for cooling the pultruded profile (Figure 5.2 and Figure 5.3).



Nº	DESIGNAÇÃO	QUANT	REFERÊNCIA	MATERIAL	FORNECEDOR
18	Cavilha Cilíndrica	2	Z25_8x20		HASCO
17	Bocal	4	Z81_9_10x1		HASCO
16	Tampão Roscado	14	Z94_M10x1		HASCO
15	Resistência de Aquecimento	10	Z110_8x80_200W		HASCO
14	Parafuso	36	Z33_M4x8		HASCO
13	Parafuso	8+8	Z32_M6x45 Z32_6x50		HASCO
12	Parafuso	8	Z32_M6x30		HASCO
11	Placa de Isolamento A6	1	Z121		HASCO
10	Placa de Isolamento A5	1	Z121		HASCO
9	Placa de Isolamento A4	1	Z121		HASCO
8	Placa de Isolamento A3	1	Z121		HASCO
7	Placa de Isolamento A2	1	Z121		HASCO
6	Placa de Isolamento A1	1	Z121		HASCO
5	Fieira de Arrefecimento Parte Inferior	1		AÇO	
4	Fieira de Arrefecimento Parte Superior	1		AÇO	
3	Fieira de Consolidação Parte Inferior	1		AÇO	
2	Fieira de Consolidação Parte Superior	1		AÇO	
1	Placa de Suporte	1		AÇO	

Figure 5.2 – Heated and cooled dies

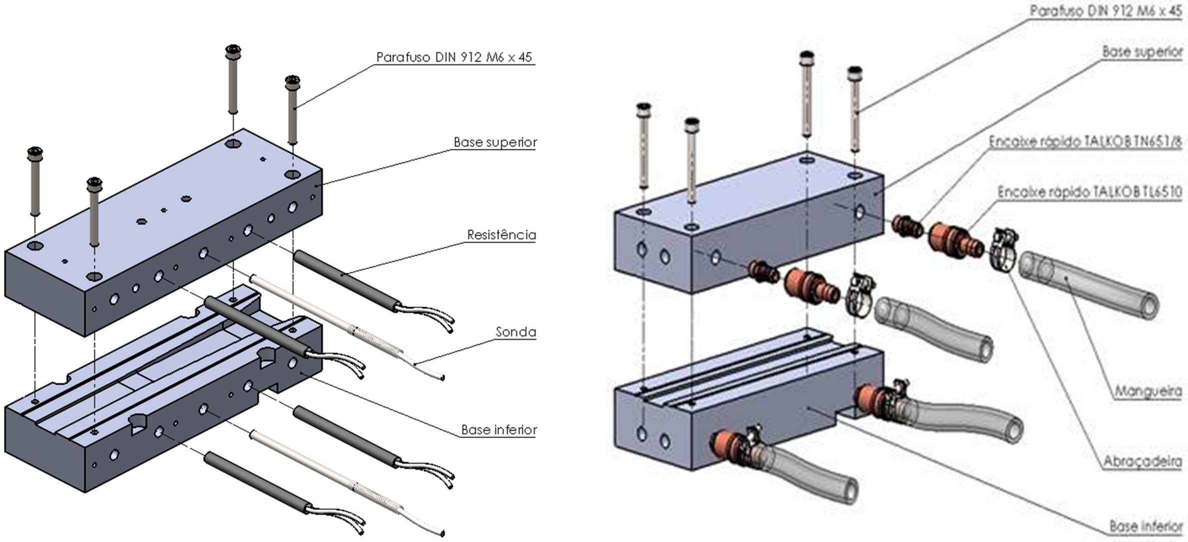


Figure 5.3 – Heated and cooled dies perpectives

To improve the temperature profile in the heated die, a balanced distribution of the electric resistances was performed (Figure 5.4).

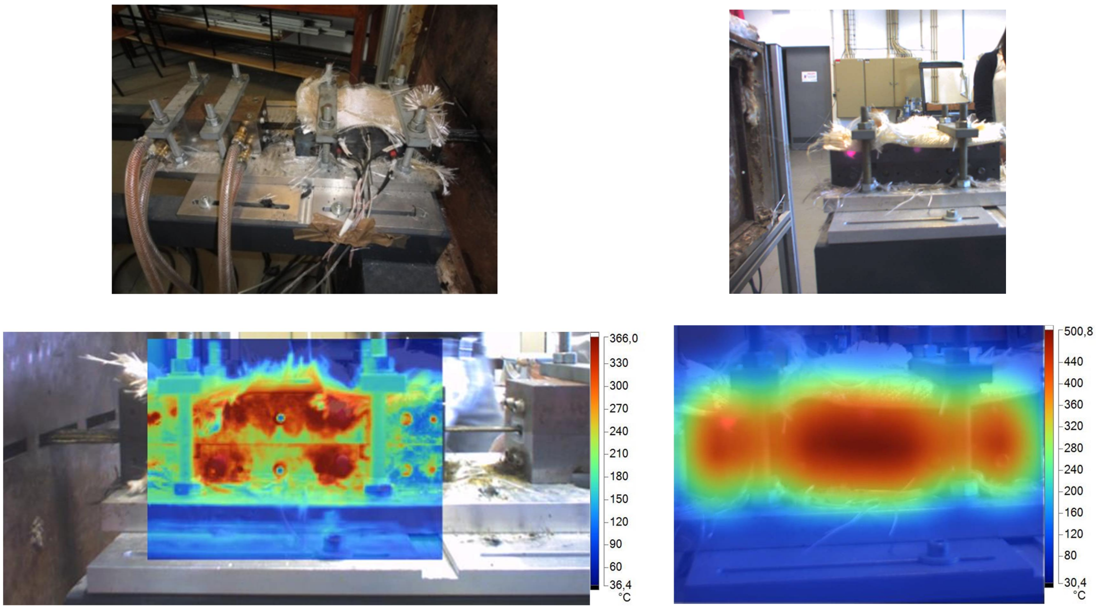


Figure 5.4 – Initial temperature profile (left) and improve temperature profile (right) in the heated die

To better analyze, in the pultrusion process, the influence of the existing process parameters and others in the final properties of the profiles was studied. Namely the pressure in the consolidation die, the pull force, as well as the distance and cooling system between the pressurization and consolidation die and the cooling die should be considered. Hence, the dies project should be improved with the inclusion of pressure and temperature sensors, the machine's measurement of the pulling force, the proper insulation of the heated die and the possibility of moving the dies keeping the alignment in order to change the distance between them (Figure 5.5).

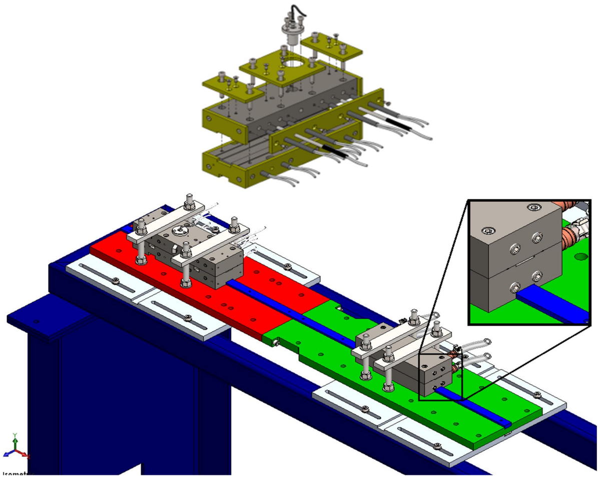


Figure 5.5 – Some changes in machine and dies to improve the process

5.3. Paper 1

ECCM15 - 15TH EUROPEAN CONFERENCE ON COMPOSITE MATERIALS
Venice, Italy, 24-28 June 2012

3.2 - DEVELOPMENT OF A NEW PULTRUSION EQUIPMENT TO MANUFACTURE THERMOPLASTIC MATRIX COMPOSITE PROFILES

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Keywords: Towpreg, pultrusion, fibreglass composites, thermoplastic matrix composites

Abstract

This paper describes the design and manufacture of a low-cost full scale pultrusion prototype equipment and discusses the production and mechanical properties of polypropylene/glass (GF/PP) reinforced composite bars fabricated by using the prototype equipment. Three different GF/PP pre-impregnated raw-materials, a commercial GF/PP comingled system from Vetrotex, a GF/PP powder coated towpreg [1-3] and, a GF/PP pre-consolidated tape (PCT) produced in our laboratories, were used in the production of composite bars that were subsequently submitted to mechanical testing in order to determine the relevant mechanical properties and quantify the consolidation quality. Samples of the different composite profiles were also observed under SEM microscopy.

1 Introduction

Pultrusion is a versatile continuous high speed production technology allowing the production of fibre reinforced complex profiles. Thermosetting resins are normally used as matrices in the production of structural constant cross section profiles. In contrast, the use of thermoplastic matrices, that can allow higher production speeds and present higher toughness, chemical resistance, damping and are more ecological, are still in an early stage [4-11].

Nevertheless, it was only recently that new technologies allowed the production of low-cost continuous fibre reinforced pre-impregnated thermoplastic raw-materials. With these technologies it is possible to replace the former expensive thermoplastic matrix prepregs (obtained by melting and solvent based processes) by cheap dry commingled fibres [12-15] and powder coated pre-impregnated materials (towpregs) [9, 16, 17]. Work is currently in progress to consolidate and process these new promising materials into final composite parts by using existing high throughput technologies, such as heated compression moulding, filament winding and pultrusion [8, 18-25].

In this work, three different GF/PP pre-impregnated raw-materials, a commercial GF/PP comingled system from Vetrotex, a GF/PP powder coated towpreg and, a GF/PP pre-consolidated tape (PCT) produced in our laboratories, were used in the production of composite bars processed in a laboratorial pultrusion equipment developed for such purpose [26].

The obtained composite profiles were subsequently submitted to mechanical testing in order to determine the relevant mechanical properties and quantify the consolidation quality. Samples of the different composite profiles were also observed under SEM microscopy. Finally, the obtained results were compared with traditional thermosetting resins reinforced with glass fibres.

2 Processing

2.1 Raw-Materials

Table 1 summarises relevant properties of the glass fibres and polypropylene used in present work to produce pre-impregnated raw materials. In the GF/PP towpregs were used 2400 Tex type E fibre rovings from Owens Corning and a Icorene® 9184B P polypropylene from ICO Polymers France. On the other hand, the PCT tapes were manufactured with glass fibres (TufRov 4599) from PPG Industries and a polypropylene (Moplen RP348U) from Basell.

Property	Units	Glass fibres	Polypropylene
Density	Mg/m^3	2.56	0.91
Tensile strength	MPa	3500	30
Tensile modulus	GPa	76	1.3
Average powder particle size	µm	-	440
Linear roving weight	Tex	2400	-

Table 1. Properties of the raw materials used to produce the GF/PP towpregs.

Commercial commingled GF/PP fibres Twintex® R PP 60 B 1870 FU from Owens Corning were also used, as reference of a current commercially available pre-impregnated product, in the production of the pultrusion thermoplastic composite profiles.

2.2 Processing the pre-impregnated raw-materials

The prototype dry powder coating equipment used to produce fibre reinforced towpregs is schematically depicted in Figure 1 [8, 27]. It consists of six main parts: a wind-off system, a fibres spreader unit, a heating section, a coating section, a consolidation unit and a wind-up section. Initially, the reinforcing fibres are wound-off and pulled through a pneumatic spreader and then coated with polymer by heating in a convection oven and made to pass into a polymer powder vibrating bath. A gravity system allows maintaining the amount of polymer powder constant. The consolidation unit oven allows softening the polymer powder and promotes its adhesion to the fibre surface. Finally, the thermoplastic matrix towpreg is cooled down and wound-up on a spool.

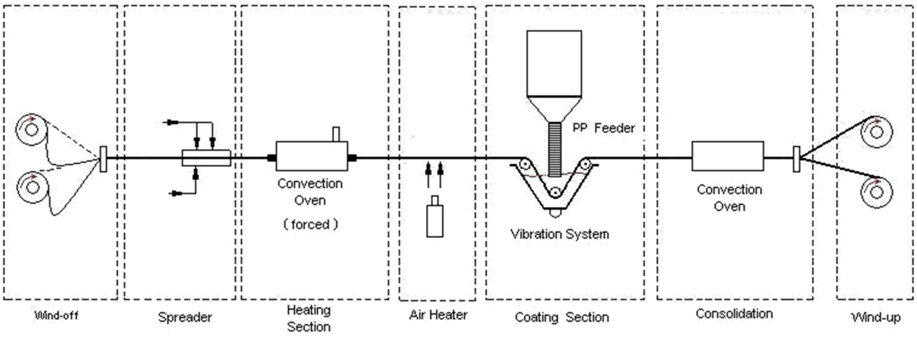


Figure 1. Powder coating line setup.

On other hand, thermoplastic pre-consolidated tapes were manufactured by using a new specially developed cross-head extrusion hot melting process (Fig. 2).

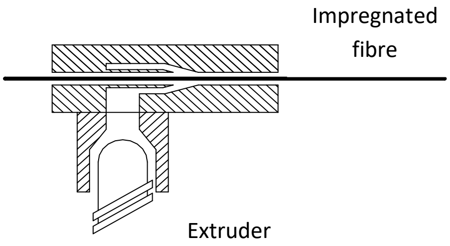


Figure 2. Cross-head extrusion.

The core of this technology is a impregnation unit in which reinforcing fibres are introduced, spread and impregnated by the polymer melt. The impregnation is achieved through the build-up of pressure acting on the molten polymer trapped between the unit's spreading elements and the fibre rovings. The apparatus consists of a creel system holding the fibre rovings, a guidance system to transport the fibre into the impregnation unit, an extruder to melt and feed the molten polymer into the impregnation unit, the impregnation unit itself, and subsequently a cooling unit, a puller, and a take-up device where the composite tape is collected. Such thermoplastic pre-consolidated tape is commercially available through the company Comp Tape Lda. [28]. An overview of such material data is given in Table 2.

Property	Description
Fibre type	E-Glass, 2400 Tex
Fibre diameter	17 μm
Fibre content	60 wt.%
Matrix type	Polypropylene (PP)
Tape width	25 mm
Tape linear density	16000 Tex

Table 2. PCT data.

2.3 Pultrusion

Figures 3 and 4 depict a schematic and a photograph of the pultrusion equipment developed in the present work. The 10 kN pultrusion line may be divided in five main parts: i) initial towpreg bobbins storing cabinet; ii) guiding system; iii) pultrusion head, that includes a pre-heating furnace and the pressurization/consolidation and cooling dies; iv) pulling system and, v) the final profile cutting system.

To produce the composite profiles, the pre-impregnated materials are guided into the pre-heating furnace to be heated up to the required temperature. Then, they enter in the pultrusion die to be heated up and consolidated to the required size in its first zone and, after cooled down in order to solidify. The pultruded material is then cut into specified lengths. In this work, a die was designed and manufactured to allow producing a 20×2 mm^2 tape-shaped profile.

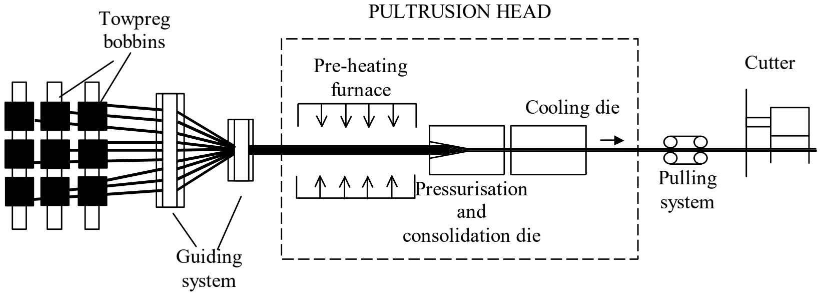


Figure 3. Schematic diagram of the proprietary pultrusion line.

Figure 4. Overview of pultrusion equipment.

The pre-heating furnace may reach a temperature of 1000 ºC and was designed to allow processing almost every type of fibre/thermoplastic-based pre-impregnated materials.

Table 3 summarises the pultrusion conditions used to process the three different pre-impregnated raw-materials into final GF/PP composite profiles.

Raw-material	**Heated die temperature** (ºC)	**Cooled die temperature** (ºC)	**Pre-heating temperature** (ºC)	**Pulling speed** (m/min)
Twintex®	300	50	170	0.2
Towpreg	275	25		
PCT	230	50		

Table 3. Pultrusion processing parameters.

As may be seen, it was already possible to produce from all GF/PP pre-impregnated raw-materials profiles at pull speeds of 0.2 m/min.

3 Tests and results

3.1 Microscopy analysis

To determine the impregnation quality of the pultruded thermoplastic composites, 2 cm-long samples were cut from the pultruded sections and were embedded in a thermoset EPIKOTE™ 04908 resin. After curing and polishing to a mirror like finish, using increasingly fine sanding paper, samples were ready for microscopy analysis. Observations were done using reflected light optical microscopy (Olympus BH-2). A digital camera (Leica DFC200) was used to image cross sectional views of the samples.

The microscopy images taken from the samples of the pultruded composites using PCT, Twintex® and towpreg, are given in Table 4.

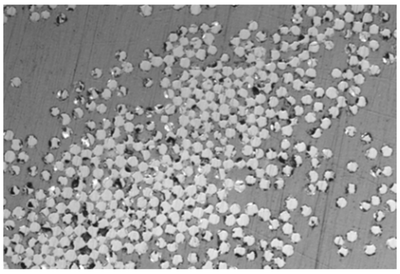
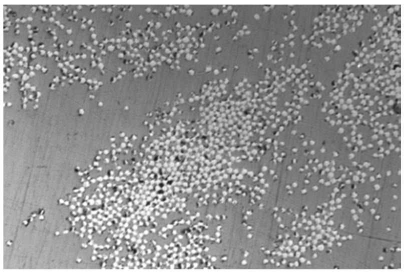
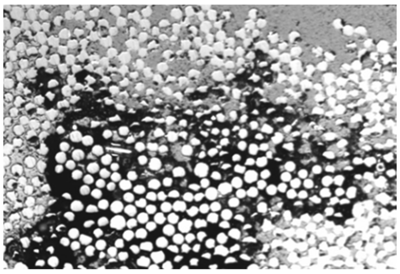
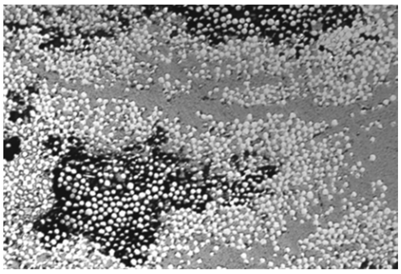
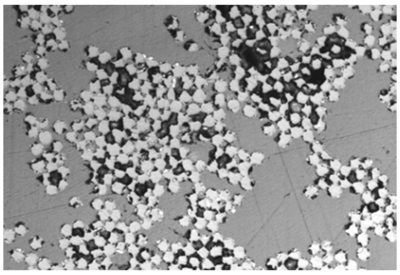
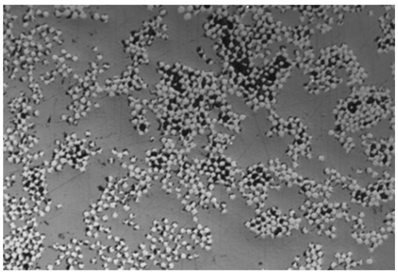
Material	Magnification	
	250 ×	130 ×
PCT		
Towpreg		
Twintex®		

Table 4. Microscope images of the pultruded profiles.

As can be seen from the images presented in table 4, all semi-finished lead to a reasonable distribution of the reinforcing fibres over the cross-section, although a small improvement in distribution can be observed going from PCT through Twintex® to towpreg composites.

However, large differences in impregnation quality occur, between the different samples that are likely to be related, directly, to the impregnation state of the semi-finished used during pultrusion. It may be seen that the impregnation quality of the PCT composite samples is excellent, presenting almost all fibres completely surrounded ('wet-out') by the polymer,. This is most likely due to the high degree of impregnation already achieved in the PCT raw-material tape prior to the pultrusion step. hardly showing any dry spots in the pultruded samples

The Twintex-based samples also show a very good impregnation of the fibre. This is likely due to the intimate contact between the individual dry glass and PP fibres prior to the final pultrusion stage, making the effective remaining impregnation distance when melting the polymer very small, which leads to an easier consolidation. Although, some larger dry spots were observed between the glass fibres at larger magnifications, showing an overall impregnation quality poor when compared with the one observed in the PCT tape based pultruded composites.

Finally, the depicted towpreg-based composite samples exhibit larger apparent dry zones. This is most likely due to the uneven distribution of the dry polymer powder in the towpreg, prior to pultrusion. Consequently, seems to be harder to bridge the large distances of dry glass fibre during pultrusion, which results on bigger unimpregnated zones in the pultruded composites.

3.2 Mechanical testing

3.2.1 Short beam shear tests

In order to obtain an indication of the composite quality after pultrusion, short beam tests have been carried out according to ASTM 2344, at room temperature, using a Universal Instron 4505 testing machine fitted with a 50 kN load cell. Five 20 x 10 x 2 mm composite samples were cut from pultruded composites processed from each pre-impregnated raw material to be tested. Figure 5 show typical force-displacement curves of the tested specimens in the short beam shear test.

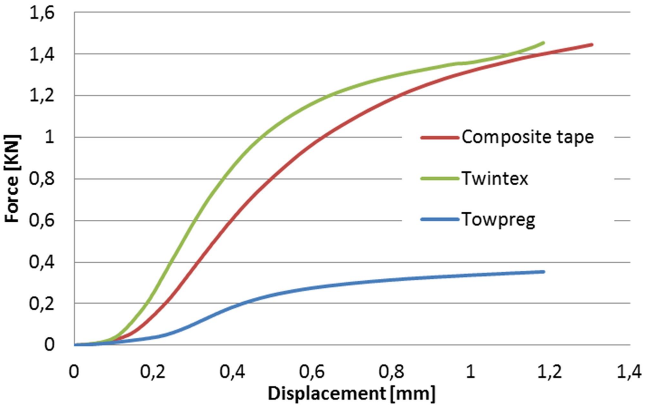


Figure 5. Short beam test results.

Those curves show that all specimens failed in plastic shear, and therefore, no breaking load could be obtained, which would allow the formal calculation of the interlaminar shear strength. Such results seem to show that a reasonable degree of adhesion between layers was obtained in the composites. Curves also show an obvious different behaviour between samples. While PCT tape and Twintex® based pultruded composites have similar load-bearing capacities, having similar shape and ultimate load curves, towpreg based samples showed lower performance. This mostly results from the already mentioned limited degree of impregnation of these samples.

3.2.2 Tensile and flexural tests

Table 5 presents the mechanical properties determined from flexural and tensile tests carried out on pultruded profiles. The fibre mass fraction and the flexural and tensile properties were determined in accordance with the ISO 1172, EN ISO 14125 and EN ISO 527-5 standards, respectively. For the former, specimens weighting approximately 20 g, cut from the profiles, were calcinated during 10 min at 600º C inside a Naberterherm® S30 muffle furnace. For the second determination, rectangular, 100 mm×20 mm×2 mm samples were submitted to three-point bending tests using a 80 mm support span, a cross-head speed of 1 mm/min and a 100 kN load cell in a Shimadzu® universal testing machine. The tensile tests were conducted on 250 mm×15 mm×2 mm rectangular samples, at a 2 mm/min cross-head speed, using the same equipment and load cell. A 50 mm length strain-gauge was used up to 0.3% strain, to allow determining accurately the tensile modulus on each sample.

Raw-material	**Tensile strength** (MPa)	**Tensile modulus** (GPa)		**Flexural strength** (MPa)		**Flexural modulus** (GPa)		**Fibre mass fraction** (%)	**Fibre volume fraction** (%)
	Av.	Av.	SD	Av.	SD	Av.	SD	Av.	Av.
Twintex®	>416	24.9	1.1	595	24	26.2	2.0	62.5	37.1
Towpreg	>305	29.9	3.5	125	11	27.1	1.2	78.8	56.8
PCT	>424	21.4	1.5	329	30	16.8	1.5	54.8	30.0

Av. – Average SD – Standard Deviation

Table 5. Results from tensile and flexural tests.

As can be seen from Table 5, similar results that are compatible with the major common and structural applications were obtained in all pultruded composites materials from both tensile and flexural tests. In any case, worse flexural strength and modulus results were found in towpreg and PCT tape based pultruded composites, respectively. These lower results obtained in the flexural tests are probably consequence of the inferior degree of impregnation observed in the towpreg based composites and, in the case of PCT tape based composites, result from the higher rich polymer regions exhibited by this material in its outside layers.

4 Conclusions

The tests made using a proprietary pultrusion equipment already allow producing in good conditions profiles from almost all commercial available thermoplastic matrix pre-impregnated raw-materials at pull speeds of 0.2 m/min. Currently, work is carried out to try increasing the pultrusion processing speed to values in the range from 2 to 6 m/min, which will equalizing the speed of the pultrusion line with that of the towpreg coating and PCT tape production lines. The use of similar operational speeds in both processes (equipments) will make possible, in future, assembling them in just one equipment.

The mechanical properties obtained in GF/PP pultruded composite profiles were also found to be adequate either for common or structural engineering applications. The experimental results also demonstrated that further work should be carried out to improve impregnation in towpreg based pultruded composites.

Acknowledgments

Authors would like to acknowledge the experimental work done by Ms. Anna Matveeva.

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5.4. Paper 2

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Special Issue on Raw Materials and Recycling

Production of thermoplastics matrix preimpregnated materials to manufacture composite pultruded profiles

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Abstract

The aim of this work is to optimize the production of new continuous carbon fibers reinforced polypropylene matrix pre-impregnated materials (towpregs) continuously processed by dry deposition of polypropylene (PP) powder by our own developed dry coating line. The processing of the produced towpregs by pultrusion, using a prototype equipment, was also optimized. The optimization of both processes was made by studying the influence of the most relevant processing parameters in the final properties of the produced towpregs and composites. The method of Taguchi/DOE (Design of Experiments) was used to allow the determination of the optimal processing windows. The possibility of using maleic anhydride as compatibilizer for polypropylene reinforced carbon fiber composites (CF/PP) was also analyzed. A pre-consolidate tape was produced by the melting cross-head extrusion process and its proprieties compared with those of towpregs. Finally, towpregs were characterized by scanning electron microscopy (SEM) and visual analysis. Their polymer mass contents were determined and the final pultruded composite profiles were also submitted to tensile, interlaminar, flexural, calcination and optical microscopy tests.

Keywords: towpreg; composite materials; thermoplastic; pultrusion; polypropylene; Taguchi/DOE.

This paper was presented at MATERIAIS 2013, Coimbra, Portugal, March 25-27, 2013

1. Introduction

During the last decades, composites have successfully replaced traditional materials in many engineering applications due to its excellent properties, mainly their excellent mechanical properties combined with low density [1,2].

Although only recently thermoplastic matrices have been used in long and continuous fiber reinforced composites replacing with success thermosetting matrices, the number of their applications is increasing due to their better ecological and mechanical performance. Composites with thermoplastic matrices offers increased fracture toughness, higher impact tolerance, short processing cycle time and excellent environmental stability. They are recyclable, post-formable and can be joined by welding. The use of long/continuous fiber reinforced thermoplastic matrix composites involves, however, great technological and scientific challenges since thermoplastics present much higher viscosity than thermosettings, which makes much difficult and complex the impregnation of reinforcements and consolidation tasks [2-8].

Today, two major technologies are being used to allow wet reinforcing fibers with thermoplastic polymers [5-8]: i) the direct melting of the polymer

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and, ii) the intimate fiber/matrix contact prior to final composite fabrication. Continuous fiber reinforced thermoplastic matrix pre-impregnated tapes (PCT´s) are, for example, produced by direct melting processes. Alternatively, intimate contact processes allow producing cheap and promising pre-impregnated materials, such as, commingled fibers, co-woven fabrics and powder coated towpregs.

Sometimes, thermoplastic compatibilizers were added to the matrices to improve their adhesion and facilitate impregnation to reinforcements [9].

2. Experimental

2.1 Raw materials

The following raw materials were used to produce CF/PP pre-impregnated materials for this work: i) a PP powder ICORENE 9184B P® and carbon fiber roving M30 SC® from the ICO Polymers and TORAY, respectively, were used to produce the CF/PP towpregs (Fig. 1a), ii) PP powder Moplen RP348U® from Basell and the carbon fiber roving already mentioned were used to manufacture the CF/PP tapes (Fig. 1b). Tables 1 and 2 present the properties of these raw-materials.

Some batches of CF/PP towpregs were also produced using PP powder (ICORENE 9184B P®) additivated with 1% in mass content of maleic anhydride, S 47 29608 707® from Merck Schuchardt OHG, in order to assess the possible enhancement of fiber/matrix adhesion [9-13].

Table 1. Properties of CF/PP towpregs raw-materials

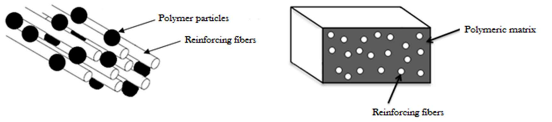
Property	PP powder (ICORENE 9184B P®)		Carbon fiber (TORAY M30 SC®)	
	Manufacturer datasheet	Experimental	Manufacturer datasheet	Typical values
Linear density (Tex)	-	-	760	-
Specific gravity (Mg/m^3)	0.91	0.91	1.73	1.75
Tensile strength (MPa)	30[1]	19[1]	5490	2600
Young Modulus (GPa)	1.3	0.98	294	170
Poisson´s ratio	-	0.21	-	-
Average powder particle size (µm)	440	163	-	-

[1] Yield Strength

Table 2. Properties of the raw-materials used to produce CF/PP tapes accordingly to manufacturers datasheets

Property	PP granules (Moplen RP348U® from Basell)	Carbon fiber roving (M30 SC® from TORAY)
Linear density (Tex)	-	760
Specific gravity (Mg/m3)	900	1.73
Tensile strength (MPa)	30[a]	5490
Young Modulus (GPa)	1.1	294

[a] Yield Strength



a) towpregs (PCT´s) b) Pre-consolidated tapes

Fig. 1. CF/PP pre-impregnated products under study.

2.2 Production of Thermoplastic Matrix Pre-Impregnated Products

2.2.1 Production of towpregs

The CF/PP towpregs were produced in a dry powder coating equipment schematically shown in Fig. 2 [14,15]. It consists of six main parts: wind-off system, fiber spreader unit, heating section, coating section, consolidation unit and a wind-up section. Initially, the reinforcing fibers are wound-off and pulled through a pneumatic spreader and then coated with polymer by heating in a convection oven and made to pass into a polymer powder vibrating bath. A gravity system allows maintaining the amount of polymer powder constant. The consolidation unit oven allows softening the polymer powder, promoting its adhesion to the fiber surface. Finally, the thermoplastic matrix towpreg is cooled down and wound-up on a spool.

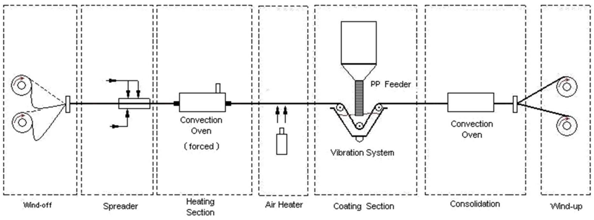


Fig. 2. Powder coating line setup.

2.2.2 Towpreg production optimization

In order to optimize the production of CF/PP powder coated towpregs, different processing variables combinations were experimented and the number of trials optimized using the Taguchi approach. The studied operational parameters were:

- heating oven temperature (600, 650 and 700 ºC);
- consolidation oven temperature (350, 400 and 450 ºC);
- linear pull speed (4, 6 and 8 m/min).

The Taguchi approach was applied to the towpregs production process in order to obtain the condition that maximizes polymer powder content.

The polymer mass fraction in the towpregs, ω_p, was determined by weighting towpreg strips produced in those different conditions, using the following equation:

$$\omega_p = \frac{W_t - W_f}{W_t} \qquad (1)$$

where W_t and W_f are the measured unit length weights of the towpreg strip and fiber roving, respectively.

Table 3 shows the used processing conditions and obtained results, according to the established design of experiments. The average polymer mass content in towpregs, established by the design of experiences was 34.5% (Table 3).

Table 3. Taguchi approach applied to towpregs manufacturing process

Experiments	Processing variables			Results:
	Heating oven temperature (ºC)	Consolidation furnace temperature (ºC)	Linear pulling speed (m/min)	Polymer mass fraction (%)
1	600	350	4	32.2
2	600	400	6	31.4
3	600	420	8	20.6
4	650	350	8	27.9
5	650	400	4	39.9
6	650	420	6	40.7
7	700	350	6	35.6
8	700	400	8	40.6
9	700	420	4	40.4
			Average	34.5

The mains effects of the processing variables on the results can be seen from Fig. 3.

The optimal condition obtained from Taguchi method application led to the following operating parameters selection: heating oven temperature and consolidation oven temperatures of 700 ºC and 400ºC respectively, and a linear pulling speed of 4 m/min. Using this optimal operative condition, the amount of polymer should increased up to 45.6%. However, the operative condition that has chosen as optimal had a line pull speed of 6 m/min allowing a high rate of production, lower processing problems and sufficiently levels of polymer content (40%, enough for the of use of towpregs in the pultrusion process). Also, the addition of 1% of maleic anhydride to the PP polymer had no influence on the towpreg polymer mass fraction.

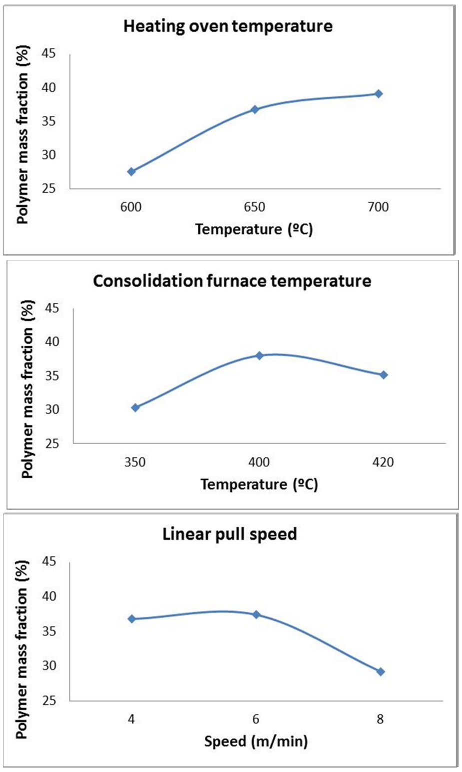


Fig. 3. Variation of towpreg polymer content with processing parameters

2.2.3 Production of pre-consolidate tapes (PCT)

The CF/PP PCT used in this work was produced in a cross-head extrusion equipment existing in our laboratories (see Fig. 4). The core of this technology is an impregnation unit where the carbon fibers are introduced, spread and impregnated by the polymer melt. Impregnation is achieved by pressurizing the molten polymer trapped between the unit's spreading elements and the fiber rovings.

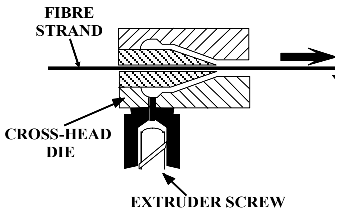


Fig. 4. Cross-head extrusion die.

The apparatus consists of a creel holding system for fiber rovings, a guidance unit allowing an adequate transport of fiber into the impregnation section, an extruder to melt and feed the molten polymer into the impregnation unit, the impregnation unit itself and, subsequently, a cooling unit, a puller, and a take-up device where the composite tape is collected [16]. Main properties of the PCTs produced by this way are given in Table 4.

Table 4. Overview of the main properties of the produced pre-consolidated tapes (PCT´s)

Property	**Description**
Fiber type	Carbon, 760 Tex
Filament diameter	5 µm
Fiber content	45 wt.%
Matrix type	Polypropylene (PP)
Tape width	25 mm
Tape linear density	14000 Tex

2.3 Processing of the pre-impregnated materials

The CF/PP pre-impregnated materials (towpregs and PCT's) were processed into composite bar profiles using a prototype pultrusion line [16, 17].

Our developed 10 kN pultrusion equipment, schematic depicted in Fig.5, consists in five main parts: i) an initial towpreg bobbins holding cabinet; ii) guiding system; iii) pultrusion head, that includes a pre-heating furnace and the pressurization/consolidation and cooling dies; iv) pulling system and, v) the final profile cutting system.

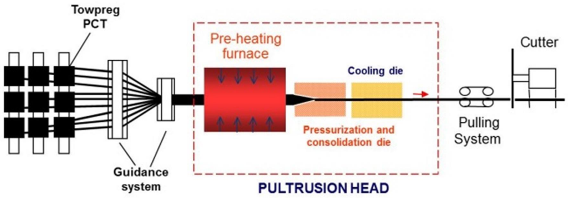


Fig. 5. Schematic diagram of the pultrusion line.

To produce composite profiles, the pre-impregnated materials are guided into the pre-heating furnace to be heated up to the required temperature. Then, they enter in the pultrusion die to be heated up and consolidated to the required size in its first zone and, after cooled down in order to solidify. The pultruded material is then cut into specified lengths.

A die with a cavity of 20 ×2 (mm) was used to produce a composite rectangular shaped bar.

2.3.1 Towpreg processing and optimization

Bar profiles were manufactured by pultrusion from different towpregs, using operating conditions in order to optimize the processing. The studied processing variables were:

-Furnace temperature (160 and 180 ºC);

-Heating die temperature (240 and 260 ºC);

-Linear pull-speed (0.2 and 0.3 m/min).

Results have shown that was not possible to produce in steady conditions pultruded profiles from towpregs at pultrusion speeds and consolidation die temperatures higher than 0.4 m/min and 260 ºC, respectively.

By using higher values in these two parameters the process became unsteady mainly due to reflux and accumulation of the thermoplastic polymer at the entrances of the consolidation and cooling dies, respectively.

Table 5 summarizes the flexural test results obtained with the studied processing conditions.

Table 5. Flexural testing results from towpregs

	Processing variables			**Flexural properties**	
Exper.	**Furnace temperature (ºC)**	**Heating die temperature (ºC)**	**Linear pulling speed (m/min)**	**Flexural modulus (GPa)**	**Flexural strength (MPa)**
1	160	240	0.2	86.7 ± 1.3	229.0 ± 7.3
2	180	240	0.2	79.5 ± 2.0	212.4 ± 12.6
3	160	260	0.2	91.0 ± 0.4	241.2 ± 1.6
4	180	260	0.2	85.1 ± 1.7	218.2 ± 9.1
5	160	240	0.3	82.1 ± 2.8	241.7 ± 13.1
6	180	240	0.3	87.5 ± 1.9	239.6 ± 13.3
7	160	260	0.3	85.0 ± 4.4	234.5 ± 11.5
8	180	260	0.3	83.7 ± 2.8	221.3 ± 7.1

The variation of the flexural modulus and strength with the selected processing parameters can be seen in Figures 6 and 7.

The optimal condition concerning flexural stiffness maximization obtained led to the following operating parameters selection: furnace and heated die oven temperatures of 160 ºC and 260ºC respectively, and a linear pulling speed of 0,2 m/min. For optimizing the flexural strength the obtained parameters combination was: furnace and heated die oven temperatures of 160 ºC and 240ºC respectively, and a linear pulling speed of 0.3 m/min.

It is possible observe that the furnace temperature of 160ºC lead to the better results. That could be explained by the lower polymer reflux on the entrance of the heated die. The optimal operating conditions to maximize both flexural proprieties (modulus and strength) were: furnace and heated die oven temperatures of 160 ºC and 260ºC respectively, and a linear pulling speed of 0.2 m/min.

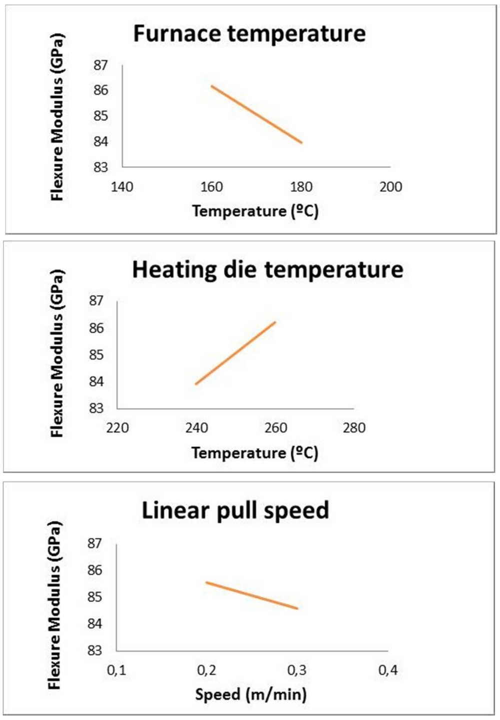


Fig. 6. Variation of the flexural modulus with the selected processing parameters.

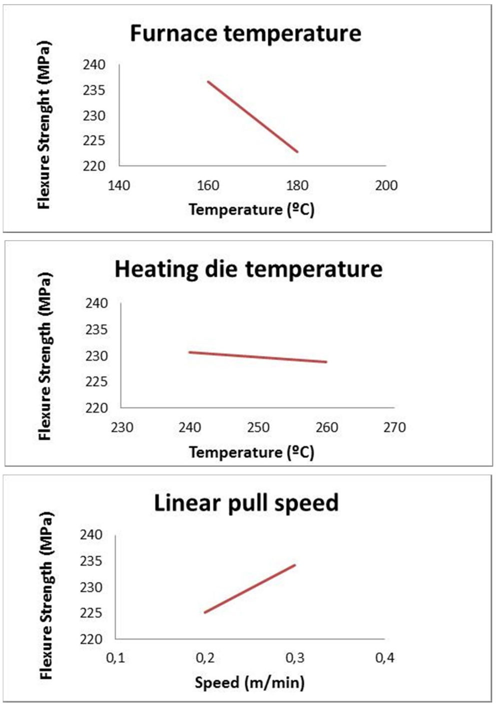


Fig. 7. Variation of the flexural strength with the selected processing parameters.

Finally, towpregs with additive were also pultruded into bars using the condition that optimizes both flexural properties and two more conditions (see Table 6).

Table 6. Flexural properties of towpregs with additive processed by pultrusion

Exper.	Processing variables			Flexural properties	
	Furnace temperature (ºC)	**Heating die temperature (ºC)**	**Linear pulling speed (m/min)**	**Flexural modulus (GPa)**	**Flexural strength (GPa)**
1	160	260	0,2	229.0 ± 7.3	87.6± 1,3
2	160	240	0,2	191.7 ± 7.8	70.4 ± 2.8
3	160	240	0,3	237.4 ± 11.8	80.5 ± 2.6

Table 7 shows the obtained results from flexural tests using towpreg pultruded bars with and without additive of maleic anhydride. It is possible to conclude that use of additive had no significant influence on the flexural properties.

Table 7. Flexural test results on towpreg bars with and without additive

Processing parameters		Flexural modulus (GPa)		Flexural strenght (GPa)	
		Without additive	**With additive**	**Without additive**	**With additive**
Furnace temperature (ºC)	160	90.1 ± 0.4	87.6 ± 1.3	241.2 ±1.6	229.0 ± 7.3
Heating die temperature (ºC)	260				
Linear pulling speed (m/min)	0,2				

2.3.2 Pre-consolidate tapes processing

CF/PP PCT were processed into composite bar profiles using the already mentioned pultrusion equipment die and the following typical operating conditions:

-Furnace temperature (160 ºC);
-Heating die temperature (260 ºC);
-Linear pull-speed (0.2 m/min).

2.4 Testing

2.4.1 Towpreg testing

Towpregs were characterized by scanning electron microscopy (SEM) and visual analysis.

Several CF/PP produced towpreg samples were analysed under a Nova NanoSEM 200 Scanning Electron Microscope to evaluate the adhesion of the polymer powder to the fibers and its distribution. Figure 8 show SEM micrographs of towpreg samples. As may be seen, a reasonable degree of adhesion between the carbon fibers and the polymer powder particles was obtained. Also, the polymer particles distribution on the fibers can be considered sufficient and eventually improved.

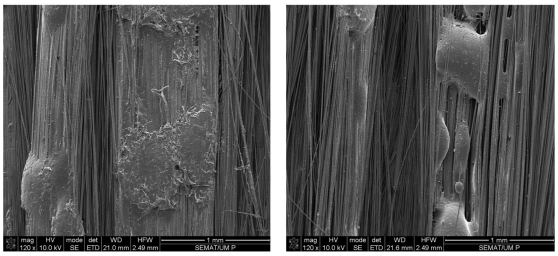


Fig. 8. Typical towpreg SEM micrographs (magnification of 120×).

2.4.2 Composites testing

Samples of pultruded bars were submitted to flexural, tensile, interlaminar and calcination tests according to the ISO standards 14125, 527, 14130 and 1172, respectively, and had their cross-sections studied under optical Microscopy (see Fig. 9). PCT's were also submitted to the same tests.

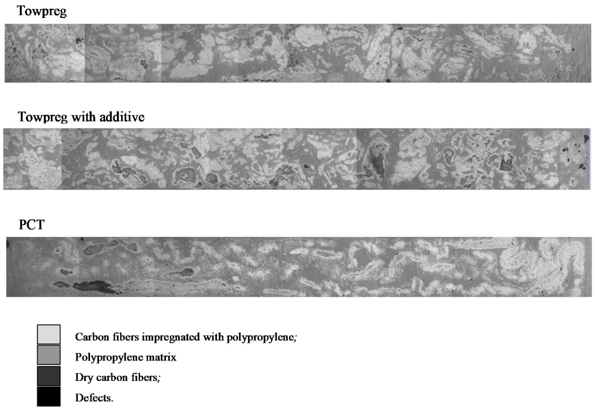


Fig. 9. Optical micrographs of the pultruded profiles cross-section (magnification of 8.75×).

The obtained mechanical properties were compared to the theoretical ones predicted by using the Rule of Mixtures (ROM).

2.4.3 Test results

Table 8 summarizes all experimentally obtained test results.

Table 8. Composite mechanical test results

Test Type	**Property**		***Pultrusion***		
			Towpreg	***Towpreg with addtive***	***PCT***
Flexural	Flexure Modulus (GPa)	Experimental	90.1±0.4	87.6±1.3	37.7±2.2
		Theoretical	85.7	85.5	54.0
	Flexure Modulus / Fiber volume fraction (GPa)		178.1±0.8	173.5±2.6	118.2±6.9
	Flexure Strength (MPa)	Experimental	241.2±1.6	229.0±7.3	158.7±4.2
		Theoretical	1311.0	1308.4	825.8
	Flexure Strength / Fiber volume fraction (MPa)		476.7±3.2	453.5±14.5	497.5±13.2
Tensile	Tensile Modulus (GPa)	Experimental	110.6±5.9	106.1±6.3	63.5±4.3
		Theoretical	85.7	85.5	54.0
	Tensile Modulus / Fiber volume fraction (GPa)		218.6±11.7	210.1±12.5	199.1±13.5
Inter-laminar Shear	Interlaminar Shear Strength (MPa)		12.3±0.3	13.0±0.4	14.0±0.2
Fiber volume fraction (%)			50.6	50.5	31.9

The tensile strength and modulus of the CF/PP plates, were predicted from the fibre and polymer properties using the well-known law of mixtures.

As can be seen from Table 8, experimental strength results are lower than those theoretically predicted. The experimental moduli obtained are in good agreement with the theoretical ones.

Conclusions

Obtained results allow concluding that all the pre-impregnated products studied in this work presented enough good properties for being employed in the major commercial engineering structural applications.

Composites processed from the PCTs demonstrated to have better mechanical strength than those produced from towpregs.

As can be seen from the Fig. 9, all profiles have a reasonable distribution of the reinforcing fibers over the cross-sections.

However, large differences in impregnation quality occur between the different samples that are likely to be related, directly, to the impregnation state of the semi-finished used on pultrusion. It may be seen that the impregnation quality of the PCT composite samples is good, presenting almost all fibers completely surrounded ('wet-out') by the polymer.

Only a few large dry spots were observed. This is most likely due to the good degree of impregnation already achieved in the PCT raw-material tape prior to the pultrusion step.

The samples of towpreg with additive show a higher quantity of dry zones than the ones without additive.

Finally, it may be noted that any of composites made from the towpregs and PCTs reached failure in the interlaminar shear tests. This fact reveals the high degree of ductility exhibited by these materials which may be relevant for many applications. Thus, the interlaminar shear strength results shown in Table 8 correspond to maximum force applied in the test.

The tests made using a proprietary pultrusion equipment already allow concluding being possible to produce in good conditions profiles from almost all commercial available thermoplastic matrix pre-impregnated raw-materials using pull speeds of 0.3 m/min.

It was possible to optimize the production of pultruded profiles and towpregs, through the use of Taguchi method, achieving optimal conditions.

The addition of the compatibilizing agent (1% maleic anhydride) did not improve the polymer mass content in towpregs and the mechanical properties on the final composites.

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5.5. Paper 3

20th International Conference on Composite Materials
Copenhagen, 19-24th July 2015

ADVANCES IN THERMOPLASTIC PULTRUDED COMPOSITES

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Keywords: Towpreg, Pultrusion, Thermoplastic Composites, Mechanical Properties

ABSTRACT

Pultrusion is a versatile continuous high speed production technology allowing the production of fibre reinforced complex profiles. Thermosetting resins are normally used as matrices in the production of structural constant cross section profiles.

Although only recently thermoplastic matrices have been used in long and continuous fibre reinforced composites replacing with success thermosetting matrices, the number of their applications is increasing due to their better ecological and mechanical performance. Composites with thermoplastic matrices offers increased fracture toughness, higher impact tolerance, short processing cycle time and excellent environmental stability. They are recyclable, post-formable and can be joined by welding. The use of long/continuous fibre reinforced thermoplastic matrix composites involves, however, great technological and scientific challenges since thermoplastics present much higher viscosity than thermosettings, which makes much difficult and complex the impregnation of reinforcements and consolidation tasks. [1]

In this work continuous fibres reinforced thermoplastic matrix towpregs were produced using equipment developed by the Institute for Polymers and Composites (IPC). The processing of the towpregs was made by pultrusion, in a developed prototype equipment existing in the Engineering School of the Polytechnic Institute of Porto (ISEP).

Different thermoplastic matrices and fibres raw-materials were used in this study to manufacture pultruded composites for commercial applications (glass and carbon fibre/ polypropylene) and for advanced markets (carbon fibre/Primospire®).

To improve the temperature distribution profile in heating die, different modifications were performed.

In order to optimize both processes, towpregs production and pultruded composites profiles were analysed to determine the influence of the most relevant processing parameters in the final properties. The final pultruded composite profiles were submitted to mechanical tests to obtain the relevant properties.

1 INTRODUCTION

During the last decades, composites have successfully replaced traditional materials in many engineering applications due to its excellent properties, mainly their excellent specific mechanical properties [1, 2].

Pultrusion is a continuous manufacturing process used to shape polymeric composite materials into parts with constant cross section. The reinforcement fibres in the form of continuous strands or mats are pulled through a guide plate and impregnated passing by a thermosetting resin bath.

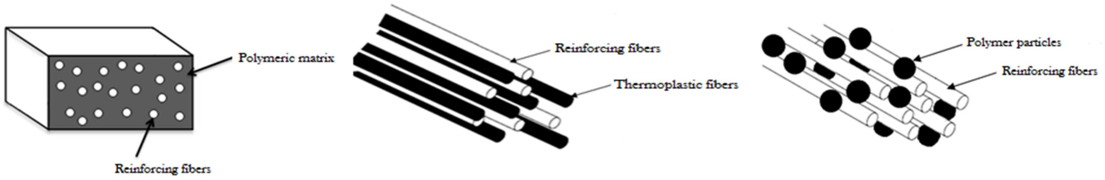
So far, almost all applications of pultrusion manufacturing technologies use thermosetting resins due to inherent difficulties associated with the use of thermoplastic matrices in this process. However, with recent developments, the use of preforms to facilitate impregnation, such as pre-consolidated tapes, commingled yarns and towpregs, allowed the thermoplastic pultrusion to gain a great interest [3].

Composites with thermoplastic matrices offers increased fracture toughness, higher impact tolerance, short processing cycle time and excellent environmental stability. They are recyclable, post-formable and can be joined by welding. The use of long/continuous fibre reinforced thermoplastic matrix composites involves, however, great technological and scientific challenges since thermoplastics present much higher viscosity than thermosettings, which makes much difficult and complex the impregnation of reinforcements and consolidation tasks [2,4-9].

Today, two major technologies are being used to allow wet reinforcing fibres with thermoplastic polymers [6-9]: i) the direct melting of the polymer and, ii) the intimate fiber/matrix contact prior to final composite fabrication. Continuous fibre reinforced thermoplastic matrix pre-impregnated tapes (PCT´s) are, for example, produced by direct melting processes. Alternatively, intimate contact processes allow producing cheap and promising pre-impregnated materials, such as, commingled fibres and powder coated towpregs (Figure 1).

Sometimes, thermoplastic compatibilizers were added to the matrices to improve their adhesion and facilitate impregnation to reinforcements [10].

Different raw-materials were used in the production of thermoplastic matrix pre-impregnated materials: those to be used in parts for highly demanding markets were based on carbon fibres and Primospire® and those for more commercial composites on carbon or glass fibres and polypropylene.



a) Pre-consolidate tapes (PCTs) b) Commingled fibres c) towpregs

Figure 1. Pre-impregnated products under study

2 Experimental

2.1 Raw Materials

The following raw materials were used to produce CF/PP pre-impregnated materials for this work: i) a PP powder ICORENE 9184B P® and carbon fibre roving M30 SC® from the ICO Polymers and TORAY, respectively, were used to produce the CF/PP towpregs, ii) PP powder Moplen RP348U® from Basell and the carbon fibre roving already mentioned were used to manufacture the CF/PP PCT tapes. On other hand, composite parts for highly demanding advanced markets were processed from towpregs manufactured by using a highly aromatic amorphous thermoplastic polymer in powder form, the PRIMOSPIRE® PR 120 from Solvay Advanced Polymers, and 760 Tex M30SC carbon fibre tows TORAY.

For the GF/PP towpregs, a 2400 Tex type E fibre rovings from Owens Corning and Icorene® 9184B P polypropylene from ICO Polymers France were used. Also, the GF/PP PCT tapes were manufactured with glass fibres (TufRov 4599) from PPG Industries and a polypropylene matrix (Moplen RP348U®) from Basell.

Commercial commingled GF/PP fibres TWINTEX® R PP 60 B 1870 FU from Owens Corning were also used in the production of pultrusion thermoplastic composite profiles, as reference of a current commercially available pre-impregnated product.

Some batches of CF/PP and GF/PP towpregs were also produced using PP powder (ICORENE 9184B P®) blended with 1% in mass content of maleic anhydride S 47 29608 707® from Merck Schuchardt OHG, in order to assess the possible enhancement of fibre/matrix adhesion [9-12].

Tables 1 and 2 summarise relevant properties of the polypropylene, glass and carbon fibres used in present work to produce pre-impregnated raw materials (towpregs and PCT´s). Table 3 shows the manufacturer datasheets properties of TWINTEX ®.

Table 1. Properties of Towpregs and PCT PP raw-materials

Property	**PP powder** (ICORENE 9184B P®)		**Primospire®**		**PP granules** (Moplen RP348U ®)
	Manufacturer datasheet	Experimental	Manufacturer datasheet	Experimental	Manufacturer datasheet
Specific gravity (Mg/m^3)	0.91	0.91	1.21	-	0.90
Tensile strength (MPa)	Yield Strength 30	Yield Strength 19	207	104	Yield Strength 30
Young Modulus (GPa)	1.3	0.98	8.3	8.0	1.1
Poisson´s ratio	-	0.21	-		-
Average powder particle size (µm)	440	163	-	139	-
Glass transition temperature (T_g)	Typical value 0-20	-	158	156	Typical value 0-20
Melting temperature (T_m)	Typical value 170	166	-	-	Typical value 170

Table 2. Properties of Towpregs and PCT fibres raw-materials

Property	**Glass fibre**			**Carbon fibre**	
	(305E-TYPE 30®)		(TufRov 4599®)	(TORAY M30 SC®)	
	Manufacturer datasheet	Experimental	Manufacturer datasheet	Manufacturer datasheet	Experimental
Linear density (Tex)	2400	-	2400	760	-
Specific gravity (Mg/m^3)	2.65	-	2.54-2.6	1.73	-
Tensile strength (MPa)	3500	1657	1900-2400	5490	2731
Young Modulus (GPa)	76	62.5	69-76	294	194.5
Average fibre diameter	17	13.7	17	5	7.37

Table 3. TWINTEX ® R PP 60 B 1870 FU from Owens Corning

Property	**Values**
Linear density (Tex)	1870
Tensile strength (MPa)	760
Young Modulus (GPa)	29.5
Fibre mass content (%)	60

2.2 Production of Thermoplastic Matrix Pre-Impregnated Products

The dry powder coating equipment used to produce fibre reinforced towpregs is schematically depicted in Figure 2 [13-15].

The pre-consolidated tapes (PCT´s) used in this work were produced in a cross-head extrusion equipment (see Figure 3) from our own laboratories [14].

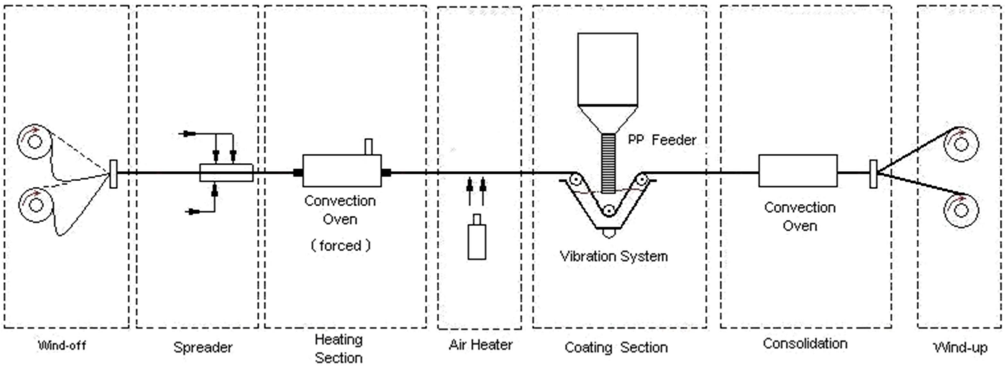


Figure 2. Powder coating line setup.

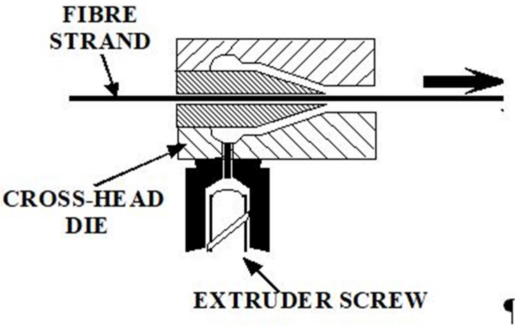


Figure 3. Cross-head extrusion die

2.2.1. CF/PP, CF/Primospire® and GF/PP towpregs production

In order to optimize the production of CF/PP powder coated towpregs, different processing variables combinations were experimented and the number of trials optimized using the Taguchi approach. The studied operational parameters were:

- heating oven temperature (600, 650 and 700 ºC); consolidation oven temperature (350, 400 and 450 ºC); linear pull speed (4, 6 and 8 m/min).

The optimal condition obtained led to the following operating parameters selection: heating oven temperature and consolidation oven temperatures of 700 ºC and 400ºC respectively, and a linear pulling speed of 4 m/min. However, the operative condition that was chosen as optimal had a line pull speed of 6 m/min allowing a high rate of production, lower processing problems and sufficiently levels of polymer mass content (40%, enough for the of use of towpregs in the pultrusion process).

To try maximizing the polymer powder content in the GF/PP towpregs the following processing conditions were varied within the next ranges: i) convective oven temperature (ºC): 650 - 700; ii) Consolidation furnace temperature (ºC): 350 – 450; iii) Coating line pulling speed (m/min): 4 – 6. From the polymer mass fractions obtained in produced towpreg strips it was possible to establish as optimal the following operating parameters: convective and consolidation oven temperatures of 700 ºC and 400ºC respectively, and a linear pulling speed of 6 m/min. In such operational conditions the GF/PP towpregs were continuously produced with polymer mass content of 30.7 %.

In order to produce CF/Primospire towpregs, the powder coating equipment was operated at different following woven temperatures and fibre linear pull speeds:

- heating oven temperature (700 ºC); consolidation oven temperature (500 - 550 ºC); linear pull speed (4 and 6 m/min). From such work the best values of the operational variables, which allow simultaneously producing towpregs in good and stable circumstances and having the maximum polymer powder content were:
- heating oven temperature - 700 ºC; consolidation oven temperature - 525 ºC and linear pull speed - 6 m/min. Using those conditions towpregs with a polymer mass content of aprox. 40% were produced.

2.3 Pultrusion of pre-impregnated materials

The towpregs, PCT's and commingled fibres were processed into composite bar profiles using the laboratorial pultrusion line, Figure 4 [15, 16].

To produce composite profiles, the pre-impregnated materials are guided into the pre-heating furnace to be heated up to the required temperature. Then, they enter in the pultrusion heated die to be heated and consolidated to the required size and, after cooled down in the cooling die to solidify.

In this work, it was designed and manufactured a die to allow producing a 20×2 mm2 bar-shaped profile.

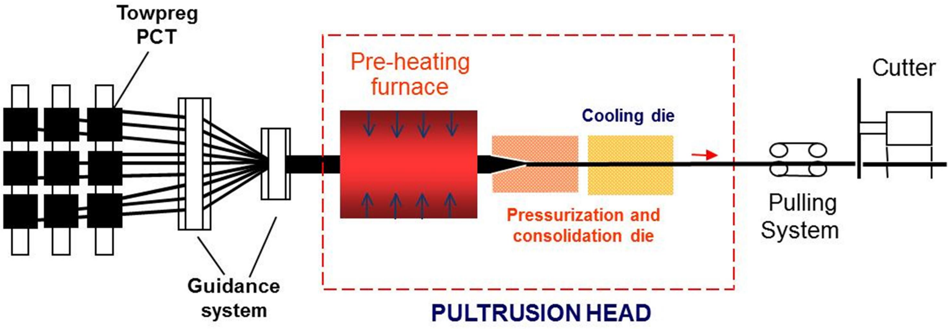
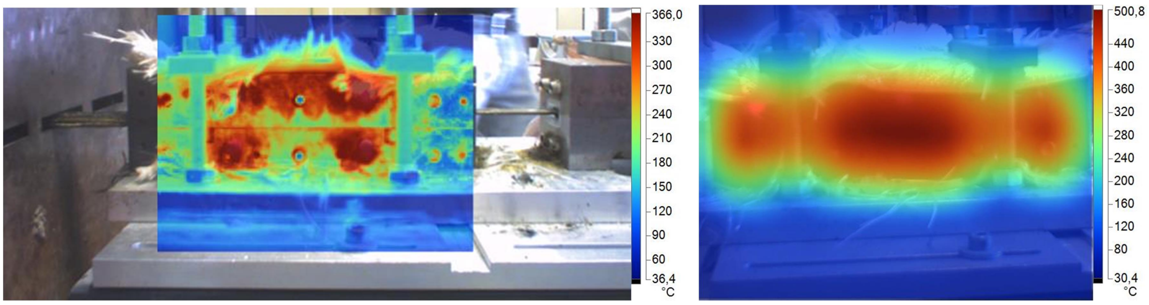


Figure 4. Schematic diagram of the pultrusion line

Those profiles were manufactured from different pre-impregnated materials, using operating conditions in order to optimize the processing. The heating elements were conveniently placed in the die improving the temperature distribution profile, as can be seen in Figure 5.



a) Initial temperature profile b) Improved temperature profile

Figure 5. Heated die temperatures distribution profiles

2.3.1 Towpreg processing

CF/PP towpregs were manufactured by pultrusion into composite bar profiles using the most relevant operating conditions. The Taguchi´s/DOE method was applied, maintaining the cooling die at 25 ºC, in order to optimize the processing parameters:

i) furnace temperature (160 or180 ºC); ii) heating die temperature (240 or 260 ºC); iii) linear pull-speed (0.2 or 0.3 m/min).

Results have shown that was not possible to produce, in steady, conditions pultruded profiles from towpregs at pultrusion speeds and consolidation die temperatures higher than 0.4 m/min and 260 ºC, respectively. By using higher values of these two parameters, the process became unsteady, mainly due to reflux and accumulation of the thermoplastic polymer at the entrances of the consolidation and cooling dies.

The found optimal operating conditions that maximize mechanical properties were: furnace and heated die oven temperatures of 160 ºC and 260ºC respectively, and a linear pulling speed of 0.2 m/min.

The CF/Primospire pultruded bars were produced in this work with the following operational conditions: i) furnace temperature (380 - 400 ºC); ii) heating die temperature (420 - 475 ºC); iii) linear pull-speed of 0.2 m/min.

To determine the best processing window for GF/PP towpregs, the main processing conditions were varied, maintaining the cooling die at 25 ºC: i) furnace temperature (ºC): 170 – 180; ii) heated die temperature (ºC): 240 – 300; iii) linear pulling speed (m/min): 0.2 - 0.4.

Results have shown that was not possible to produce, in steady conditions, profiles from towpregs at pultrusion speeds and heated die temperatures higher than 0.3 m/min and 280 ºC, respectively. By using higher values the process became unsteady as it was already found for CF/PP towpregs processing. Problems also occurred for temperatures below 270º C in the heated die.

It was concluded to use as optimal pultrusion operating window for GF/PP towpregs the following one: i) furnace temperature (ºC): 170 – 180; ii) heated die temperature (ºC): 280; iii) cooling die temperature (ºC): 25; iv) linear pulling speed (m/min): 0.2 - 0.3.

2.3.2 Pre-consolidate tapes(PCT´s) and Twintex® processing

PCT´s and Twintex® were processed into rectangular 20×2 (mm2) bar using the already mentioned pultrusion equipment being operating conditions shown in Table 4.

Table 4. Pultrusion processing parameters for PCT´s and Twintex®

Raw-material	Heated die temperature (ºC)	Cooled die temperature (ºC)	Furnace temperature (ºC)	Pulling speed (m/min)
CF/PP PCT	230	50	160	0.2
GF/PP PCT	230		170	
Twintex®	300		170	

2.4 Testing

Bar samples were submitted to flexural, tensile and interlaminar testing according to the ISO standards 14125, 527 and 14130, respectively.

The mechanical properties were compared to the theoretical ones predicted by using the Rule of Mixtures (ROM).

Tensile tests were conducted, according to ISO 527, in a 100 kN universal testing machine at the crosshead speed of 2 mm/min using 180×20×2 mm3 rectangular samples.

The tensile modulus was determined from the slope of the initial linear portion of the experimental stress/strain curve. A SG Shimadzu® 50 mm length strain-gauge was used up to 0.3% strain, for accurate determination of the tensile modulus.

Regarding the determination of tensile strength, it was not possible to proceed with the test until specimen failure due to grip slippage. Hence, new specimen geometry was designed and tested with good results (Figure 6).

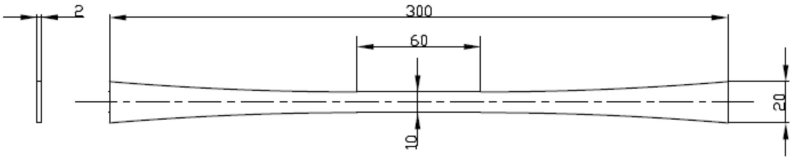


Figure 6. Geometry of the tensile test specimens

Three-point flexural tests were also conducted on five 100 × 20 × 2 (mm3) composite specimens, using 100 kN universal testing machine and a distance between supports of 80 mm, according to ISO 14125, at a crosshead speed of 1 mm/min.

Samples with dimensions of 20 × 20 × 2 (mm3), cut from composites processed from each pre-impregnated raw material, were submitted to interlaminar shear tests according to ISO 14130. The tests were conducted in a 50 kN universal testing machine by using an initial pre-load of 1 N at the crosshead speed of 1 mm/min and a 10 mm span between supports.

Carbon and glass fibre composites mass content was determined by using calcination tests according to the EN ISO 1172. Composite samples, weighting approximately 2 g, were submitted to calcination inside a crucible in a muffle furnace during 10 min at 625° C.

3 Results and Discussion

Tables 5, 6 and 7 summarize all experimentally results obtained from the CF/PP, CF/Primospire® and GF/PP composites processed by pultrusion from the pre-impregnated products under study. To better evaluate and compare the mechanical properties obtained on the composites processed from the different pre-impregnated products studied, tables also present theoretical expected values and relative values of specific properties.

As can be seen from Tables 5 and 6, the experimental moduli obtained from de CF/PP and GF/PP composites are in good agreement with the predicted theoretical ones. Some experimental values are even higher than the theoretical expected ones. This can be explained considering that the volume fraction content of some samples can be higher than the determined by the calcination tests.

Using the proposed new geometry (Figure 6) for the tensile test specimens, it was possible to reach breaking loads and therefore determine their tensile strengths.

Analysing Table 5, one can conclude that composites processed from the CF/PP PCT´s demonstrated to have better flexural and interlaminar shear strengths than those produced from CF/PP towpregs. Concerning the interlaminar shear tests, the CF/Primospire composites shown a much higher value than CF/PP probably due to the better mechanical properties that the Primospire matrix exhibits. As it may be seen and expected, the CF/Primospire® towpregs required the use of much higher temperatures than the CF/PP ones in pre-heating furnace and pressurization/consolidation die. Due to such higher temperatures, tests still continue being done to optimise the operational conditions and, consequently, the obtained mechanical properties.

From Table 6, it is possible to conclude that commingled fibres (TWINTEX®) presented, in general, better properties and had also shown to be more adjusted to commercial application demands and to be easily processed into final composites by the currently used manufacturing methods, probably because their easy consolidation.

In any case, worse flexural strength and modulus results were found in GF/PP towpreg and PCT pultruded composites, respectively. These lower results obtained in the flexural tests are probably consequence of the inferior degree of impregnation observed in the towpreg based composites and, in the case of PCT tape based composites, result from the higher rich polymer regions exhibited by this material in its outside layers.

Table 5. CF/PP composite mechanical test results

Test Type	Property		*Pultrusion*		
			Towpreg	***Towpreg with additive***	***PCT***
Flexural	Flexure Modulus (GPa)	Experimental	90.1±0.4	87.6±1.3	37.7±2.2
		Theoretical	98.9	98.7	62.7
	Flexure Modulus / Fibre volume fraction (GPa)		178.1±0.8	173.5±2.6	118.2±6.9
	Flexure Strength (MPa)	Experimental	241.2±1.6	229.0±7.3	158.7±4.2
	Flexure Strength / Fibre volume fraction (MPa)		476.7±3.2	453.5±14.5	497.5±13.2
Tensile	Tensile Modulus (GPa)	Experimental	110.6±5.9	106.1±6.3	63.5±4.3
		Theoretical	98.9	98.7	62.7
	Tensile Modulus / Fibre volume fraction (GPa)		218.6±11.7	210.1±12.5	199.1±13.5
	Tensile Strength (MPa)	Experimental	1060.8±43.1	1129.3±34.6	636.9±38.4
	Tensile Strength / Fibre volume fraction (MPa)		2096.4±85.2	2236.2±68.5	1996.6±120.4
Interlaminar Shear	Interlaminar Shear Strength (MPa)		12.3±0.3	13.0±0.4	14.0±0.2
Fibre volume fraction (%)			50.6	50.5	31.9

Table 6. Test results on the processed GF/PP composites

Test Type	Property		*Pultrusion*		
			Commingled fibres	***Towpregs***	***PCT***
Flexural	Flexure Modulus (GPa)	Experimental	26.2±2.0	28.6±0.9	16.8±1.5
		Theoretical	23.8	33.1	19.1
	Flexure Modulus / Fibre volume fraction (GPa)		70.6±5.4	54.9±1.7	56.0±5.0
	Flexure Strength (MPa)	Experimental	595.0±24	158.0±12.3	329.0±30
	Flexure Strength / Fibre volume fraction (MPa)		1603.8±64.7	303.3±23.6	1096.7±100
Tensile	Tensile Modulus (GPa)	Experimental	24.9±1.1	33.9±1.5	21.4±1.5
		Theoretical	23.8	33.1	19.1
	Tensile Modulus / Fibre volume fraction (GPa)		67.1±3.0	63.5±2.9	71.3±5.0
	Tensile Strength (MPa)	Experimental	545.9±31.7	>336.3±22.3	355.8±53.2
	Tensile Strength / Fibre volume fraction (MPa)		1471.4±85.4	>645.5±42.8	1186.0±177.3
Interlaminar Shear	Interlaminar Shear Strength (MPa)		26.8±1.7	7.5±0.1	27.8±0.6
Fibre volume fraction (%)			37.1	52.1	30.0

Table 7. Test results on the processed CF/Primospire® composites

Test Type	***Property***	***Pultrusion***
		Towpreg FC/Primospire
Flexural	Flexure Modulus (GPa)	56.1±2.9
	Flexure Strength (MPa)	253.6±16.1
Tensile	Tensile Modulus (GPa)	92.2±5.6
	Tensile Strength (MPa)	839.2±28.7
Inter-laminar Shear	Interlaminar Shear Strength (MPa)	25.4±2.1
Fibre volume fraction (%)		~ 45%

Nevertheless, the GF/PP pre-impregnated products produced in our laboratories (towpregs and PCTs) have already demonstrated very good mechanical behaviour, namely, in terms of stiffness. In fact, the composites manufactured from these products presented experimental moduli values very closed to the theoretical expected ones. While composites processed from the PCTs demonstrated to have better mechanical strength, those produced from towpregs presented higher moduli. As mechanical strength values are more affected by small defects than those from moduli, the composites manufactured from PCTs seem to profit from the pre-consolidate state already presented by this product before final processing. Finally, it may be noted that any of composites made from pre-impregnated materials under study reached failure in the interlaminar shear tests. This fact reveals the high degree of ductility exhibited by these materials which may be relevant for many applications. Thus, the interlaminar shear strength results shown in Tables 5 and 6 correspond to maximum force applied in the test.

4 Conclusions

The tests made using a proprietary pultrusion equipment already allow to conclude that is possible to produce, in good conditions, profiles from almost all available thermoplastic matrix pre-impregnated raw-materials using pull speeds of 0.3 m/min.

Existing powder-coating equipment was shown to be suitable to produce CF/PP, CF/Primospire® and GF/PP towpregs that could be adequately processed into pultruded profiles. From the tests made, the towpregs can be easily and continuously produced at industrial production speeds between 2 a 8 m/min.

It was possible to optimize the production of CF/PP pultruded profiles and CF/PP towpregs, through the use of Taguchi/DOE method, achieving optimal conditions.

A process window was established for the production of PCT´s and towpregs and for the pultrusion of towpregs, PCT's and commingled fibres.

The mechanical properties of the composites processed from all those three GF/PP pre-impregnated were determined and evaluated. All of them demonstrated to have mechanical properties compatible with the requirements of the major current structural engineering applications. In general, commingled fibres TWINTEX® presented slight better mechanical properties and have shown to be more adjusted for composite processing than the other pre-impregnated products.

In particular, very good agreement was found between the experimental moduli values of all composites produced and the theoretical ones.

More research must be done in order to increase the processing speeds of CF/PP, CF/Primospire® and GF/PP towpregs as well as PCT's and to improve the impregnation, uniformity and dispersion of raw-materials in the composites.

CF/Primospire® composites showed a higher value for the interlaminar strength than all other ones. Due to higher processing temperatures, further tests should be done to optimise the operational conditions and further improve the obtained composite mechanical properties.

The mechanical properties obtained in all pultruded composites allow predicting their adequate use either in general or structural engineering applications.

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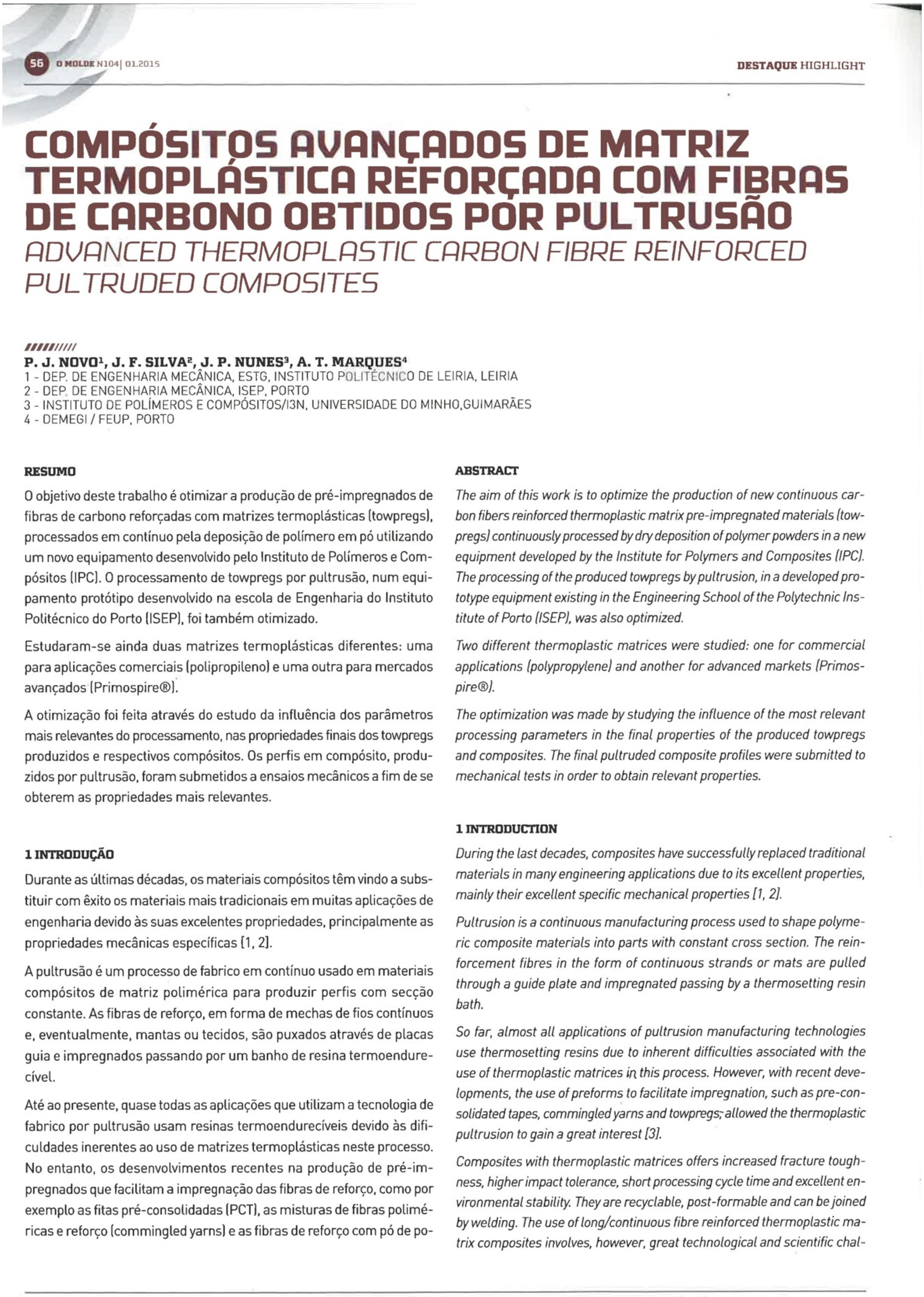
5.6. Paper 4



COMPÓSITOS AVANÇADOS DE MATRIZ TERMOPLÁSTICA REFORÇADA COM FIBRAS DE CARBONO OBTIDOS POR PULTRUSÃO

ADVANCED THERMOPLASTIC CARBON FIBRE REINFORCED PULTRUDED COMPOSITES

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RESUMO

O objetivo deste trabalho é otimizar a produção de pré-impregnados de fibras de carbono reforçadas com matrizes termoplásticas (towpregs), processados em contínuo pela deposição de polímero em pó utilizando um novo equipamento desenvolvido pelo Instituto de Polímeros e Compósitos (IPC). O processamento de towpregs por pultrusão, num equipamento protótipo desenvolvido na escola de Engenharia do Instituto Politécnico do Porto (ISEP), foi também otimizado.

Estudaram-se ainda duas matrizes termoplásticas diferentes: uma para aplicações comerciais (polipropileno) e uma outra para mercados avançados (Primospire®).

A otimização foi feita através do estudo da influência dos parâmetros mais relevantes do processamento, nas propriedades finais dos towpregs produzidos e respectivos compósitos. Os perfis em compósito, produzidos por pultrusão, foram submetidos a ensaios mecânicos a fim de se obterem as propriedades mais relevantes.

1 INTRODUÇÃO

Durante as últimas décadas, os materiais compósitos têm vindo a substituir com êxito os materiais mais tradicionais em muitas aplicações de engenharia devido às suas excelentes propriedades, principalmente as propriedades mecânicas específicas [1, 2].

A pultrusão é um processo de fabrico em contínuo usado em materiais compósitos de matriz polimérica para produzir perfis com secção constante. As fibras de reforço, em forma de mechas de fios contínuos e, eventualmente, mantas ou tecidos, são puxados através de placas guia e impregnados passando por um banho de resina termoendurecível.

Até ao presente, quase todas as aplicações que utilizam a tecnologia de fabrico por pultrusão usam resinas termoendurecíveis devido às dificuldades inerentes ao uso de matrizes termoplásticas neste processo. No entanto, os desenvolvimentos recentes na produção de pré-impregnados que facilitam a impregnação das fibras de reforço, como por exemplo as fitas pré-consolidadas (PCT), as misturas de fibras poliméricas e reforço (commingled yarns) e as fibras de reforço com pó de po-

ABSTRACT

The aim of this work is to optimize the production of new continuous carbon fibers reinforced thermoplastic matrix pre-impregnated materials (towpregs) continuously processed by dry deposition of polymer powders in a new equipment developed by the Institute for Polymers and Composites (IPC). The processing of the produced towpregs by pultrusion, in a developed prototype equipment existing in the Engineering School of the Polytechnic Institute of Porto (ISEP), was also optimized.

Two different thermoplastic matrices were studied: one for commercial applications (polypropylene) and another for advanced markets (Primospire®).

The optimization was made by studying the influence of the most relevant processing parameters in the final properties of the produced towpregs and composites. The final pultruded composite profiles were submitted to mechanical tests in order to obtain relevant properties.

1 INTRODUCTION

During the last decades, composites have successfully replaced traditional materials in many engineering applications due to its excellent properties, mainly their excellent specific mechanical properties [1, 2].

Pultrusion is a continuous manufacturing process used to shape polymeric composite materials into parts with constant cross section. The reinforcement fibres in the form of continuous strands or mats are pulled through a guide plate and impregnated passing by a thermosetting resin bath.

So far, almost all applications of pultrusion manufacturing technologies use thermosetting resins due to inherent difficulties associated with the use of thermoplastic matrices in this process. However, with recent developments, the use of preforms to facilitate impregnation, such as pre-consolidated tapes, commingled yarns and towpregs, allowed the thermoplastic pultrusion to gain a great interest [3].

Composites with thermoplastic matrices offers increased fracture toughness, higher impact tolerance, short processing cycle time and excellent environmental stability. They are recyclable, post-formable and can be joined by welding. The use of long/continuous fibre reinforced thermoplastic matrix composites involves, however, great technological and scientific chal-

Tabela 1. Propriedades das matérias-primas usadas nos towpregs

Propriedades	PP em pó (ICORENE 9184B P®)		Primospire ®		Fibra de carbono (TORAY M30 SC ®)	
	Informação do fornecedor	Experimental	Informação do fornecedor	Experimental	Informação do fornecedor	Experimental
Densidade linear (Tex)	-	-	-	-	760	-
Peso específico (Mg/m^3)	0.91	0.91	1.21	-	1.73	-
Tensão de rotura (MPa)	Tensão de cedência 30	Tensão de cedência 19	207	104.0	5490	2731^a
Módulo de Young (GPa)	1.3	0.98	8.3	8.0	294	194,5
Coeficiente de Poisson	-	0.21	-	-	-	-
Tamanho médio das partículas de pó (μm)	440	163	-	139	-	-
Temperatura de transição vítrea (T_g)	-	-	158	156	-	-
Temperatura de fusão (T_m)	Valor típico 170	166	-	-	-	-
Diâmetro médio das fibras (μm)	-	-	-	-	5	7,37

a - obtido de [illegible] de fibras longas

Table 1 - Properties of towpregs raw-materials

Property	PP powder (ICORENE 9184B P®)		Primospire ®		Carbon fiber (TORAY M30 SC ®)	
	Manufacturer datasheet	Experimental	Manufacturer datasheet	Experimental	Manufacturer datasheet	Experimental
Linear density (Tex)	-	-	-	-	760	-
Specific gravity (Mg/m^3)	0.91	0.91	1.21	-	1.73	-
Tensile strength (MPa)	Yield Strength 30	Yield Strength 19	207	104.0	5490	2731
Young Modulus (GPa)	1.3	0.98	8.3	8.0	294	194,5
Poisson's ratio	-	0.21	-	-	-	-
Average powder particle size (μm)	440	163	-	139	-	-
Glass transition temperature (T_g)	-	-	158	156	-	-
Melting temperature (T_m)	Typical value 170	166	-	-	-	-
Average fiber diameter	-	-	-	-	-	7,37

límero (towpregs), têm permitido que a pultrusão com matrizes termoplásticas ganhe um interesse crescente [3].

Os compósitos com matrizes termoplásticas apresentam elevada tenacidade à fratura, maior tolerância ao dano, tempo de ciclo mais reduzido e excelente resistência em meios corrosivos. Estes compósitos são recicláveis, re-processáveis e podem ser facilmente ligados por soldadura.

A utilização de compósitos de matriz termoplástica reforçada com fibras longas ou contínuas envolve, no entanto, grandes desafios tecnológicos e científicos pois as matrizes termoplásticas apresentam muito maior viscosidade que as termoendurecíveis, tornando muito difícil e complexa a impregnação do reforço e as tarefas de consolidação [2,4-9].

Atualmente, as duas principais tecnologias que estão a ser usadas para permitir a adesão do polímero termoplástico às fibras de reforço [6-9], são: i) a fusão direta do polímero e, ii) a mistura de fibras de reforço e de polímero termoplástico antes da fabricação do compósito final. Alternativamente, estes últimos processos permitem a produção de materiais pré-impregnados mais baratos e promissores, tais como, commingled yarns, tecidos e towpregs.

Por vezes, para melhorar a adesão dos reforços às matrizes e facilitar a sua impregnação são adicionados a estas compatibilizadores termoplásticos [10].

Neste trabalho utilizaram-se duas matérias-primas na produção de towpregs de matriz termoplástica: fibras de carbono e Primospire®, para mercados altamente exigentes e fibras de carbono e polipropileno para mercados mais comerciais.

2 PARTE EXPERIMENTAL

2.1 MATÉRIAS-PRIMAS

Neste trabalho, para mercados comerciais os pré-impregnados de FC/PP produzidos (towpregs) utilizaram as seguintes matérias-primas: i) pó de PP ICORENE 9184B P® e mechas de fibras de carbono M30 SC® fornecidos pela ICO polymers e TORAY, respetivamente (Fig. 1), ii) pó de PP (ICORENE 9184B P ®) com 1% de teor em massa de anidrido maleico S 47 29608 707® da Merck Schuchardt OHG, a fim de avaliar a possibibildade de melhoria da adesão entre a fibra e a matriz [10-14].

lenges since thermoplastics present much higher viscosity than thermosettings, which makes much difficult and complex the impregnation of reinforcements and consolidation tasks [2,4-9].

Today, two major technologies are being used to allow wet reinforcing fibres with thermoplastic polymers [6-9]: i) the direct melting of the polymer and, ii) the intimate fibre/matrix contact prior to final composite fabrication. Alternatively, intimate contact processes allow the production of cheap and promising pre-impregnated materials, such as, commingled fibres, co-woven fabrics and powder coated towpregs.

Sometimes, thermoplastic compatibilizers were added to the matrices to improve their adhesion and facilitate impregnation to reinforcements [10].

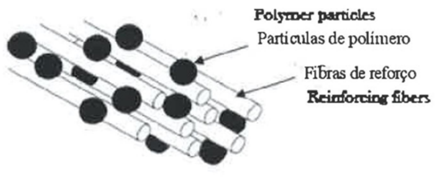
In this work two different raw-materials were used in the production of the thermoplastic matrix towpregs, those to be used in parts for highly demanding markets were based on carbon fibres and Primospire® and those for more commercial composites on carbon fibre and polypropylene.

2 EXPERIMENTAL

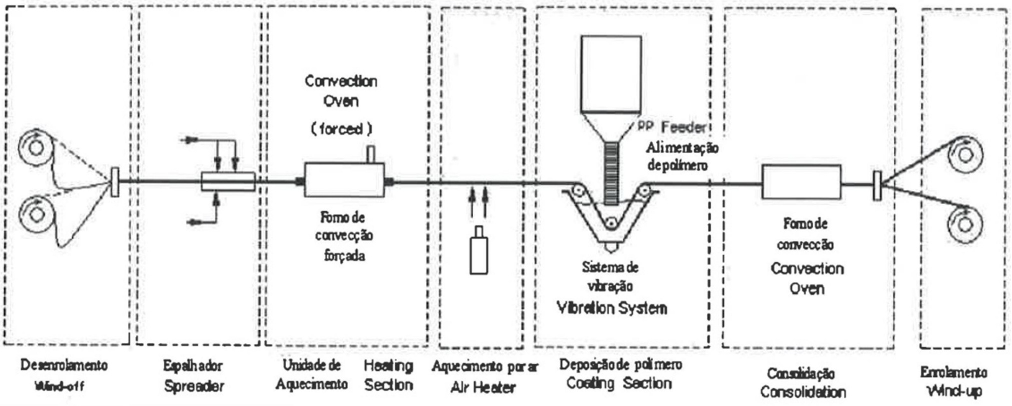
2.1 RAW-MATERIALS

The following raw materials were used to produce CF/PP pre-impregnated materials for this work, for commercial markets: i) a PP powder ICORENE 9184B P® and carbon fibre roving M30 SC® from the ICO Polymers and TORAY, respectively, were used to produce the CF/PP towpregs (Fig. 1), ii) Some batches of CF/PP towpregs were also produced using PP powder (ICORENE 9184B P®) with 1% in mass content of maleic anhydride additive, S 47 29608 707® from Merck Schuchardt OHG, in order to assess the possible enhancement of fibre/matrix adhesion [10-14].

On other hand, composite parts for highly demanding advanced markets



F1 - Towpregs de FC/PP e FC/Primospire.
CF/PP and CF/Primospire pre-impregnated products.



F2 – Esquema da linha de deposição de polímero em pó.
Powder coating line setup.

Por outro lado, foram processados a partir dos towpregs fabricados, peças em material compósito para mercados avançados de elevado desempenho, utilizando um polímero termoplástico amorfo altamente aromático em forma de pó, o PRIMOSPIRE ® PR 120 fornecido pela Solvay Advanced Polymers e mechas de fibras de carbono 760 Tex M30SC fornecidas pela TORAY. A tabela 1 apresenta as propriedades mais relevantes das matérias-primas utilizadas.

2.2 PRODUCÃO DE TOWPREGS

Os towpregs foram produzidos utilizando um equipamento de deposição de polímero seco em pó, esquematicamente representado na Fig. 2 [14,15]. Esta máquina é composta por seis partes principais: sistema de desenrolamento, espalhador de fibras, unidade de aquecimento, secção de deposição de polímero, unidade de consolidação e sistema de enrolamento. Inicialmente, as fibras de reforço são desenroladas e puxadas atravessando um espalhador pneumático, sendo posteriormente revestidas com polímero através do aquecimento das fibras num forno de convecção, fazendo-as passar num banho em vibração de polímero seco em pó. Um sistema de gravidade possibilita manter, no banho, uma quantidade constante de polímero. O forno da unidade de consolidação permite amolecer o polímero em pó, melhorando a sua adesão à superfície da fibra. Finalmente, o towpreg é arrefecido e enrolado numa bobine.

were processed from towpregs manufactured by using a highly aromatic amorphous thermoplastic polymer in powder form, the PRI-MOSPIRE® PR 120 from Solvay Advanced Polymers, and 760 Tex M30SC carbon fibre tows from TORAY. Table 1 presents the most relevant proper-ties determined for these raw materials.

2.2 PRODUCTION OF TOWPREGS

Towpregs were produced in a dry powder coating equipment schematically shown in Fig. 2 [14,15]. It consists of six main parts: wind-off system, fiber spreader unit, heating section, coating section, consolidation unit and a wind-up section. Initially, the reinforcing fibers are wound off and pulled through a pneumatic spreader and then coated with polymer by heating in a convection oven and made to pass into a polymer powder vibrating bath. A gravity system allows maintaining the amount of polymer powder constant. The consolidation unit oven allows softening the polymer powder, promoting its adhesion to the fiber surface. Finally, the thermoplastic matrix towpreg is cooled down and wound-up on a spool.

2.3 TOWPREG CF/PP PRODUCTION OPTIMIZATION

In order to optimize the production of CF/PP powder coated towpregs, different processing variables combinations were experimented and the number of trials optimized using the Taguchi approach. The studied operational parameters were:

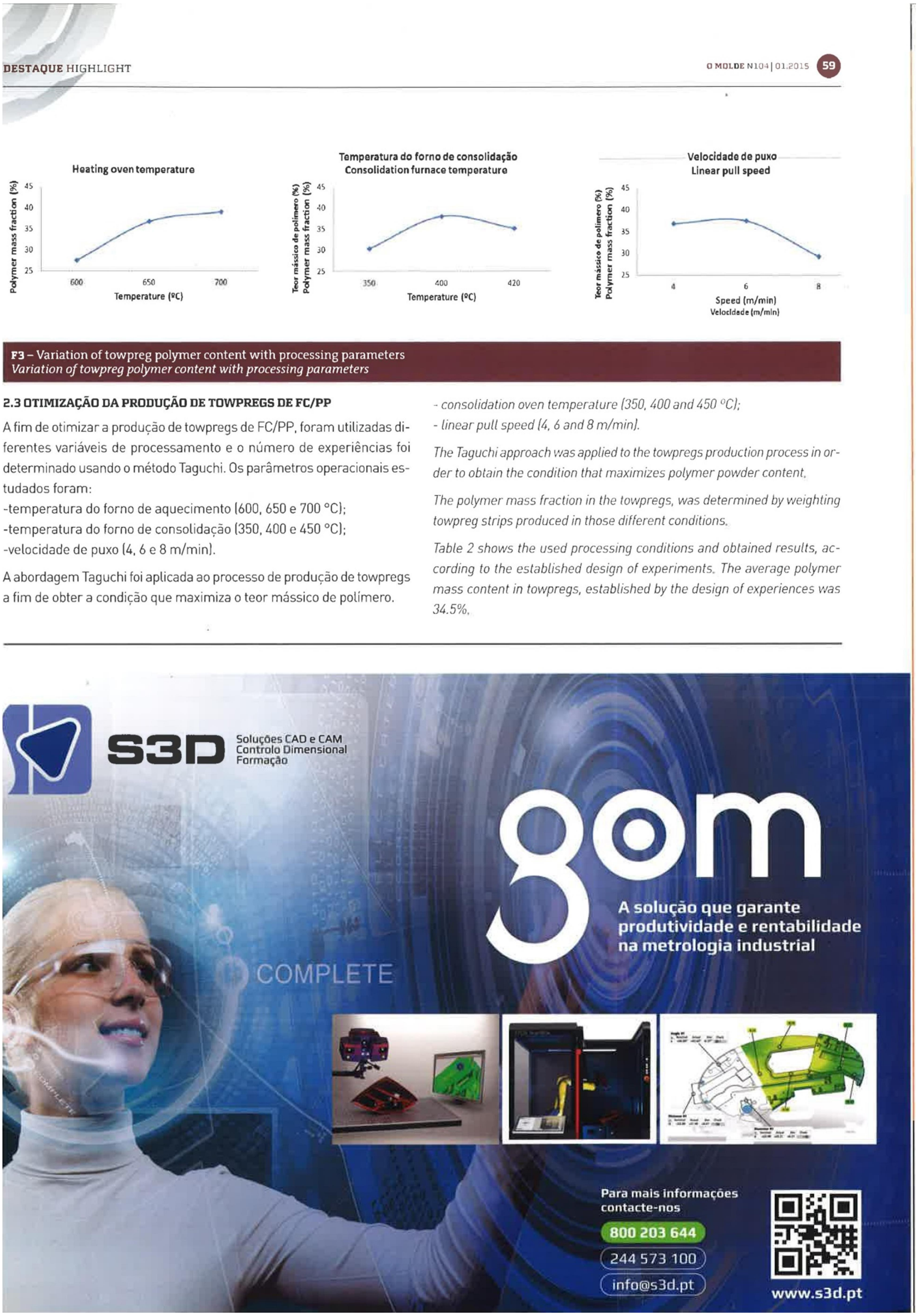
- heating oven temperature (600, 650 and 700 °C);

Tabela 2 – Método Taguchi aplicado ao processo de fabrico de towpregs

	Variáveis de processo			Resultados
Experiências	Temperatura do forno de aquecimento (°C)	Temperatura do forno de consolidação (°C)	Velocidade de puxo (m/min)	Fração mássica de polimero (%)
1	600	350	4	32.2
2	600	400	6	31.4
3	600	420	8	20.6
4	650	350	8	27.9
5	650	400	4	39.9
6	650	420	6	40.7
7	700	350	6	35.6
8	700	400	8	40.6
9	700	420	4	40.4
			Média	34.5

Table 2 – Taguchi approach applied to towpregs manufacturing process

	Processing variables			Results :
Experiments	Heating oven temperature (°C)	Consolidation furnace temperature (°C)	Linear pulling speed (m/min)	Polymer mass fraction (%)
1	600	350	4	32.2
2	600	400	6	31.4
3	600	420	8	20.6
4	650	350	8	27.9
5	650	400	4	39.9
6	650	420	6	40.7
7	700	350	6	35.6
8	700	400	8	40.6
9	700	420	4	40.4
			Average	34.5



F3 – Variation of towpreg polymer content with processing parameters
Variation of towpreg polymer content with processing parameters

2.3 OTIMIZAÇÃO DA PRODUÇÃO DE TOWPREGS DE FC/PP

A fim de otimizar a produção de towpregs de FC/PP, foram utilizadas diferentes variáveis de processamento e o número de experiências foi determinado usando o método Taguchi. Os parâmetros operacionais estudados foram:

-temperatura do forno de aquecimento (600, 650 e 700 °C);
-temperatura do forno de consolidação (350, 400 e 450 °C);
-velocidade de puxo (4, 6 e 8 m/min).

A abordagem Taguchi foi aplicada ao processo de produção de towpregs a fim de obter a condição que maximiza o teor mássico de polímero.

- consolidation oven temperature (350, 400 and 450 °C);
- linear pull speed (4, 6 and 8 m/min).

The Taguchi approach was applied to the towpregs production process in order to obtain the condition that maximizes polymer powder content.

The polymer mass fraction in the towpregs, was determined by weighting towpreg strips produced in those different conditions.

Table 2 shows the used processing conditions and obtained results, according to the established design of experiments. The average polymer mass content in towpregs, established by the design of experiences was 34.5%.

Tabela 3 - As melhores condições operatórias para produzir towpregs usados em compósitos destinados a mercados avançados

Variáveis de processamento	Unidades	Valores
		Towpregs de FC/Primospire ®
Temperatura do forno de aquecimento	°C	700
Temperatura do forno de consolidação	°C	500-550
Velocidade de puxo	m/min	4-6

A fração mássica de polímero nos towpregs foi obtida pela determinação da massa de segmentos de towpregs produzidos em diferentes condições.

A tabela 2 mostra as condições de processamento utilizadas e os resultados obtidos, de acordo com o desenho de experiências estabelecido. A média do teor mássico de polímero nos towpregs foi 34,5%.

Os principais efeitos das variáveis de processamento nos resultados obtidos podem ser vistos na Fig. 3.

A condição ótima obtida a partir da aplicação do método Taguchi conduziu à seguinte seleção de parâmetros operacionais: temperatura do forno aquecimento e temperatura de forno de consolidação de 700°C e 400 °C, respetivamente e uma velocidade de puxo de 4 m/min. Usando esta condição operacional ótima, a quantidade de polímero deveria aumentar até 45,6%. No entanto, a condição operativa que foi escolhida como ótima tinha uma velocidade de puxo de 6 m/min, permitindo assim uma alta taxa de produção, menores problemas de processamento e níveis suficientes de teores mássicos de polímero (40%, é suficiente nos towpregs a serem utilizados no processo de pultrusão). Além disso, a adição de 1% de anidrido maleico ao PP não teve nenhuma influência sobre a fração mássica de polímero no towpreg.

2.4 PRODUÇÃO DE TOWPREGS DE FC/ PRIMOSPIRE®

No sentido de produzir towpregs de FC/Primospire, o equipamento de deposição de polímero em pó foi operado com diferentes temperaturas dos fornos e velocidades de puxo (ver tabela 3). Deste trabalho, os melhores valores das variáveis operacionais que permitiram simultaneamente produzir towpregs em condições estáveis e que maximizaram o

Table 3 - Best conditions to produce towpregs used in composites for advanced markets.

Variable	Units	Values
		CF/Primospire ® towpregs
Convective oven temperature	°C	700
Consolidation furnace temperature	°C	500-550
Coating line pulling speed	m/min	4-6

The mains effects of the processing variables on the results can be seen from Fig. 3.

The optimal condition obtained from Taguchi method application led to the following operating parameters selection: heating oven temperature and consolidation oven temperatures of 700 °C and 400°C respectively, and a linear pulling speed of 4 m/min. Using this optimal operative condition, the amount of polymer should increase up to 45.6%. However, the operative condition that has chosen as optimal had a line pull speed of 6 m/min allowing a high rate of production, lower processing problems and sufficiently levels of polymer content (40%, enough for the of use of towpregs in the pultrusion process). Also, the addition of 1% of maleic anhydride to the PP polymer had no influence on the towpreg polymer mass fraction.

2.4 TOWPREG CF/ PRIMOSPIRE® PRODUCTION

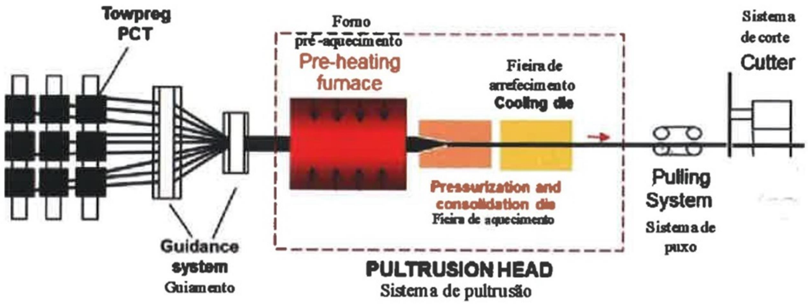
In order to produce CF/Primospire towpregs, the powder coating equipment was operated at different woven temperatures and fibre linear pull speeds (see Table 3). From such work the best values of the operational variables, which allow simultaneously producing towpregs in good and stable circumstances and having the maximum polymer powder content were:

- *heating oven temperature - 700 °C;*
- *consolidation oven temperature - 525 °C;*
- *linear pull speed - 6 m/min.*

Using those conditions towpregs with a polymer mass content of aprox. 40% were produced.

2.5 PRE-IMPREGNATED MATERIALS PROCESSING

Towpregs were processed into composite bar profiles using a 10 kN proto-



F4 - Esquema de uma linha de pultrusão.
Schematic diagram of the pultrusion line.

Tabela 4 – Resultados do ensaio de flexão dos perfis produzidos obtidos a partir de towpregs FC/PP

Experiências	Variáveis de processamento			Propriedades de flexão	
	Temperatura do forno de pré-aquecimento (°C)	Temperatura da fieira de aquecimento (°C)	Velocidade de puxo (m/min)	Módulo à flexão (GPa)	Tensão de rotura (MPa)
1	160	240	0.2	86.7 ± 1.3	229.0 ± 7.3
2	180	240	0.2	79.5 ± 2.0	212.4 ± 12.6
3	160	260	0.2	91.0 ± 0.4	241.2 ± 1.6
4	180	260	0.2	85.1 ± 1.7	218.2 ± 9.1
5	160	240	0.3	82.1 ± 2.8	241.7 ± 13.1
6	180	240	0.3	87.5 ± 1.9	239.6 ± 13.3
7	160	260	0.3	85.0 ± 4.4	234.5 ± 11.5
8	180	260	0.3	83.7 ± 2.8	221.3 ± 7.1

teor mássico de polímero, foram:

-temperatura do forno de aquecimento - 700 °C;
-temperatura do forno de consolidação - 525 °C;
-velocidade de puxo - 6 m/min.

Usando essas condições foram produzidos towpregs com um teor mássico de polímero de aproximadamente 40%.

2.5 PROCESSAMENTO DE MATERIAIS PRÉ-IMPREGNADOS

Os towpregs foram processados em perfis em material compósito num equipamento protótipo de pultrusão de 10kN [16, 17], esquematicamente representado na Fig. 4. O equipamento consiste em cinco partes principais: i) uma estante inicial para armazenagem de towpregs; ii) sistema de guiamento; iii) sistema de pultrusão, que inclui um forno de pré-aquecimento e fieiras de pressurização/consolidação e de arrefecimento; e iv) sistema de puxo e, v) o sistema de corte do perfil produzido.

Para produzir perfis compósitos, os materiais pré-impregnados são guiados para o interior de um forno de pré-aquecimento para serem aquecidos até uma temperatura desejada. Em seguida, entram na primeira fieira onde são aquecidos e pressurizados/consolidados nas dimensões requeridas e posteriormente são arrefecidos na fieira seguinte para solidificarem. Os perfis pultrudidos são então cortados em comprimentos especificados.

Foi utilizada uma fieira, com uma cavidade de 20 × 2 (mm), para produzir uma barra retangular.

Table 4 – Flexural testing results from CF/PP towpregs

Exper.	Processing variables			Flexural properties	
	Furnace temperature (°C)	Heating die temperature (°C)	Linear pulling speed (m/min)	Flexural modulus (GPa)	Flexural strength (MPa)
1	160	240	0.2	86.7 ± 1.3	229.0 ± 7.3
2	180	240	0.2	79.5 ± 2.0	212.4 ± 12.6
3	160	260	0.2	91.0 ± 0.4	241.2 ± 1.6
4	180	260	0.2	85.1 ± 1.7	218.2 ± 9.1
5	160	240	0.3	82.1 ± 2.8	241.7 ± 13.1
6	180	240	0.3	87.5 ± 1.9	239.6 ± 13.3
7	160	260	0.3	85.0 ± 4.4	234.5 ± 11.5
8	180	260	0.3	83.7 ± 2.8	221.3 ± 7.1

type pultrusion line equipment [16, 17], schematic depicted in Fig.4. The equipment consists in five main parts: i) an initial towpreg bobbins holding cabinet; ii) guiding system; iii) pultrusion head, that includes a pre-heating furnace and the pressurization/consolidation and cooling dies; iv) pulling system and, v) the final profile cutting system.

To produce composite profiles, the pre-impregnated materials are guided into the pre-heating furnace to be heated up to the required temperature. Then, they enter in the pultrusion die to be heated up and consolidated to the required size in its first zone and, after cooled down in order to solidify. The pultruded material is then cut into specified lengths.

A die with a cavity of 20 ×2 (mm) was used to produce a composite rectangular shaped bar.

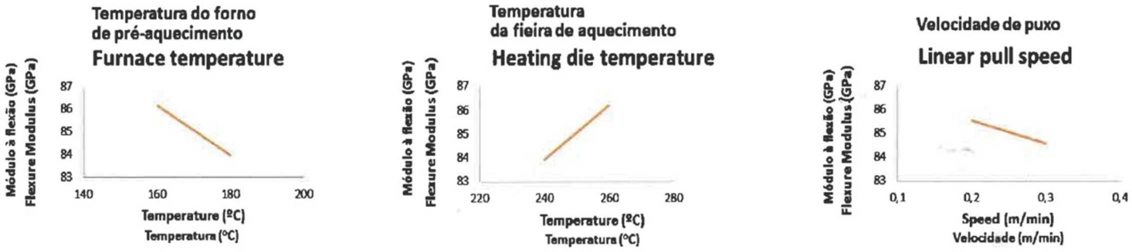
2.5.1 TOWPREG CF/PP PROCESSING AND OPTIMIZATION

Bar profiles were manufactured by pultrusion from different towpregs, using operating conditions in order to optimize the processing. The studied processing variables were:

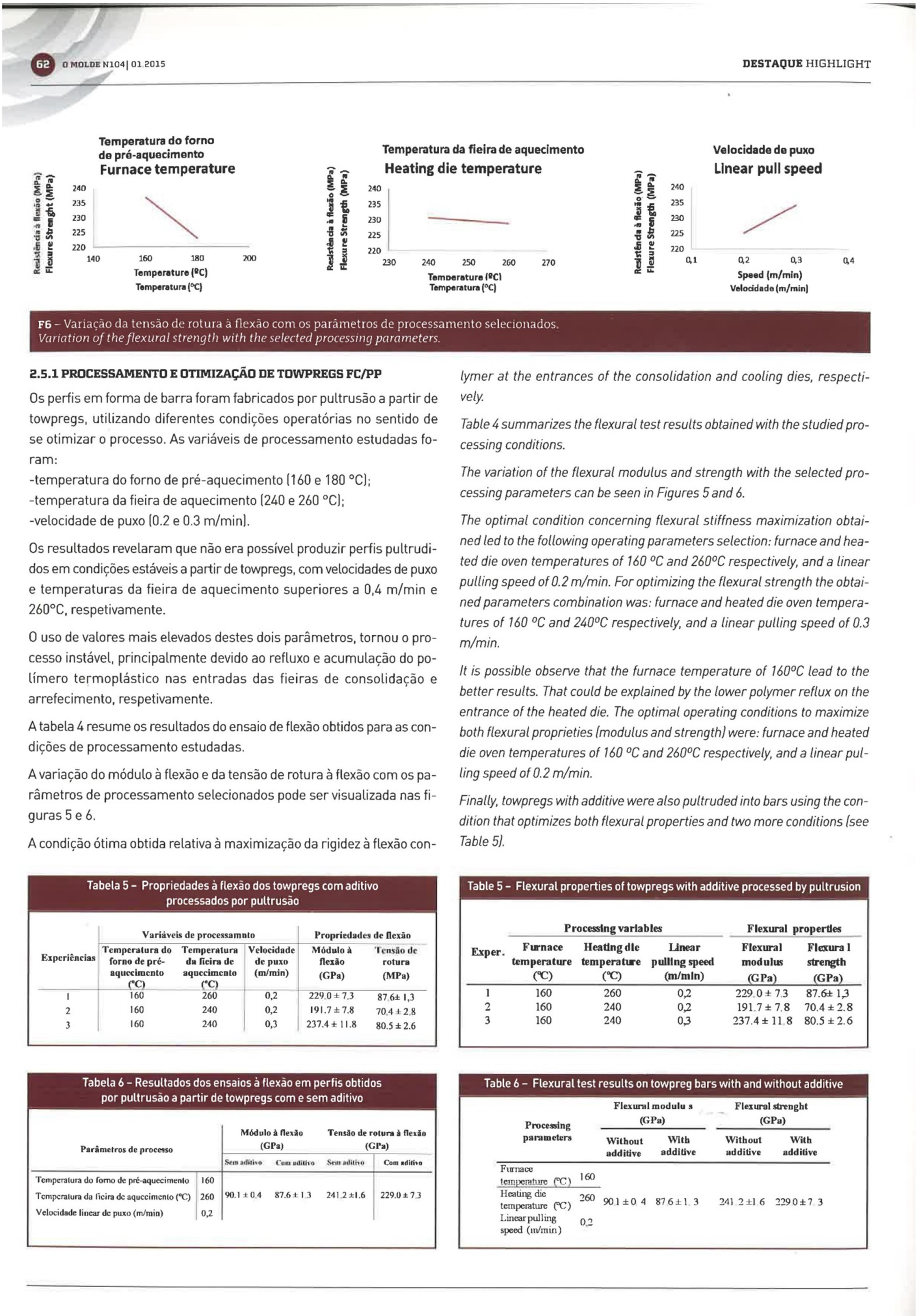
-Furnace temperature (160 and 180 °C);
-Heating die temperature (240 and 260 °C);
-Linear pull-speed (0.2 and 0.3 m/min).

Results have shown that was not possible to produce in steady conditions pultruded profiles from towpregs at pultrusion speeds and consolidation die temperatures higher than 0.4 m/min and 260 °C, respectively.

By using higher values in these two parameters the process became unsteady mainly due to reflux and accumulation of the thermoplastic po-



F5 – Variação do módulo à flexão com os parâmetros de processamento selecionados.
Variation of the flexural modulus with the selected processing parameters.



F6 – Variação da tensão de rotura à flexão com os parâmetros de processamento selecionados.
Variation of the flexural strength with the selected processing parameters.

2.5.1 PROCESSAMENTO E OTIMIZAÇÃO DE TOWPREGS FC/PP

Os perfis em forma de barra foram fabricados por pultrusão a partir de towpregs, utilizando diferentes condições operatórias no sentido de se otimizar o processo. As variáveis de processamento estudadas foram:

-temperatura do forno de pré-aquecimento (160 e 180 °C);
-temperatura da fieira de aquecimento (240 e 260 °C);
-velocidade de puxo (0.2 e 0.3 m/min).

Os resultados revelaram que não era possível produzir perfis pultrudidos em condições estáveis a partir de towpregs, com velocidades de puxo e temperaturas da fieira de aquecimento superiores a 0,4 m/min e 260°C, respetivamente.

O uso de valores mais elevados destes dois parâmetros, tornou o processo instável, principalmente devido ao refluxo e acumulação do polímero termoplástico nas entradas das fieiras de consolidação e arrefecimento, respetivamente.

A tabela 4 resume os resultados do ensaio de flexão obtidos para as condições de processamento estudadas.

A variação do módulo à flexão e da tensão de rotura à flexão com os parâmetros de processamento selecionados pode ser visualizada nas figuras 5 e 6.

A condição ótima obtida relativa à maximização da rigidez à flexão con-

lymer at the entrances of the consolidation and cooling dies, respectively.

Table 4 summarizes the flexural test results obtained with the studied processing conditions.

The variation of the flexural modulus and strength with the selected processing parameters can be seen in Figures 5 and 6.

The optimal condition concerning flexural stiffness maximization obtained led to the following operating parameters selection: furnace and heated die oven temperatures of 160 ºC and 260ºC respectively, and a linear pulling speed of 0.2 m/min. For optimizing the flexural strength the obtained parameters combination was: furnace and heated die oven temperatures of 160 ºC and 240ºC respectively, and a linear pulling speed of 0.3 m/min.

It is possible observe that the furnace temperature of 160ºC lead to the better results. That could be explained by the lower polymer reflux on the entrance of the heated die. The optimal operating conditions to maximize both flexural proprieties (modulus and strength) were: furnace and heated die oven temperatures of 160 ºC and 260ºC respectively, and a linear pulling speed of 0.2 m/min.

Finally, towpregs with additive were also pultruded into bars using the condition that optimizes both flexural properties and two more conditions (see Table 5).

Tabela 5 – Propriedades à flexão dos towpregs com aditivo processados por pultrusão

Experiências	Variáveis de processamnto			Propriedades de flexão	
	Temperatura do forno de pré-aquecimento (°C)	Temperatura da fieira de aquecimento (°C)	Velocidade de puxo (m/min)	Módulo à flexão (GPa)	Tensão de rotura (MPa)
1	160	260	0,2	229.0 ± 7.3	87.6± 1,3
2	160	240	0,2	191.7 ± 7.8	70.4 ± 2.8
3	160	240	0,3	237.4 ± 11.8	80.5 ± 2.6

Table 5 – Flexural properties of towpregs with additive processed by pultrusion

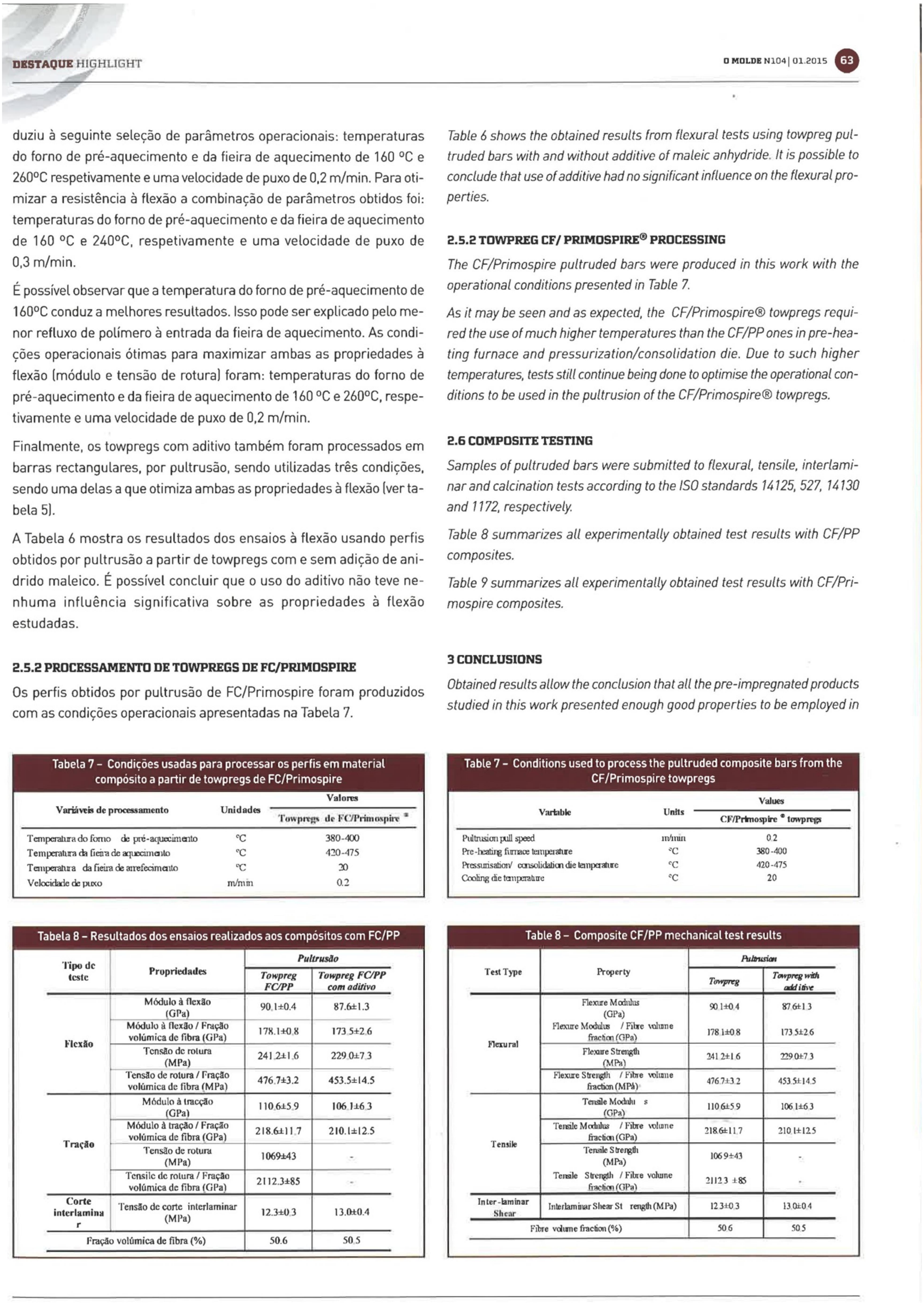
Exper.	Processing variables			Flexural properties	
	Furnace temperature (°C)	Heating die temperature (°C)	Linear pulling speed (m/min)	Flexural modulus (GPa)	Flexura l strength (GPa)
1	160	260	0,2	229.0 ± 7.3	87.6± 1,3
2	160	240	0,2	191.7 ± 7.8	70.4 ± 2.8
3	160	240	0,3	237.4 ± 11.8	80.5 ± 2.6

Tabela 6 – Resultados dos ensaios à flexão em perfis obtidos por pultrusão a partir de towpregs com e sem aditivo

Parâmetros de processo		Módulo à flexão (GPa)		Tensão de rotura à flexão (GPa)	
		Sem aditivo	Com aditivo	Sem aditivo	Com aditivo
Temperatura do forno de pré-aquecimento	160	90.1 ± 0.4	87.6 ± 1.3	241.2 ±1.6	229.0 ± 7.3
Temperatura da fieira de aquecimento (°C)	260				
Velocidade linear de puxo (m/min)	0,2				

Table 6 – Flexural test results on towpreg bars with and without additive

Processing parameters		Flexural modulu s (GPa)		Flexural strenght (GPa)	
		Without additive	With additive	Without additive	With additive
Furnace temperature (°C)	160	90.1 ± 0.4	87.6 ± 1.3	241.2 ±1.6	229.0 ± 7.3
Heating die temperature (°C)	260				
Linear pulling speed (m/min)	0,2				



duziu à seguinte seleção de parâmetros operacionais: temperaturas do forno de pré-aquecimento e da fieira de aquecimento de 160 °C e 260°C respetivamente e uma velocidade de puxo de 0,2 m/min. Para otimizar a resistência à flexão a combinação de parâmetros obtidos foi: temperaturas do forno de pré-aquecimento e da fieira de aquecimento de 160 °C e 240°C, respetivamente e uma velocidade de puxo de 0,3 m/min.

É possível observar que a temperatura do forno de pré-aquecimento de 160°C conduz a melhores resultados. Isso pode ser explicado pelo menor refluxo de polímero à entrada da fieira de aquecimento. As condições operacionais ótimas para maximizar ambas as propriedades à flexão (módulo e tensão de rotura) foram: temperaturas do forno de pré-aquecimento e da fieira de aquecimento de 160 °C e 260°C, respetivamente e uma velocidade de puxo de 0,2 m/min.

Finalmente, os towpregs com aditivo também foram processados em barras rectangulares, por pultrusão, sendo utilizadas três condições, sendo uma delas a que otimiza ambas as propriedades à flexão (ver tabela 5).

A Tabela 6 mostra os resultados dos ensaios à flexão usando perfis obtidos por pultrusão a partir de towpregs com e sem adição de anidrido maleico. É possível concluir que o uso do aditivo não teve nenhuma influência significativa sobre as propriedades à flexão estudadas.

2.5.2 PROCESSAMENTO DE TOWPREGS DE FC/PRIMOSPIRE

Os perfis obtidos por pultrusão de FC/Primospire foram produzidos com as condições operacionais apresentadas na Tabela 7.

Table 6 shows the obtained results from flexural tests using towpreg pultruded bars with and without additive of maleic anhydride. It is possible to conclude that use of additive had no significant influence on the flexural properties.

2.5.2 TOWPREG CF/ PRIMOSPIRE® PROCESSING

The CF/Primospire pultruded bars were produced in this work with the operational conditions presented in Table 7.

As it may be seen and as expected, the CF/Primospire® towpregs required the use of much higher temperatures than the CF/PP ones in pre-heating furnace and pressurization/consolidation die. Due to such higher temperatures, tests still continue being done to optimise the operational conditions to be used in the pultrusion of the CF/Primospire® towpregs.

2.6 COMPOSITE TESTING

Samples of pultruded bars were submitted to flexural, tensile, interlaminar and calcination tests according to the ISO standards 14125, 527, 14130 and 1172, respectively.

Table 8 summarizes all experimentally obtained test results with CF/PP composites.

Table 9 summarizes all experimentally obtained test results with CF/Primospire composites.

3 CONCLUSIONS

Obtained results allow the conclusion that all the pre-impregnated products studied in this work presented enough good properties to be employed in

Tabela 7 – Condições usadas para processar os perfis em material compósito a partir de towpregs de FC/Primospire

Variáveis de processamento	Unidades	Valores
		Towpregs de FC/Primospire ®
Temperatura do forno de pré-aquecimento	°C	380-400
Temperatura da fieira de aquecimento	°C	420-475
Temperatura da fieira de arrefecimento	°C	20
Velocidade de puxo	m/min	0.2

Table 7 – Conditions used to process the pultruded composite bars from the CF/Primospire towpregs

Variable	Units	Values
		CF/Primospire ® towpregs
Pultrusion pull speed	m/min	0.2
Pre-heating furnace temperature	°C	380-400
Pressurisation/ consolidation die temperature	°C	420-475
Cooling die temperature	°C	20

Tabela 8 – Resultados dos ensaios realizados aos compósitos com FC/PP

Tipo de teste	Propriedades	*Pultrusão*	
		Towpreg FC/PP	*Towpreg FC/PP com aditivo*
Flexão	Módulo à flexão (GPa)	90.1±0.4	87.6±1.3
	Módulo à flexão / Fração volúmica de fibra (GPa)	178.1±0.8	173.5±2.6
	Tensão de rotura (MPa)	241.2±1.6	229.0±7.3
	Tensão de rotura / Fração volúmica de fibra (MPa)	476.7±3.2	453.5±14.5
Tração	Módulo à tracção (GPa)	110.6±5.9	106.1±6.3
	Módulo à tração / Fração volúmica de fibra (GPa)	218.6±11.7	210.1±12.5
	Tensão de rotura (MPa)	1069±43	-
	Tensile de rotura / Fração volúmica de fibra (GPa)	2112.3±85	-
Corte interlaminar	Tensão de corte interlaminar (MPa)	12.3±0.3	13.0±0.4
Fração volúmica de fibra (%)		50.6	50.5

Table 8 – Composite CF/PP mechanical test results

Test Type	Property	*Pultrusion*	
		Towpreg	*Towpreg with additive*
Flexural	Flexure Modulus (GPa)	90.1±0.4	87.6±1.3
	Flexure Modulus / Fibre volume fraction (GPa)	178.1±0.8	173.5±2.6
	Flexure Strength (MPa)	241.2±1.6	229.0±7.3
	Flexure Strength / Fibre volume fraction (MPa)	476.7±3.2	453.5±14.5
Tensile	Tensile Modulus (GPa)	110.6±5.9	106.1±6.3
	Tensile Modulus / Fibre volume fraction (GPa)	218.6±11.7	210.1±12.5
	Tensile Strength (MPa)	106.9±43	-
	Tensile Strength / Fibre volume fraction (GPa)	2112.3 ±85	-
Inter-laminar Shear	Interlaminar Shear Strength (MPa)	12.3±0.3	13.0±0.4
Fibre volume fraction (%)		50.6	50.5

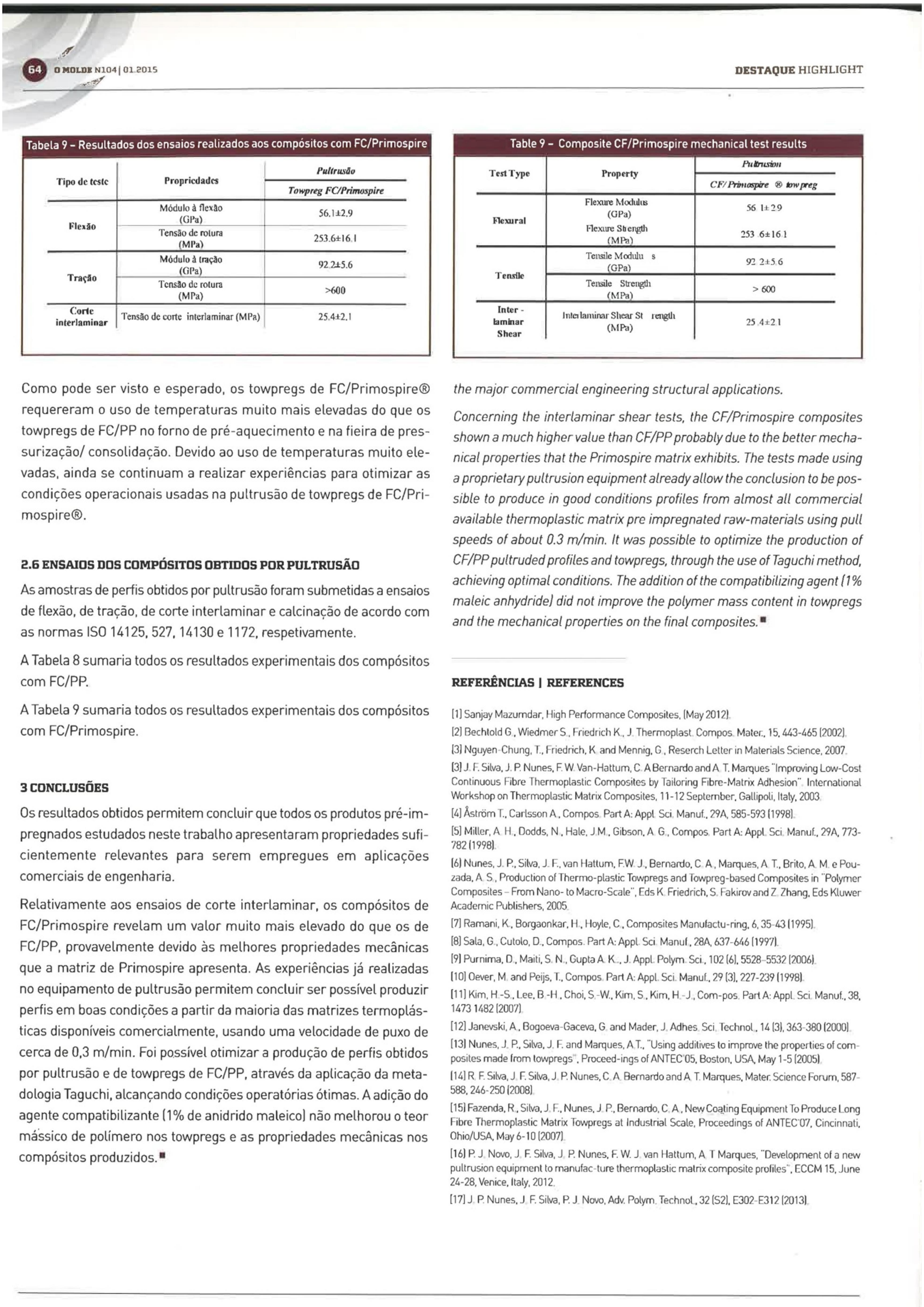


Tabela 9 – Resultados dos ensaios realizados aos compósitos com FC/Primospire

Tipo de teste	Propriedades	*Pultrusão*
		Towpreg FC/Primospire
Flexão	Módulo à flexão (GPa)	56.1±2.9
	Tensão de rotura (MPa)	253.6±16.1
Tração	Módulo à tração (GPa)	92.2±5.6
	Tensão de rotura (MPa)	>600
Corte interlaminar	Tensão de corte interlaminar (MPa)	25.4±2.1

Table 9 – Composite CF/Primospire mechanical test results

Test Type	Property	*Pultrusion*
		CF/ Primospire ® towpreg
Flexural	Flexure Modulus (GPa)	56 1±2.9
	Flexure Strength (MPa)	253 6±16.1
Tensile	Tensile Modulu s (GPa)	92 2±5.6
	Tensile Strength (MPa)	> 600
Inter - laminar Shear	Interlaminar Shear St rength (MPa)	25 4±2.1

Como pode ser visto e esperado, os towpregs de FC/Primospire® requereram o uso de temperaturas muito mais elevadas do que os towpregs de FC/PP no forno de pré-aquecimento e na fieira de pressurização/ consolidação. Devido ao uso de temperaturas muito elevadas, ainda se continuam a realizar experiências para otimizar as condições operacionais usadas na pultrusão de towpregs de FC/Primospire®.

2.6 ENSAIOS DOS COMPÓSITOS OBTIDOS POR PULTRUSÃO

As amostras de perfis obtidos por pultrusão foram submetidas a ensaios de flexão, de tração, de corte interlaminar e calcinação de acordo com as normas ISO 14125, 527, 14130 e 1172, respetivamente.

A Tabela 8 sumaria todos os resultados experimentais dos compósitos com FC/PP.

A Tabela 9 sumaria todos os resultados experimentais dos compósitos com FC/Primospire.

3 CONCLUSÕES

Os resultados obtidos permitem concluir que todos os produtos pré-impregnados estudados neste trabalho apresentaram propriedades suficientemente relevantes para serem empregues em aplicações comerciais de engenharia.

Relativamente aos ensaios de corte interlaminar, os compósitos de FC/Primospire revelam um valor muito mais elevado do que os de FC/PP, provavelmente devido às melhores propriedades mecânicas que a matriz de Primospire apresenta. As experiências já realizadas no equipamento de pultrusão permitem concluir ser possível produzir perfis em boas condições a partir da maioria das matrizes termoplásticas disponíveis comercialmente, usando uma velocidade de puxo de cerca de 0,3 m/min. Foi possível otimizar a produção de perfis obtidos por pultrusão e de towpregs de FC/PP, através da aplicação da metadologia Taguchi, alcançando condições operatórias ótimas. A adição do agente compatibilizante (1% de anidrido maleico) não melhorou o teor mássico de polímero nos towpregs e as propriedades mecânicas nos compósitos produzidos. ■

the major commercial engineering structural applications.

Concerning the interlaminar shear tests, the CF/Primospire composites shown a much higher value than CF/PP probably due to the better mechanical properties that the Primospire matrix exhibits. The tests made using a proprietary pultrusion equipment already allow the conclusion to be possible to produce in good conditions profiles from almost all commercial available thermoplastic matrix pre impregnated raw-materials using pull speeds of about 0.3 m/min. It was possible to optimize the production of CF/PP pultruded profiles and towpregs, through the use of Taguchi method, achieving optimal conditions. The addition of the compatibilizing agent (1% maleic anhydride) did not improve the polymer mass content in towpregs and the mechanical properties on the final composites. ■

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5.7. Paper 5

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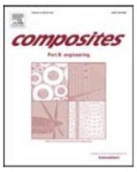

Pultrusion of fibre reinforced thermoplastic pre-impregnated materials

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ABSTRACT

Fibre reinforced thermoplastic pre-impregnated materials produced continuously by diverse methods and processing conditions were used to produce composites using pultrusion. The processing windows used to produce these materials and composites profiles were optimized by using the Taguchi/DOE (Design of Experiments) methods. Those composites were then submitted to mechanical testing and microscopy analysis. The obtained results were compared with the expected theoretical ones predicted from the Rule Of Mixtures (ROM) and with those of similar engineering conventional available materials. The results obtained shown that produced composites have adequate properties for applications in common and structural engineering markets.

1. Introduction

Although only recently thermoplastic matrices have been used in long and continuous fibre reinforced composites as alternative to thermosetting matrices, the number of their applications is increasing due to their better ecological and mechanical performance [1]. Composites with thermoplastic matrices offer increased fracture toughness, higher damage tolerance, short processing cycle times and excellent environmental stability. They are recyclable, post-formable and can be joined by welding. The use of long/continuous fibre reinforced thermoplastic matrix composites involves, however, great technological and scientific challenges since thermoplastics present much higher viscosity than thermosettings, which makes much difficult and complex the impregnation of reinforcements and consolidation tasks [1–6].

Today, two major technologies are being used to allow wet reinforcing fibres with thermoplastic polymers [1,4–6]: i) the direct melting of the polymer and, ii) the intimate fibre/matrix contact prior to final composite fabrication. Continuous fibre reinforced thermoplastic matrix pre-impregnated tapes (PCT's) are, for example, produced by direct melting processes. Alternatively, intimate contact processes allow producing cheap and promising pre-impregnated materials, such as, commingled fibres and powder coated towpregs. Sometimes, thermoplastic compatibilizers are added to the matrices to improve their adhesion and facilitate impregnation to reinforcements [7].

This work studies and compares the processability of final composite parts by using three different pre-impregnated materials produced by each one of the above mentioned wetting techniques. One is a pre-consolidated tape (Fig. 1 a)) that was produced by the melting process (cross-head extrusion) [8]. From the other two produced by fibre/matrix intimate contact methods, one is a commercially available commingled fibres product (Fig. 1 b) and the other a towpreg (Fig. 1 c)) produced by our own developed dry coating line [9]. All studied pre-impregnated materials were based on a continuous carbon and glass fibres reinforced polypropylene matrix system. Pultrusion was the selected manufacturing method for processing all these pre-impregnated materials into composite parts. It is a versatile continuous high speed production technology, allowing the production of fibre reinforced complex profiles. Nowadays crucial challenges in pultrusion such as the residual

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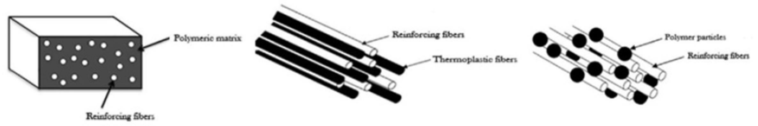


a) Pre-consolidate tapes (PCTs) b) Commingled fibres c) towpregs

Fig. 1. Pre-impregnated products under study.

Table 1
Properties of towpregs and PCT PP raw-materials.

Property	PP powder (ICORENE 9184B P®)		PP granules (Moplen RP348U ®)
	Manufacturer datasheet	Experimental	Manufacturer datasheet
Specific gravity (Mg/m^3)	0.91	0.91	0.90
Tensile strength (MPa)	Yield Strength 30	Yield Strength 19	Yield Strength 30
Young Modulus (GPa)	1.3	0.98	1.1
Poisson's ratio	–	0.21	–
Average powder particle size (μm)	440	163	–
Glass transition temperature (T_g)	Typical value 0–20	–	Typical value 0–20
Melting temperature (T_m)	Typical value 170	166	Typical value 170

Table 2
Properties of towpregs and PCT fibres raw-materials.

Property	Glass fibre			Carbon fibre	
	(305E-TYPE 30®)		(TufRov 4599®)	(TORAY M30 SC®)	
	Manufacturer datasheet	Experimental	Manufacturer datasheet	Manufacturer datasheet	Experimental
Linear density (Tex)	2400	–	2400	760	–
Specific gravity (Mg/m^3)	2.65	–	2.54–2.6	1.73	–
Tensile strength (MPa)	3500	1657	1900–2400	5490	2731
Young Modulus (GPa)	76	62.5	69–76	294	194.5
Average fibre diameter	17	13.7	17	5	7.37

stresses in the product which may induce damage or premature cracks and delamination are being studied [10–12].

The optimization of the pultrusion process was made by studying the influence of the most relevant processing parameters in the final properties of the produced pre-impregnated materials and composites. The method of Taguchi/DOE (Design of Experiments) was used to achieve this aim.

The possibility of using maleic anhydride as compatibilizer of carbon and glass fibre reinforced polypropylene composites was also analysed in the present work.

Towpregs were characterized by scanning electron microscopy (SEM), visual analysis and their polymer mass contents were determined. The final composite parts were also submitted to tensile, interlaminar and flexural tests, as well as calcination and optical microscopy tests and the results were compared with theoretical ones that can be predicted by using the ROM (Rule Of Mixtures) and other engineering traditional materials (steel, aluminium and several polymers).

2. Experimental

2.1. Raw materials

The following raw materials were used to produce carbon reinforced polypropylene (CF/PP) pre-impregnated materials for this work: i) a PP powder ICORENE 9184B P® and carbon fibre roving M30 SC® from the ICO Polymers and TORAY, respectively, were used to produce the CF/PP towpregs, ii) PP powder Moplen RP348U® from Basell and the carbon fibre roving already mentioned were used to manufacture the CF/PP PCT tapes.

For the glass reinforced polypropylene (GF/PP) towpregs, a 2400 Tex type E fibre rovings from Owens Corning and Icorene® 9184B P polypropylene from ICO Polymers France were used. Also, the GF/PP PCT tapes were manufactured with glass fibres (TufRov 4599) from PPG Industries and a polypropylene matrix (Moplen RP348U) from Basell.

Commercial commingled GF/PP fibres TWINTEX® R PP 60 B 1870 FU from Owens Corning were also used in the production of pultrusion thermoplastic composite profiles, as reference of a current commercially available pre-impregnated product.

Some batches of CF/PP and GF/PP towpregs were also produced using PP powder (ICORENE 9184B P®) blended with 1% in mass content of maleic anhydride S 47 29608 707® from Merck Schuchardt OHG, in order to assess the possible enhancement of fibre/matrix adhesion [13–16].

Tables 1 and 2 summarise relevant properties of the polypropylene, glass and carbon fibres used in present work to produce pre-impregnated raw materials (towpregs and PCT's). Table 3 shows the manufacturer datasheets properties of TWINTEX ®.

Table 3
TWINTEX ® R PP 60 B 1870 FU from Owens Corning.

Property	Values
Linear density (Tex)	1870
Tensile strength (MPa)	760
Young Modulus (GPa)	29.5
Fibre mass content (%)	60

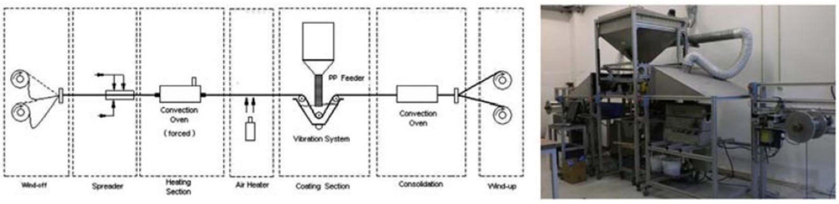


Fig. 2. Powder coating line setup.

2.2. Production of thermoplastic matrix pre-impregnated products

The dry powder coating equipment used to produce fibre reinforced towpregs is depicted in Fig. 2 [9,17].

The pre-consolidated tapes (PCT's) used in this work were produced in a cross-head extrusion equipment (see Fig. 3) from our own laboratories [8]. Using this equipment, it was possible to produce the tapes (PCT's) pre-impregnated raw-materials. The overview of their main properties is given in Table 4.

2.2.1. CF/PP towpregs production and optimization

In order to optimize the production of CF/PP powder coated towpregs, different processing variables combinations were experimented and the number of trials optimized using the Taguchi approach. The studied operational parameters were:

- Heating oven temperature (600, 650 and 700 °C); consolidation oven temperature (350, 400 and 450 °C); linear pull speed (4, 6 and 8 m/min).

The Taguchi approach was applied to the towpregs production process in order to obtain the condition that maximizes polymer powder content.

The polymer mass fraction in the towpregs, ω_p, was determined by weighting towpreg strips produced in those different conditions, using equation (1):

$$\omega_p = \frac{W_t - W_f}{W_t} \tag{1}$$

where W_t and W_f are the measured unit length weights of the towpreg strip and fibre roving, respectively.

Table 5 shows the used processing conditions and obtained results, according to the established design of experiments. The average polymer mass content in towpregs, established by the design of experiences was 34.5% (Table 5).

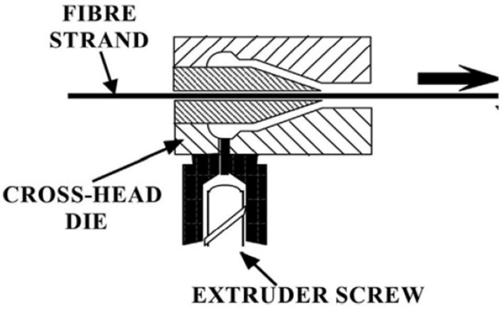


Fig. 3. Cross-head extrusion die.

In Fig. 4 an average plot is obtained by plotting the average polymer mass fraction effect against the corresponding main processing variables (temperatures/linear pull speed) levels.

The optimal condition obtained from Taguchi method application led to the following operating parameters selection: heating oven temperature and consolidation oven temperatures of 700 °C and 400 °C respectively, and a linear pulling speed of 6 m/min. Using this optimal operative condition, the amount of polymer should increase up to 45.6%. However, it was found that the average polymer content in continuous towpreg production was only 40.0% (enough for the of use of towpregs in the pultrusion process, where a limit value of polymer mass content of 22% should be achieved as minimum, if only rovings are used [18]). Also, the addition of 1% of maleic anhydride to the PP polymer had no influence on the towpreg polymer mass fraction. Table 6 summarizes the determined properties on towpregs produced using the optimal combination of parameters.

2.2.2. GF/PP towpregs production and optimization

To try maximizing the polymer powder content in the towpregs the following processing conditions were varied within the next ranges: i) convective oven temperature (°C): 650–700; ii) Consolidation furnace temperature (°C): 350–450; iii) Coating line pulling speed (m/min): 4–6.

From the polymer mass fractions obtained in produced towpreg strips it was possible to establish as optimal the following operating parameters: convective and consolidation oven temperatures of 700 °C and 400 °C respectively, and a linear pulling speed of 6 m/min. In such operational conditions the GF/PP towpregs were continuously produced with polymer mass content of 30.7%.

Unexpectedly, very low polymer mass fractions (~10%–16%) were obtained when PP powder with 1% of maleic anhydride was used to produce GF/PP towpregs. Hence, the idea of using this additive to improve adhesion of the PP matrix to the glass fibres was abandoned. Table 6 summarizes the determined towpreg properties obtained with the combination of selected parameters.

2.3. Pultrusion of pre-impregnated materials

The towpregs, PCT's and commingled fibres were processed into composite rectangular bar profiles using the laboratorial pultrusion line, Fig. 5 [8,19].

Table 4
Overview of the main properties of the produced pre-consolidated tapes (PCT's).

Property	CF/PP	GF/PP
Fibre type	Carbon, 760 Tex	E-Glass, 2400 Tex
Filament diameter	7 μm	17 μm
Fibre content	45 wt.%	60 wt.%
Matrix type	Polypropylene (PP)	Polypropylene (PP)
Tape width	25 mm	25 mm
Tape linear density	14 000 Tex	16 000 Tex

Table 5
Taguchi approach applied to towpregs manufacturing process.

Experiments	Processing variables			Results
	Heating oven temperature (°C)	Consolidation furnace temperature (°C)	Linear pulling speed (m/min)	Polymer mass fraction (%)
1	600	350	4	32.2
2	600	400	6	31.4
3	600	420	8	20.6
4	650	350	8	27.9
5	650	400	4	39.9
6	650	420	6	40.7
7	700	350	6	35.6
8	700	400	8	40.6
9	700	420	4	40.4
Average				34.5

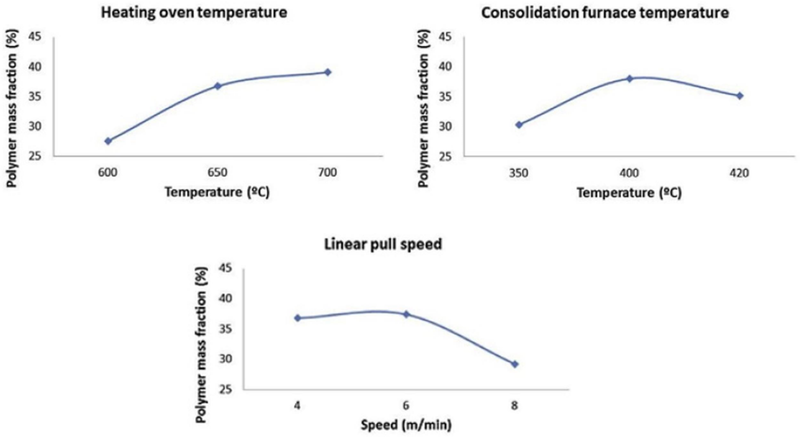


Fig. 4. Variation of towpreg polymer content with processing parameters.

To produce composite profiles, the pre-impregnated materials are guided into the pre-heating furnace to be heated up to the required temperature. Then, they enter in the pultrusion heated die to be heated and consolidated to the required size and, after cooled down in the cooling die to solidify. The control of the die temperatures was made using two PT 100 sensors, one in each half-die. The die temperature distribution profile, obtained with a FLUKE TI45FT infrared camera, can be seen in Fig. 6.

In this work, it was designed and manufactured a die to allow producing a 20 × 2 mm^2 bar-shaped profile.

2.3.1. Towpreg processing

CF/PP towpregs were manufactured by pultrusion into composite bar profiles using the most relevant operating conditions. The Taguchi's/DOE method was applied, maintaining the cooling die at 25 °C, in order to optimize the processing parameters: i) furnace temperature (160 or180 °C); ii) heating die temperature (240 or 260 °C); iii)linear pull-speed (0.2 or 0.3 m/min).

Table 6
Overview of the main properties of towpregs produced using the optimal condition.

Property	CF/PP	GF/PP
Fibre type	Carbon, 760 Tex	E-Glass, 2400 Tex
Filament diameter	7 μm	17 μm
Fibre content	60.0 wt.%	69.3 wt.%
Matrix type	Polypropylene (PP)	Polypropylene (PP)
Tape width	5 mm	5 mm
Tape linear density	1270 Tex	3460 Tex

Results have shown that it was not possible to produce pultruded profiles from towpregs in steady conditions at linear pull-speeds and consolidation die temperatures higher than 0.4 m/min and 260 °C, respectively. By using higher values for those two parameters, the process became unsteady, mainly due to the thermoplastic polymer reflux at the entrance of the consolidation die and also to their accumulation at the entrance of the cooling die.

Table 7 summarizes the processing conditions according to established in the design of experiments. The variations of the flexural modulus and strength (determined according to the procedure described in paragraph 2.4.2) with the selected processing parameters, needed for achieving the optimal condition, can be seen in Figs. 7 and 8.

The optimal condition concerning flexural stiffness maximization obtained from Taguchi method application led to the following operating parameters selection: furnace and heated die oven temperatures of 160 °C and 260 °C respectively, and a linear pulling speed of 0.2 m/min. For optimizing the flexural strength the obtained parameters combination were: furnace and heated die oven temperatures of 160 °C and 240 °C respectively, and a linear pulling speed of 0.3 m/min.

It is possible to observe that the furnace temperature of 160 °C lead to the better results. That could be explained by the lower polymer reflux on the entrance of the heated die. The optimal operating conditions to maximize both flexural properties were:

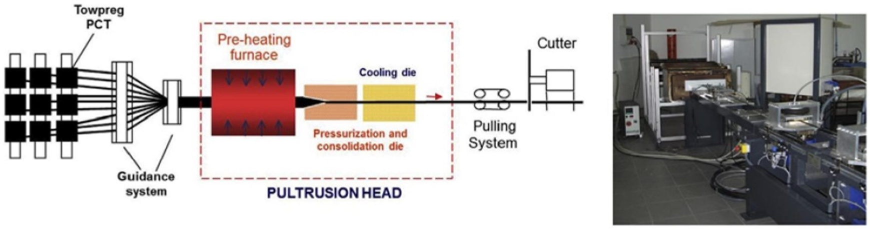


Fig. 5. Schematic diagram and overview of the pultrusion line.

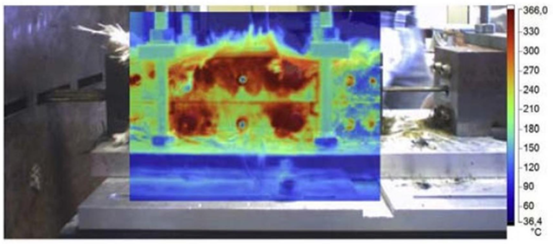


Fig. 6. Heated die temperature distribution profile.

furnace and heated die oven temperatures of 160 °C and 260 °C respectively, and a linear pulling speed of 0.2 m/min.

Finally, towpregs with additive were also pultruded into composite bars using the condition that optimizes both flexural properties (Table 8, experiment 1) and two other experiments (Table 8, experiments 2 and 3). The results from flexural testing shown in Table 9 allow concluding that the use of such additive had no significant influence on the flexural properties.

GF/PP pre-impregnated towpreg rovings were processed by pultrusion into rectangular 20 × 2 (mm^2) profiles. To determine the best processing window, the main processing conditions were varied, maintaining the cooling die at 25 °C: i) pre-heating temperature (°C): 170–180; ii) pressurization/consolidation die temperature (°C): 240–300; iii) linear pultrusion speed (m/min): 0.2–0.4.

Results have shown that it was not possible to produce, in steady conditions, profiles from towpregs at pultrusion speeds and pressurization/consolidation die temperatures higher than 0.3 m/min and 280 °C, respectively. By using higher, values the process became unsteady as it was already found for CF/PP towpregs processing. The same problems also occurred for temperatures below 270 °C in the pressurization/consolidation die. By maintaining constant the temperatures in the cooling and pressurization/consolidation dies at 25 °C and 280 °C, respectively, profiles pultruded in different processing conditions were submitted to the flexural tests (see 2.4.2). As it is seen in Table 10, very similar values of flexural moduli and strengths were found by using pre-heating furnace temperatures and linear pultrusion pulling speeds in the ranges of 170–180 (°C) and 0.2–0.3 m/min, respectively. While the slower pultrusion pulling speed of 0.2 m/min seemed to generate profiles with higher absolute values, this was not confirmed by the flexural properties divided by the determined fibre volume fraction depicted in two last the columns of Table 10. On the other hand, higher flexural strength values were obtained at the higher temperature of 180 °C in pre-heating furnace, even if flexural strength relative values were considered (ratio between the flexural strength and the fibre volume fraction). Hence, it was concluded that the GF/PP towpreg pultrusion operating window should be the following one: i) pre-heating temperature (°C): 170–180; ii) pressurization/consolidation die temperature (°C): 280; iii) cooling die temperature (°C): 25; iv) linear pultrusion speed (m/min): 0.2–0.3.

2.3.2. *Pre-consolidate tapes(PCT's) and Twintex® processing*

PCT's and Twintex® were processed into rectangular 20 × 2 (mm^2) bar using the already mentioned pultrusion equipment being operating conditions shown in Table 11.

2.4. *Testing*

2.4.1. *Microscopy analysis*

CF/PP and GF/PP towpreg samples were characterized by scanning electron microscopy (SEM) to evaluate the adhesion of the polymer powder to the fibres and its distribution. In order to prevent charge build-up by electron absorbed by the samples, those were coated with a layer of gold with approximately 6.5 μm thick, before the observation.

To determine the impregnation quality and to evaluate the fibre distribution and fibre/matrix adhesion of the thermoplastic composites, their cross-sections were studied under optical microscopy. Observations were done using reflected light optical microscopy (Olympus BH-2). A digital camera (Leica DFC200) was used to get the image cross sectional views of the samples.

Table 7
Taguchi approach applied to towpreg processing by pultrusion.

Experiments	Processing variables			Bending properties	
	Furnace temperature (°C)	Heating die temperature (°C)	Linear pulling speed (m/min)	Flexural modulus (GPa)	Flexural strength (MPa)
1	160	240	0.2	86.7 ± 1.3	229.0 ± 7.3
2	180	240	0.2	79.5 ± 2.0	212.4 ± 12.6
3	160	260	0.2	91.0 ± 0.4	241.2 ± 1.6
4	180	260	0.2	85.1 ± 1.7	218.2 ± 9.1
5	160	240	0.3	82.1 ± 2.8	241.7 ± 13.1
6	180	240	0.3	87.5 ± 1.9	239.6 ± 13.3
7	160	260	0.3	85.0 ± 4.4	234.5 ± 11.5
8	180	260	0.3	83.7 ± 2.8	221.3 ± 7.1

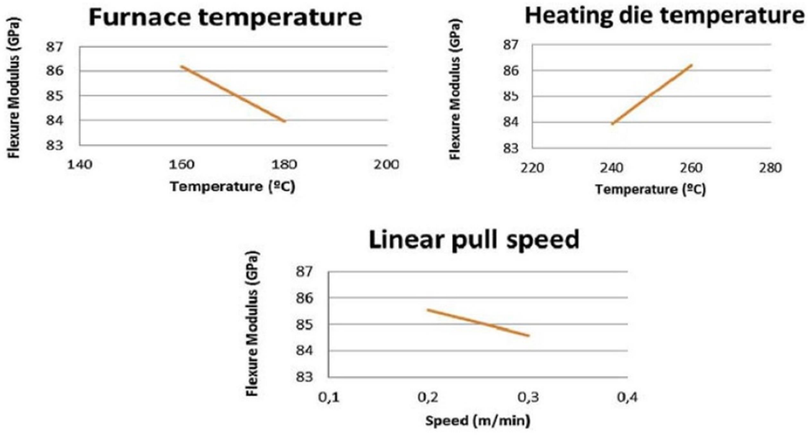


Fig. 7. Variation of the flexural modulus with the selected processing parameters.

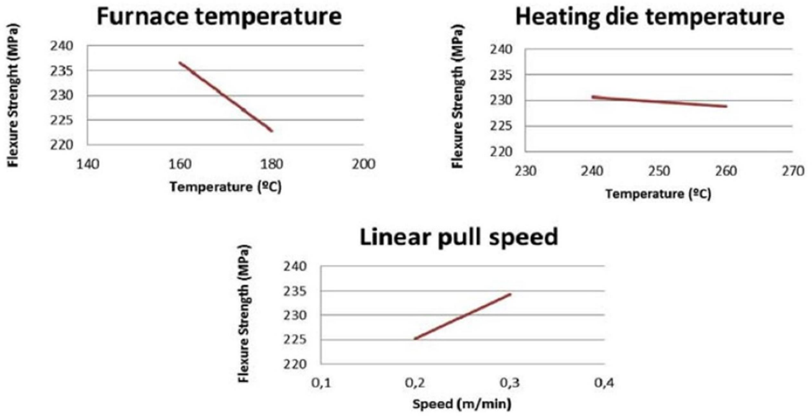


Fig. 8. Variation of the flexural strength with the selected processing parameters.

Table 8
Taguchi approach applied to towpregs processed with additive.

Experiments	Processing variables			Flexural properties	
	Furnace temperature (°C)	Heating die temperature (°C)	Linear pulling speed (m/min)	Flexural strength (MPa)	Flexural modulus (GPa)
1	160	260	0.2	229.0 ± 7.3	87.6 ± 1.3
2	160	240	0.2	191.7 ± 7.8	70.4 ± 2.8
3	160	240	0.3	237.4 ± 11.8	80.5 ± 2.6

Table 9
Flexural test results on composite bars with and without additive from CF/PP towpregs.

Processing parameters		Flexural modulus (GPa)		Flexural strength (MPa)	
		Without additive	With additive	Without additive	With additive
Furnace temperature (°C)	160	90.1 ± 0.4	87.6 ± 1.3	241.2 ± 1.6	229.0 ± 7.3
Heating die temperature (°C)	260				
Linear pulling speed (m/min)	0.2				

Table 10
Influence of pultrusion conditions on the flexural properties of profiles made from GF/PP towpregs.

Pultrusion conditions		Flexural properties		Fibre content		Flexural properties/fibre volume fraction	
Pre-heating temperature (°C)	Pultrusion speed (m/min)	Modulus (GPa)	Strength (MPa)	Mass (%)	Volume (%)	Relative modulus (GPa)	Relative strength (MPa)
170	0.2	29.1 ± 0.6	149.2 ± 14.4	76.1	52.2	55.7 ± 1.2	285.2 ± 27.6
170	0.3	28.6 ± 1.2	142.3 ± 16.2	75.4	51.3	55.8 ± 2.3	255.0 ± 31.6
180	0.2	29.5 ± 0.1	156.1 ± 5.1	76.5	52.8	55.9 ± 0.2	295.6 ± 9.7
180	0.3	28.6 ± 0.9	157.7 ± 12.3	76.0	52.1	54.9 ± 1.7	302.7 ± 23.6

Table 11
Pultrusion processing parameters for PCT's and Twintex®.

Raw-material	Heated die temperature (°C)	Cooled die temperature (°C)	Pre-heating temperature (°C)	Pulling speed (m/min)
CF/PP PCT	230	50	160	0.2
GF/PP PCT	230		170	
Twintex®	300		170	

2.4.2. Mechanical testing

Bar samples were submitted to flexural, tensile and interlaminar testing according to the ISO standards 14125, 527 and 14130, respectively. The mechanical properties obtained were compared to the theoretical ones predicted by using the Rule of Mixtures (ROM).

Tensile tests were conducted, according to ISO 527, in a 100 kN universal testing machine at the crosshead speed of 2 mm/min using 180 × 20 × 2 mm^3 rectangular samples. The tensile modulus was determined from the slope of the initial linear portion of the experimental stress/strain curve. A SG Shimadzu® 50 mm length strain-gauge was used up to 0.3% strain, for accurate determination of the tensile modulus. Regarding the determination of tensile strength, it was not possible to proceed with the test until specimen failure due to grip slippage. Hence, new specimen geometry (see Fig. 9) was designed and tested with good results, allowing determining the samples tensile strengths.

Three-point flexural tests were also conducted on five 100 × 20 × 2 (mm^3) composite specimens, using 100 kN universal testing machine and a distance between supports of 80 mm, according to ISO 14125, at a crosshead speed of 1 mm/min.

Samples with dimensions of 20 × 20 × 2 (mm^3), cut from composites processed from each pre-impregnated raw material, were submitted to interlaminar shear tests according to ISO 14130. These three point bending tests were conducted in a 50 kN universal testing machine by using an initial pre-load of 1 N at the crosshead speed of 1 mm/min and a 10 mm span between supports.

2.4.3. Calcination testing

Carbon and glass fibre composites mass content was determined by using calcination tests according to the EN ISO 1172. Composite samples, weighting approximately 2 g, were submitted to calcination inside a crucible in a muffle furnace during 10 min at 620 °C.

3. Results and discussion

Fig. 10 shows SEM micrographs of CF/PP and GF/PP towpregs samples. A good degree of adhesion between both carbon and glass fibres and the polymer powder particles was obtained. Also, a reasonable polymer powder distribution on the fibres was achieved at the optimised operating conditions.

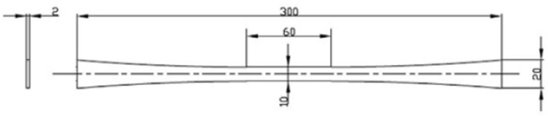


Fig. 9. Geometry of the tensile test specimens.

The cross-sections of the pultruded composites were studied under optical Microscopy. As can be seen from Fig. 11, all CF/PP composite profiles from towpregs (with and without additive) and PCT's have a reasonable distribution of the reinforcing fibres over the cross-sections. However, large differences in impregnation quality occur between the different samples that are likely to be related, directly, to the impregnation state of pre-impregnated materials used in pultrusion. It may be seen that the impregnation quality of the PCT composite samples is good, presenting almost all fibres completely surrounded ('wet-out') by the polymer. Only a few large dry spots were observed. This is most likely due to the good degree of impregnation already achieved in the PCT raw-material tape prior to the pultrusion step.

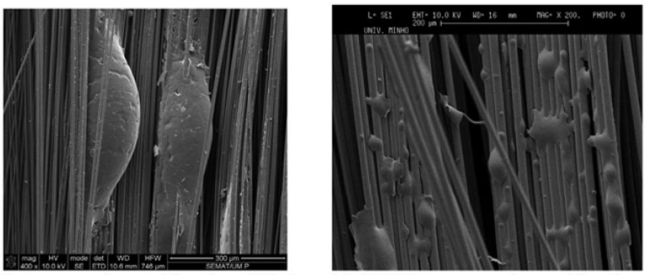
The samples from CF/PP towpreg with additive show a higher quantity of dry zones than the ones without additive. This could be due to some lack of compatibility between the fibre sizing and the used maleic anhydride coupling agent.

As Fig. 12 shows, it was still possible to distinguish discontinuities on the cross section of pultruded composites from GF/PP towpregs, where it may be seen zones very rich in polymer contrasting with others with much higher quantity of fibres.

The microscopy images taken from the samples of the pultruded composites using GF/PP PCT, TWINTEX® and GF/PP towpreg, are given in Table 12. All pre-impregnated materials lead to a reasonable distribution of the reinforcing fibres over the cross-sections, although small improvements in fibre distribution can be observed going from PCT through TWINTEX® to towpreg composites. A good fibre distribution means that the fibres are uniformly spread on the polymeric matrix, without significant agglomeration areas.

It may be seen that the impregnation quality of the PCT composite samples is excellent, presenting almost all fibres completely surrounded ('wet-out') by the polymer, hardly showing any dry spots in the pultruded samples.

The TWINTEX® -based samples also show a very good impregnation of the fibre. This is likely due to the intimate contact between the individual dry glass and PP fibres prior to the final pultrusion stage, making very small the effective remaining impregnation distance between polypropylene and glass fibres which leads to an easier consolidation. However, some larger dry spots were observed between the glass fibres at larger magnifications (see Table 12), showing an overall impregnation quality poor when compared with the one observed in the PCT tape based



a) CF/PP towpreg (magnification 400×) b) GF/PP towpreg (magnification 200×)

Fig. 10. Typical CF/PP and GF/PP towpreg SEM micrographs.

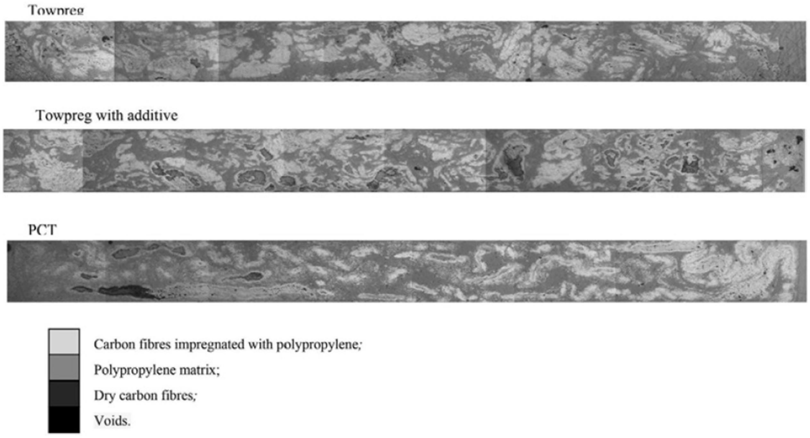


Fig. 11. Optical micrographs of the CF/PP pultruded profiles cross-sections (20 × 2 mm^2) (magnification of 6.25×).

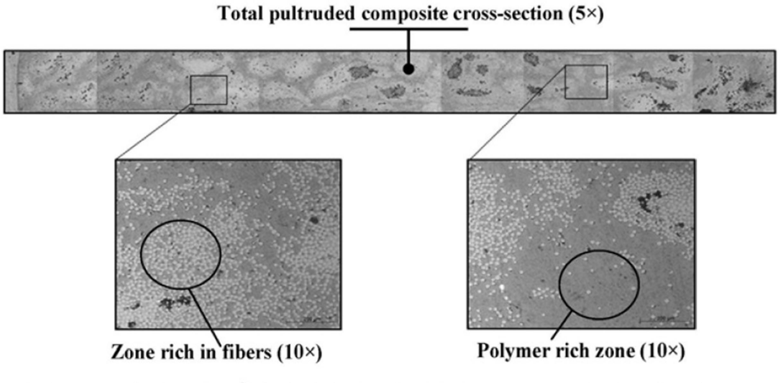
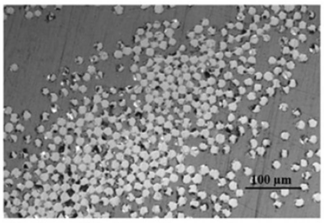
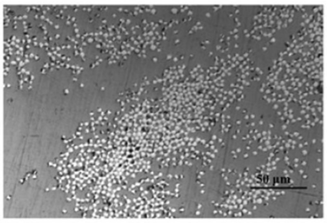
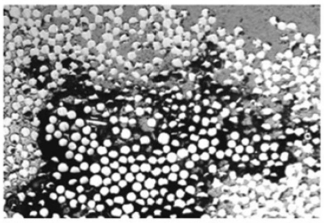
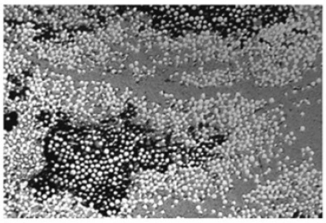
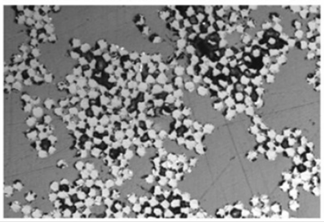
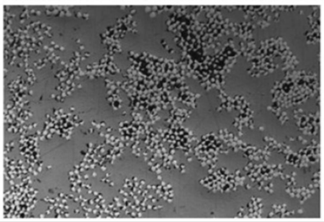


Fig. 12. Cross-section (20 × 2 mm^2) of pultruded profiles from GF/PP towpregs observed under optical microscopy.

pultruded composites. Finally, the depicted towpreg-based composite samples exhibit larger apparent dry zones. This is most likely due to the uneven distribution of the dry polymer powder in the towpreg, prior to pultrusion. It seems to be harder to bridge the large distances of dry glass fibre during pultrusion, which results on bigger unimpregnated zones in the pultruded composites.

Tables 13 and 14 summarize all experimentally results obtained from the CF/PP and GF/PP unidirectional composites processed by pultrusion, from the pre-impregnated products under study. To better evaluate and compare the mechanical properties obtained on the composites processed from the different pre-impregnated products studied, Tables 13 and 14 also present theoretical expected values and relative values of specific properties.

Table 12
Microscope images of GF/PP pultruded profiles.

Material	Magnification	
	250 ×	130 ×
PCT		
Towpreg		
TWINTEX®		

☐ Glass fibres ▨ Polypropylene matrix ■ Voids

The theoretical values of moduli, E, were directly obtained from the rule of mixtures using the raw-material properties presented in Tables 1–3, following the Eq. (2):

$$E = E_f \cdot \nu_f + E_p \cdot \left(1 - \nu_f\right) \tag{2}$$

where, E_f, E_p and ν_p are the fibre modulus, polymer modulus and fibre volume fraction, respectively.

As can be seen from Tables 13 and 14, the experimental moduli obtained from de CF/PP and GF/PP composites are in good agreement with the predicted theoretical ones. Some experimental values are even higher than the theoretical expected ones. This can be explained considering that the volume fraction content of some samples can be higher than the determined by the calcination tests.

Table 13
CF/PP composite mechanical test results.

Test type	Property		Pultrusion		
			Towpreg	Towpreg with additive	PCT
Flexural	Flexure Modulus (GPa)	Experimental	90.1 ± 0.4	87.6 ± 1.3	37.7 ± 2.2
		Theoretical	98.9	98.7	62.7
	Flexure Modulus/Fibre volume fraction (GPa)		178.1 ± 0.8	173.5 ± 2.6	118.2 ± 6.9
	Flexure Strength (MPa)	Experimental	241.2 ± 1.6	229.0 ± 7.3	158.7 ± 4.2
	Flexure Strength/Fibre volume fraction (MPa)		476.7 ± 3.2	453.5 ± 14.5	497.5 ± 13.2
Tensile	Tensile Modulus (GPa)	Experimental	110.6 ± 5.9	106.1 ± 6.3	63.5 ± 4.3
		Theoretical	98.9	98.7	62.7
	Tensile Modulus/Fibre volume fraction (GPa)		218.6 ± 11.7	210.1 ± 12.5	199.1 ± 13.5
	Tensile Strength (MPa)	Experimental	1060.8 ± 43.1	1129.3 ± 34.6	636.9 ± 38.4
	Tensile Strength/Fibre volume fraction (MPa)		2096.4 ± 85.2	2236.2 ± 68.5	1996.6 ± 120.4
Inter-laminar Shear	Interlaminar shear strength (MPa)		12.3 ± 0.3	13.0 ± 0.4	14.0 ± 0.2
Fibre volume fraction (%)			50.6	50.5	31.9

Table 14
Test results on the processed GF/PP composites.

Test type	Property		Pultrusion		
			Commingled fibres	Towpregs	PCT
Flexural	Flexure Modulus (GPa)	Experimental	26.2 ± 2.0	28.6 ± 0.9	16.8 ± 1.5
		Theoretical	23.8	33.1	19.1
	Flexure Modulus/Fibre volume fraction (GPa)		70.6 ± 5.4	54.9 ± 1.7	56.0 ± 5.0
	Flexure Strength (MPa)	Experimental	595.0 ± 24	158.0 ± 12.3	329.0 ± 30
	Flexure Strength/Fibre volume fraction (MPa)		1603.8 ± 64.7	303.3 ± 23.6	1096.7 ± 100
Tensile	Tensile Modulus (GPa)	Experimental	24.9 ± 1.1	33.9 ± 1.5	21.4 ± 1.5
		Theoretical	23.8	33.1	19.1
	Tensile Modulus/Fibre volume fraction (GPa)		67.1 ± 3.0	63.5 ± 2.9	71.3 ± 5.0
	Tensile Strength (MPa)	Experimental	545.9 ± 31.7	>336.3 ± 22.3	355.8 ± 53.2
	Tensile Strength/Fibre volume fraction (MPa)		1471.4 ± 85.4	>645.5 ± 42.8	1186.0 ± 177.3
Inter-laminar Shear	Interlaminar Shear Strength (MPa)		26.8 ± 1.7	7.5 ± 0.1	27.8 ± 0.6
Fibre volume fraction (%)			37.1	52.1	30.0

Using the proposed new geometry (Fig. 9) for the tensile test specimens, it was possible to reach failure loads and therefore determine their tensile strengths.

Analysing Table 13, one can conclude that composites processed from the CF/PP PCT's demonstrated to have better flexural and interlaminar shear strengths than those produced from CF/PP towpregs. From Table 14, it is possible to conclude that commingled fibres (TWINTEX®) presented, in general, better properties and had also shown to be more adjusted to commercial application demands and to be easily processed into final composites by the currently used manufacturing methods, probably due to their easy consolidation.

In any case, worse flexural strength and modulus results were found in GF/PP towpreg and GF/PP PCT's pultruded composites, respectively, when compared to TWINTEX®. These lower results obtained in the flexural tests are probably consequence of the inferior degree of impregnation observed in the towpreg based composites and, in the case of GF/PP PCT's based composites, result from the higher rich polymer regions exhibited by this material in its outside layers, decreasing the flexural properties.

Nevertheless, the GF/PP pre-impregnated products produced in our laboratories (towpregs and PCTs) have already demonstrated very good mechanical behaviour, namely, in terms of stiffness. In fact, the composites manufactured from these products presented experimental moduli values very closed to the theoretical expected ones. While composites processed from the PCTs demonstrated to have better mechanical strength, those produced from towpregs presented higher moduli. However, if the fibre volume fractions were considered, then the relative moduli (flexure modulus/fibre volume fraction) of PCT's and towpregs exhibit similar values. As mechanical strength values are more affected by small defects than those from moduli, the composites manufactured from PCTs seem to profit from the pre-consolidate state already presented by this product before final processing. Finally, it may be noted that none of the composites made from pre-impregnated materials reached failure in the three point bending interlaminar shear tests. This fact reveals the high degree of ductility exhibited by these materials which may be relevant for many applications. Thus, the interlaminar shear strength results shown in Tables 13 and 14 correspond to maximum force applied in the test.

Fig. 13 shows a typical force-displacement curves of the GF/PP composites tested specimens in the short beam shear test, from towpregs, PCT's and TWINTEX®. Those curves show that all specimens failed in plastic shear. Therefore, no breaking load could be obtained, which would allow the formal calculation of the interlaminar shear strength. Such results seem to show that a reasonable degree of adhesion between layers was obtained in the composites. Curves also show an obvious different behaviour between samples. While PCT tape and TWINTEX® pultruded composites have similar force-displacement behaviour, towpreg based samples showed lower performance. This is due to the results from the already mentioned limited degree of impregnation of these samples.

The flexural properties of composite materials under study were compared with those of common use and technical materials, in particular metals, polymers and polymer matrix composites and as it can be seen in Table 15 [20–25] the results of produced composites bars are higher than traditional materials, revealing a possible growing interest in its application.

4. Conclusions

The tests made using a proprietary pultrusion equipment already allow to conclude that is possible to produce, without major production problems, profiles from almost all available thermoplastic matrix pre-impregnated raw-materials using pull speeds of 0.3 m/min. Currently, work is carried out to increase the pultrusion processing speed to values in the range from 2 to 6 m/min. This will equalize the speed of the pultrusion line with that of the towpreg coating and PCT tape production lines. With the use of similar operational speeds in both processes (equipments) it will be possible, in future, combining them in one.

Existing powder-coating equipment was shown to be suitable to produce CF/PP and GF/PP towpregs that could be adequately processed into pultruded profiles. From the tests made, the towpregs can be easily and continuously produced at industrial production speeds between 2 a 6 m/min.

It was possible to optimize the production of CF/PP pultruded profiles and CF/PP towpregs, through the use of Taguchi/DOE

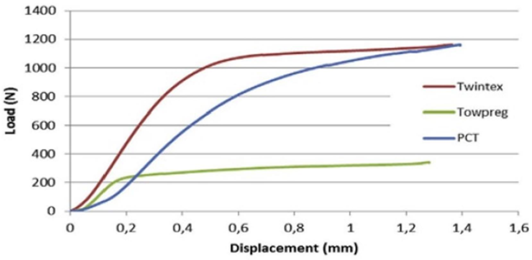


Fig. 13. Short beam test results of pultruded composites from GF/PP pre-impregnated materials.

Table 15
Compared the flexural properties of composite materials under study with those of common use and technical materials.

Material	Density (kg/m^3)	Flexural properties				
		Strength (MPa)	Specific strength (kN*m/Kg)	Modulus (GPa)	Specific modulus (MN*m/Kg)	Modulus$^{1/2}$/Density (GPa)$^{1/2}$/(Mg/m^3)
CF/PP (from towpreg) [66%][a]	1322.5	241.2	182.4	90.1	68.1	7.2
GF/PP (from towpreg) [76%][a]	1767.3	158.0	89.4	28.6	16.1	3.0
GF/PP (from Twintex®) [63%][a]	1519.0	595.0	391.7	26.2	17.2	3.4
CF/Epoxy laminate (from prepeg hand layup – AS4 continuous tows) [74%][a]	1560.0	1724.0	1105.1	134.0	85.9	7.4
Kevlar/Epoxy UD	1360.0	655.0	481.6	67.0	49.2	6.0
GF/PP compression moulded (from UD melt-impregnated prepegs) [60%][a]	1480.0	570.0	385.1	22.0	14.9	3.2
GF Pultrusion [60–80%][a]	2016.0–2288.0	345.0–552.0	171.1–241.3	31.0-41.0[e]	15.3–17.9	2.8–3.2
Stainless steel (304)[b]	8000.0	517.0[d]	64.6	193.0[e]	24.1	1.7
Carbon Steel (1020)[b]	7870.0	400.0[d]	50.8	206.0[e]	26.2	1.8
Aluminium alloy (5052-H34)[c]	2680.0	262.0[d]	97.8	70.0[e]	26.1	3.1
Aluminium alloy (3003-H14)[c]	2730.0	152.0[d]	55.6	69.0[e]	25.2	3.0
Aluminium (1100)[b]	2710.0	90.0[d]	33.2	69.0[e]	25.5	3.1
Epoxy	1150.0	110.0–115.0	95.7–100	3.0–3.2	2.6–2.8	1.5–1.6
Polyester	1200.0	80.0–123.0	66.7–102.5	3.0–3.5	2.9	1.5
PEEK	1292.0	110.2	85.2	3.9–2.8	2.2–3.0	1.4
PPS	1350.0	96.0–151.0	71.1–111.9	3.4–4.1	2.5–3.0	1.4–1.5
PA-6	1115.0	69.0–117.3	61.8–105.2	1.9–2.8	1.7–2.5	1.2–1.5
PC	1215.0	81.4–93.2	66.9–76.7	2.1–2.4	1.8–2.0	1.2–1.3
PP	909.5	44.8–55.2	49.3–60.7	0.8–1.7	0.9–1.7	1.0–1.4

[a] Fibre mass content.
[b] Annealed.
[c] At temper.
[d] Tensile strength.
[e] Tensile Modulus.

method, achieving optimal conditions. The addition of the compatibilizing agent (1% maleic anhydride) did not improve the polymer mass content in towpregs neither the mechanical properties on the final composites.

Three different commercial promising glass fibre reinforced thermoplastic matrix pre-impregnated materials were easily processed by pultrusion: a commercial available GF/PP commingled fibres product and also GF/PP towpregs and tapes manufactured in our own laboratories.

A process window was established for the production of PCT's and towpregs and for the processing of towpregs, PCT's and commingled fibres.

The mechanical properties of the composites processed from all those three GF/PP pre-impregnated (TWINTEX®, towpregs and PCT's) were determined and evaluated. All of them demonstrated to have mechanical properties compatible with the requirements of the major current structural engineering applications. In general, commingled fibres TWINTEX® presented slightly better mechanical properties and have shown to be more suitable for composite processing than the other pre-impregnated products.

In particular, very good agreement was found between the experimental moduli values of all composites produced and the theoretical ones.

More research must be done in order to increase the processing speeds of CF/PP and GF/PP towpregs as well as PCT's and to improve the impregnation, uniformity and dispersion of raw-materials in the composites.

The mechanical properties obtained in the pultruded composites allow predicting their adequate use either in general or structural engineering applications.

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5.8. Paper 6

Processing Thermoplastic Matrix Towpregs by Pultrusion

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ABSTRACT: In the work reported herein, glass fiber reinforced polypropylene towpregs, produced continuously at different processing conditions in a dry powder coating equipment (towpregger), were processed into final composite parts in a specially developed prototype pultrusion equipment. The influence of the towpregger fiber pull speed and the furnace temperature on the polymer content of the final towpregs was determined. The towpregs' quality was also assessed using optical microscopy and scanning electron microscopy. They were then processed into composite profiles in the pultrusion machine, and the influence of the pull speed and dies' temperatures on their mechanical and other relevant physical properties was studied. Finally, the best processing window and the optimization of the final composite profiles are discussed. © 2012 Wiley Periodicals, Inc. Adv Polym Techn 32: E306–E312, 2013; View this article online at wileyonlinelibrary.com. DOI 10.1002/adv.21279

KEY WORDS: Composites, Mechanical properties, Processing, Pultrusion, Thermoplastic matrix towpregs

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Introduction

Nowadays, thermosetting matrices are being successfully replaced by thermoplastics in continuous fiber reinforced composites for advanced applications. This trend led to more durable and recyclable products, with higher thermal and mechanical properties, not involving hazardous chemical reactions during processing.[1–7] Nevertheless, it was only recently that new technologies allowed the production of low-cost continuous fiber-reinforced preimpregnated thermoplastic raw materials. With these technologies, it is possible to replace the former expensive thermoplastic matrix prepregs (obtained by melting and solvent-based processes) by cheap dry commingled fibers[8–11] and powder-coated preimpregnated materials (towpregs).[5,12,13] Work is currently in progress to consolidate and process these new promising materials into final composite parts by using existing high throughput technologies, such as heated compression molding, filament winding, and pultrusion.[4,14–21]

In this work, a pultrusion equipment was built to continuously produce composite profiles from glass fiber reinforced polypropylene (GF/PP) towpregs that had been made in a proprietary dry coating equipment (towpregger).[5,22,23] The towpregs' processing window was optimized by varying the fiber pull speed and furnace temperature in the coating line and determining the influence of these parameters on the final polymer mass fraction. Two different pultrusion head tools (dies) were also designed to be used in the pultrusion equipment, allowing the production of profiles with two different shapes. Finally, the performance of the profiles was evaluated by mechanical testing. From the preliminary results obtained, it was concluded that they have adequate properties for application in common and structural engineering markets.

Experimental

POWDER COATING AND PULTRUSION EQUIPMENTS

The prototype powder coating equipment used to produce fiber-reinforced towpregs is schematically depicted in Fig. 1.[5,23] It consists of six main parts: a wind-off system, a fibers spreader unit, a heating section, a coating section, a consolidation unit, and a wind-up section. Initially, the reinforcing fibers are wound-off and pulled through a pneumatic spreader and then coated with polymer by heating in a convection oven and made to pass into a polymer powder vibrating bath. A gravity system allows maintaining the amount of polymer powder constant. The consolidation unit oven allows softening of the polymer powder, promoting its adhesion to the fiber surface. Finally, the thermoplastic matrix towpreg is cooled down and wound up on a spool.

Figure 2 shows a general overview of the existing powder coating equipment. Figures 3 and 4 depict a schematic and a photograph, respectively, of the pultrusion equipment developed in the present work.

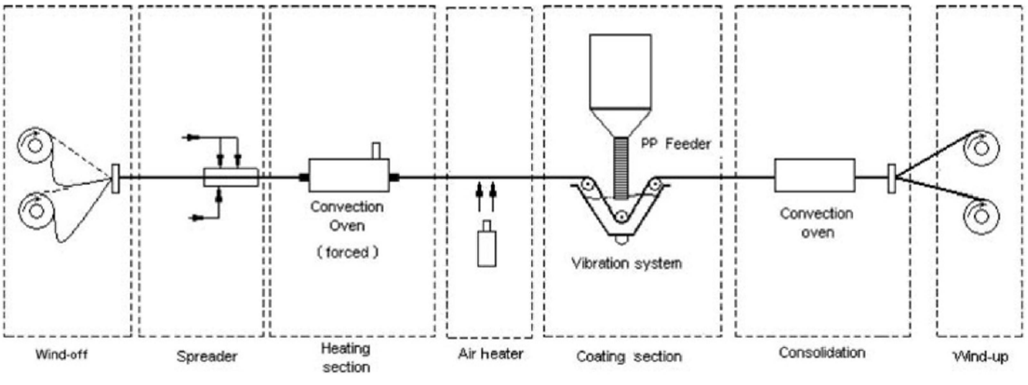

FIGURE 1. Schematic diagram of the powder coating line setup.

FIGURE 2. General overview of the powder coating equipment.

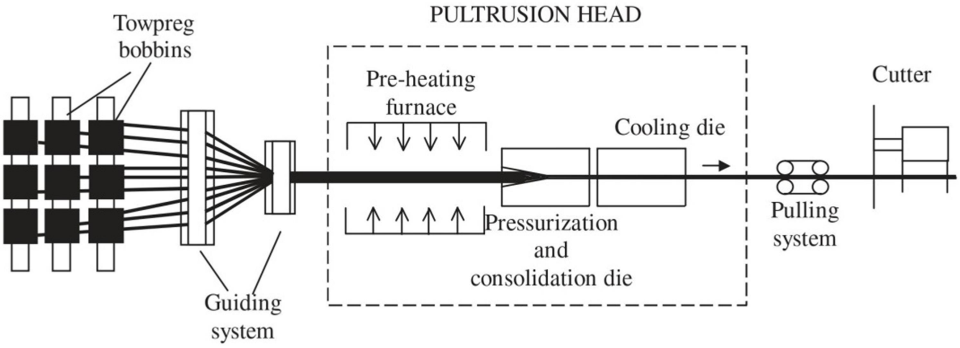

FIGURE 3. Schematic diagram of the proprietary pultrusion line.

FIGURE 4. Overview of the proprietary pultrusion equipment.

The 10-kN pultrusion line may be divided into five main parts:

- **i.** initial towpreg bobbins storing cabinet,
- **ii.** guiding system,
- **iii.** pultrusion head that includes a preheating furnace and the pressurization/consolidation and cooling dies,
- **iv.** pulling system, and
- **v.** the final profile cutting system.

To produce the composite profiles, the towpregs are guided into the preheating furnace, where the material is heated up to the required temperature. The towpregs then enter in the pultrusion die; in its first zone, the material is heated up and consolidated, and in the second it is cooled down to the required size. After solidification, the pultruded material is cut into specified lengths.

The preheating furnace, which may reach a temperature of 1000°C, was designed to allow processing almost every type of fiber/thermoplastic-based towpregs.

Two different groups of dies (pressurization/consolidation and cooling dies) were already designed. One produces the U-shaped profile shown in Fig. 5 and the other a 20 × 2 mm tape-shaped profile.

RAW MATERIALS

The GF/PP towpregs used in the present work were produced by using 2400 Tex type E glass fiber rovings and a polypropylene (ICORENE® 9184B P) from Owens Corning (Chambery, France) and ICO Polymers France (Montereau, France), respectively. The most relevant properties of both materials are summarized in Table I.

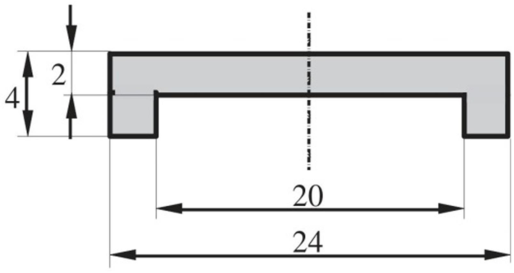

FIGURE 5. U-shaped profile considered in the die design.

TABLE I
Properties of the Raw Materials Used to Produce the GF/PP Towpregs

Property	Units	Glass Fibers	Polypropylene
Density	Mg/m^3	2.56	0.91
Tensile strength	MPa	3500	30
Tensile modulus	GPa	76	1.3
Average powder particle size	μm	–	440
Linear roving weight	Tex	2400	–

GF/PP TOWPREG PROCESSING CONDITIONS

Figure 6 shows the variation of the experimental polymer mass fraction determined in towpregs obtained with the coating line at different oven temperatures and fiber pull speeds. The determination was done by cutting and weighting 1-m length of towpreg strips and using the following expression:

$$\omega_{\mathrm{p}} = \left(1 - \frac{W_{\mathrm{f}}}{W_{\mathrm{T}}}\right) \times 100 \tag{1}$$

where ω_{p} is the polymer mass fraction (in%), W_{f} is the fiber roving linear weight per meter (in kg; see Table I), and W_{T} is the total weight measured per meter of towpreg (in kg).

As it may be seen in Fig. 6, the polymer mass fraction decreases with increasing fiber pull speed, as expected. Maxima polymer depositions were obtained when temperatures between 400 and 450°C were used in the convection oven. Such temperatures do not correspond to the actual towpreg

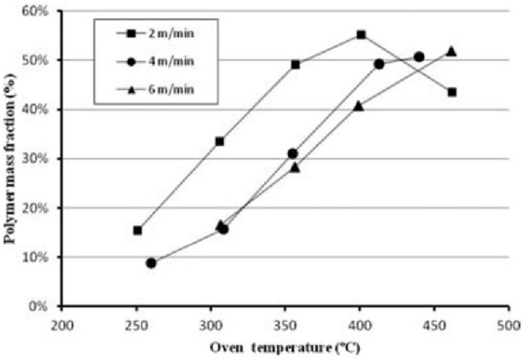

FIGURE 6. Variation of the polymer mass fraction with the oven temperature and fiber pull speed.

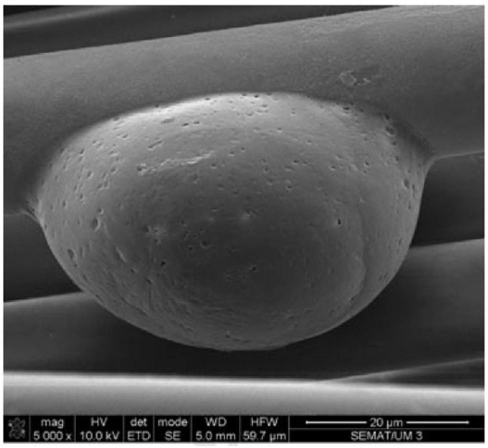

FIGURE 7. SEM micrograph of a polymer droplet adhered to a fiber in the towpreg (magnification of 5000×).

surface temperature, which is necessarily lower, but to that measured by the thermocouples inside the oven.

Several towpreg samples were analyzed under a Nova NanoSEM 200 scanning electron microscope (SEM) to evaluate the adhesion of the polymer powder to the fibers and its distribution. Figures 7 and 8 show SEM micrographs of towpreg samples produced using a temperature in the convection oven around 400°C and a fiber pull speed of 4 m/min. As may be seen, good polymer melting and adhesion (see Fig. 7) and a reasonable polymer powder distribution (see Fig. 8) on the glass fibers were achieved at these optimized operating conditions.

PULTRUSION

The GF/PP profiles were produced in the pultrusion equipment using the typical operating conditions presented in Table II.

TABLE II
Typical Pultrusion Operating Conditions

Variable	Units	Value
Pultrusion pull speed	m/min	0.2–0.8
Preheating furnace temperature	°C	160–250
Die temperature	°C	250–380
Cooling die temperature	°C	25–60

As may be seen, in the preliminary tests, it was already possible to produce GF/PP profiles in good conditions at pull speeds of 0.2 m/min. The optical micrograph in Fig. 9 shows that quite a homogeneous fiber/matrix distribution was obtained along the profile cross section.

Currently, experiments are increasing the pultrusion pull speed to values in the range between 2 and 6 m/min, which would enable producing the GF/PP profiles directly at the end of the dry coating towpreg line. In fact, the possibility of assembling a pultrusion head to the towpregger will be a major achievement of this future work. For this, it will be necessary to process the final GF/PP profiles at pulling speeds similar to those used in the towpreg equipment. This ultimate goal is yet to be achieved.

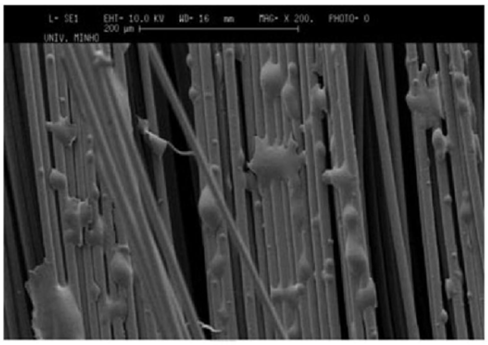

FIGURE 8. SEM micrograph showing the polymer powder distribution in the towpreg (magnification of 200×).

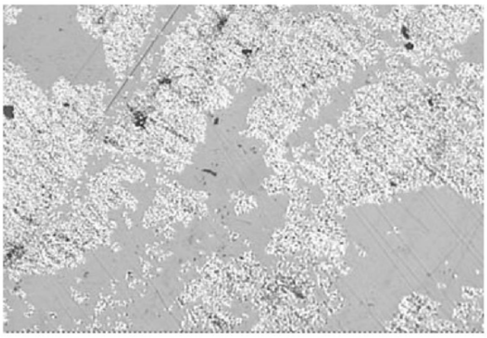

FIGURE 9. Optical micrograph of the pultruded profile cross section (magnification of 50×).

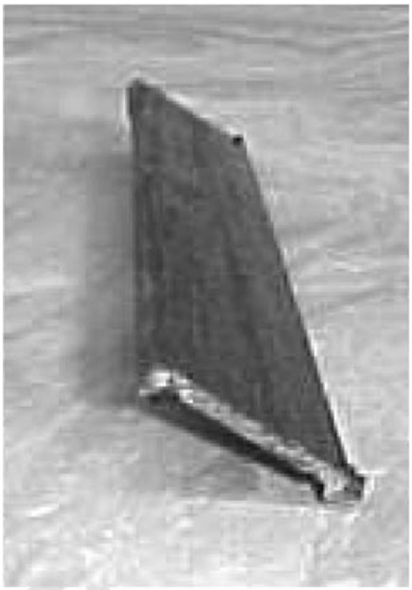

FIGURE 10. U-Shaped pultruded profile.

As shown in Fig. 10, the pultruded rectangular profiles present well-defined and smooth surfaces. However, some imperfections are still detectable (a few naked fibers can be observed on the surface), which seem to result from the nonuniform distribution of the polymer particles that had been observed in the initial towpregs.

MECHANICAL PROPERTIES OF THE PULTRUSION PROFILES

Table III presents the mechanical properties determined from flexural and tensile tests carried out on pultruded profiles with a fiber volume content around 55%. The fiber mass fraction and the flexural and tensile properties were determined in accordance with the ISO 1172, EN ISO 14125, and EN ISO 527-5 standards, respectively. For the former, specimens weighting approximately 20 g, cut from the profiles, were calcinated during 10 min at 600°C inside a Naberterherm® S30 muffle furnace (Naberterherm, Lilienthal, Germany). For the second determination, rectangular, 100 mm × 20 mm × 2 mm samples were submitted to three-point bending tests using an 80-mm support span, a cross-head speed of 1 mm/min and a 100-kN load cell in a Shimadzu® universal testing machine (Shimadzu Europa GmbH, Duisburg, Germany). The tensile tests were conducted on 250 mm × 15 mm × 2 mm rectangular samples, at a 2-mm/min cross-head speed, using the same equipment and load cell. A SG Shimadzu® 50–mm length strain gauge was used up to 0.3% strain to allow determining accurately the tensile modulus on each sample.

The tensile strength and modulus in the direction of the fibers of the GF/PP plates, σ_1 and E_1, respectively, were predicted from the fibers and polymer properties via the well-known law of mixtures:

$$\sigma_1 = \sigma_f v_f + \sigma_m (1 - v_f) \tag{2}$$

and

$$E_1 = E_f v_f + E_m (1 - v_f) \tag{3}$$

where σ_f, E_f, and v_f are the glass fibers' tensile strength, modulus, and volume fraction, respectively, and E_m and σ_m and are the matrix modulus and tensile strength at the fiber strain to break, respectively.

As can be seen from Table III, experimental strength results lower than the theoretical ones were obtained. In any case, such results seem to be compatible with the major commercial applications expected of GF/PP composites. On the contrary, the experimental moduli obtained are already in good agreement with the theoretical ones.

TABLE III
Mechanical Properties of GF/PP Composites

	Tensile Strength (MPa)		Tensile Modulus (GPa)		Flexural Strength (MPa)		Flexural Modulus (GPa)		Fiber Mass Fraction (%)		Fiber Volume Fraction (%)	
Kind of Data	Av.	SD	Av.	SD	Av.	SD	Av.	SD	Av.	SD	Av.	SD
Determined	>305	26	29.9	3.5	124.6	4.3	27.1	0.3	78.4	1.4	56.2	2.8
Theoretical	661.6	219	35.6	7.4	661.6	219	35.6	7.4				

Av.: average; SD: standard deviation.

Conclusions

An existing powder coating equipment was shown to be suitable to produce GF/PP towpregs that could be adequately processed into composite pultruded profiles. From the tests made, the towpregs can be easily and continuously produced at industrial production speeds between 2 and 6 m/min. An optimized oven temperature range between 400 and 450°C was determined for processing of these towpregs.

The preliminary tests made using a proprietary pultrusion equipment already allow producing profiles at pull speeds until 0.8 m/min. Currently, work is carried out to increase the pultrusion processing speed to values in the range from 2 to 6 m/min, which will allow using the same production rate in both pultrusion and powder coating equipments. In the future, the use of similar operational speeds in both processes (equipments) will make assembling them possible using just one equipment.

The mechanical properties of GF/PP profiles processed from these towpregs were also found to be adequate either for common or structural engineering applications. In particular, very good agreement was found between the experimental moduli and the theoretical ones.

Acknowledgment

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5.9. Conclusions

It has been possible to produce pultrude profiles from almost all available thermoplastic matrix pre-impregnated raw materials using pull speeds of 0.3 m/min. Currently, work is carried out to increase the pultrusion processing speed to values in the range from 2 to 6 m/min. This will equalize the speed of the pultrusion line with that of the towpreg coating and PCT tape production lines.

Existing powder-coating equipment was shown to be suitable to produce CF/PP, GF/PP towpregs and CF/PRIMOSPIRE® that could be adequately processed at industrial production speeds between 2 a 6 m/min and subsequently transformed into pultruded profiles.

It was possible to optimize the production of CF/PP pultruded profiles and CF/PP towpregs, through the use of Taguchi/DOE method, achieving optimal conditions. The addition of the compatibilizing agent (1% maleic anhydride) did not improve the polymer mass content in towpregs neither the mechanical properties on the final composites.

A process window was established for the production of PCT´s and towpregs and for the processing of towpregs, PCT's and commingled fibres.

The mechanical properties of the composites processed from all those three GF/PP pre-impregnated (TWINTEX®, towpregs and PCT´s) were determined and evaluated. All of them demonstrated to have mechanical properties compatible with the requirements of the major current structural engineering applications. In particular, very good agreement was found between the experimental moduli values of all composites produced and the theoretical ones.

More research must be done in order to increase the processing speeds of CF/PP and GF/PP towpregs as well as PCT's and to improve the impregnation, uniformity and dispersion of raw-materials in the composites.

Chapter 6

HEATED COMPRESSION MOULDING OF THERMOPLASTIC COMPOSITES

6.1. Introduction

Different raw-materials were used in the production of thermoplastic matrix pre-impregnated materials: those for parts in highly demanding markets were based on carbon fibres and PRIMOSPIRE® and those for more commercial composites on carbon fibres and polypropylene, as well as glass fibres with polypropylene.

Heated compression moulding and pultrusion were the processing methods used to obtain final composite parts. Thus, the efficient processing windows allowing producing continuously the thermoplastic matrix commingled fibres, towpregs, PCT´s and tapes and also transform them into composites were established [6.1-6.13].

The aim of *paper 1* was to study and compare the processing conditions and final mechanical properties of continuous glass-fibre reinforced polypropylene composites (GF/PP) manufactured by using available thermoplastic pre-impregnated materials produced by different methods. Pultrusion and compression moulding were the selected manufacturing methods for processing all these pre-impregnated materials into composite parts. To assess the quality of the three different GF/PP pre-impregnated materials, the final manufactured composite parts were finally submitted to mechanical testing and microscopy analysis. The obtained properties were compared between each other and to those theoretical ones that can be predicted by using the Classical Lamination Theory (CLT). The aim of *paper* 2 has been to produce and optimize the processing of carbon fibres thermoplastic matrix pre-impregnated materials (towpregs and PCT´s) by pultrusion and heated compression moulding. The optimization of those processes was made using the Taguchi Method - DOE for Design of Experiments which allowed making more rational choices of processing windows. The composite relevant mechanical properties were determined and discussed. Heated compression moulding and pultrusion were also used to produce composite plates and profiles in *paper 3*. The optimization of those processes was made by studying the influence of the most relevant processing parameters in the final properties of the produced carbon fibres thermoplastic matrix pre-impregnated materials and composites. The composite relevant mechanical properties were determined and the final composites were submitted to Dynamic Mechanical Analysis (DMA), Scanning Electron Microscope (SEM), optical microscopy and calcination tests. The determination of the fibre volume fraction of all studied composite was obtained comparing the results of thermogravimetric analysis (TGA), SEM and calcination tests. In the *paper 4*, four different pre-impregnated materials were used in this study: towpregs and tapes (PCT´s), both produced in our manufacturing lines and commingled fibres (TWINTEX®)) and tapes (CompTape®) supplied by external companies. The laboratory made pre-impregnated materials consisted of carbon and glass fibres and a polypropylene thermoplastic matrix. Pultrusion and heated compression moulding processes were used to obtain composite profiles and plates and were described in this paper. One interesting target to be achieved was the increase of pultrusion speeds to meet the industrial needs. This was possible particularly with the thermoplastic composite tape due to its consistency. Other aim was increasing the Tex of carbon fibre to study this effect in mechanical properties of CF/PP pultruded profiles from the towpregs. The composite relevant mechanical properties were determined and the final composites were observed by optical microscopy and calcination tests.

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6.2. Paper 1

THE 19TH INTERNATIONAL CONFERENCE ON COMPOSITE MATERIALS

PROCESSING CONDITIONS AND PROPERTIES OF CONTINUOUS FIBER REINFORCED GF/PP THERMOPLASTIC MATRIX COMPOSITES MANUFACTURED FROM DIFFERENT PRE-IMPREGNATED MATERIALS

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Keywords: *thermoplastic matrix composites; pre-impregnated; pultrusion; compressing molding; polypropylene; glass fibers; mechanical properties*

1 Introduction

The aim of the present work was to study and compare the processing conditions and final mechanical properties of continuous glass-fiber reinforced polypropylene composites (GF/PP) manufactured by using available thermoplastic pre-impregnated materials produced by different methods.

In the last years, thermoplastic matrices have been replacing with success thermosetting matrices in long/continuous fiber reinforced composites in almost markets due to the numerous advantages they present. However, it remains a challenge developing cost-effective technologies to allow wetting and impregnating fibers with thermoplastic matrices, characterized for being much more viscous than thermosets [1- 3].

Today, two major technologies are being used to allow wet reinforcing fibers with thermoplastic polymers [2, 3]: i) the direct melting of the polymer and, ii) the intimate fiber/matrix contact prior to final composite fabrication. Continuous fiber reinforced thermoplastic matrix pre-impregnated tapes are, for example, produced by direct melting processes. Alternatively, intimate contact processes allow producing cheap and promising pre-impregnated materials, such as, commingled fibers, co-woven fabrics and towpregs.

This work studies and compares the processability of final composite parts by using three different pre-impregnated materials produced by each one of both above mentioned wetting techniques. All studied pre-impregnated materials were based on a continuous glass fibers reinforced polypropylene matrix (GF/PP) system. One is a pre-consolidate tape (Fig. 1 b)) that was produced by the melting process (cross-head extrusion) in a previous work [4] and, from the other two produced by fiber/matrix intimate contact methods, one is a commercial available commingled fibers product (Fig. 1 c) and the other a towpreg (Fig. 1 a)) produced by our own developed dry coating prototype line [5]. Pultrusion and compression molding were the selected manufacturing methods for processing all these pre-impregnated materials into composite parts.

To assess the quality of the three different GF/PP pre-impregnated materials, the final manufactured composite parts were finally submitted to mechanical testing and microscopy analysis. The obtained properties were compared between each other and to those theoretical ones that can be predicted by using the Classical Lamination Theory (CLT).

2 Experimental

2.1 Raw Materials

The following raw materials were used to produce GF/PP pre-impregnated materials in the course of this work: i) a PP powder ICORENE 9184B P® and Type E glass fiber direct rovings 305E-TYPE 30® from the ICO Polymers and Owens Corning, respectively, were used to produce the GF/PP towpregs (Fig. 1 a)), ii) the PP Moplen RP348U® and the type E glass fiber roving TufRov 4599® from the Basell and PPG Industries, respectively, were used to manufacture the GF/PP tapes (Fig. 1 b)). Tables 1 and 2 present the properties of these raw-materials.

The commercial available Twintex® R PP 60 B 1870 FU from Owens Corning was the commingled fibers product used (see Fig. 1 c)). Table 3 shows properties of this product mentioned in the manufacturer datasheets.

Being well-known that maleic anhydride usually enhances the fiber/matrix adhesion [6-10], some batches of GF/PP towpregs were also produced using the PP powder (ICORENE 9184B P®) additivated with 1% mass content of maleic anhydride, S 47 29608 707® from Merck Schuchardt OHG, to confirm that effect.

2.2 Production of Thermoplastic Matrix Pre-Impregnated Products

The GF/PP towpregs were produced in a developed dry powder coating equipment schematically shown in Fig. 2 and illustrated in the photo of Fig. 3 [5, 11]. It consists of six main parts: wind-off system, fiber spreader unit, heating section, coating section, consolidation unit and a wind-up section. Initially, the reinforcing fibers are wound-off and pulled through a pneumatic spreader and then coated with polymer by heating in a convection oven and made to pass into a polymer powder vibrating bath. A gravity system allows maintaining the amount of polymer powder constant. The consolidation unit oven allows softening the polymer powder, promoting its adhesion to the fiber surface. Finally, the thermoplastic matrix towpreg is cooled down and wound-up on a spool.

To try maximizing the polymer powder content in the towpregs the following processing conditions were varied within the next ranges: i) convective oven temperature (ºC): 650 - 700; ii) Consolidation furnace temperature (ºC): 350 – 450; iii) Coating line pulling speed (m/min): 4 – 6.

The polymer mass fraction in the towpregs, ωp, was determined by weighting towpreg strips produced in those different conditions and using the following equation:

$$\omega_p = \frac{W_t - W_f}{W_t} \tag{1}$$

where Wt and Wf are the measured unit length weights of the towpreg strip and fiber roving, respectively.

From the polymer mass fractions obtained in produced towpreg strips it was possible to establish as optimal the following operating parameters: convective and consolidation oven temperatures of 700 ºC and 400ºC respectively, and a linear pulling speed of 6 m/min. In such operational conditions the GF/PP towpregs were continuously produced with polymer mass content of 30.0 % ± 7.2 %.

Unexpectedly, very low polymer mass fractions (~10 % - 16 %) were obtained when the PP powder add with 1% of maleic anhydride was used in the production of the GF/PP towpregs. Thus, the idea of using this additive to improve adhesion of the PP matrix to the glass fibers was abandoned.

The GF/PP pre-consolidated tapes (PCT) used in this work were, on other hand, produced in a cross-head extrusion equipment (see Fig. 4) from our own laboratories [4]. The core of this technology is an impregnation unit where the glass fibers are introduced, spread and impregnated by the polymer melt. Impregnation is achieved by building-up the pressure acting on the molten polymer trapped between the unit's spreading elements and the fiber rovings.

The apparatus consists of a creel holding system for fiber rovings, a guidance unit allowing an adequate transport of fiber into the impregnation section, an extruder to melt and feed the molten polymer into the impregnation unit, the impregnation unit itself and, subsequently, a cooling unit, a puller, and a take-up device where the composite tape is collected. An overview of main properties of the PCTs produced by this means is given in Table 4.

Today, some pre-consolidated thermoplastic matrix tapes (PCTs) produced in similar way are commercially available through the company Comp Tape Lda. [12].

2.3 Composites Processing

All three GF/PP pre-impregnated materials were then process into composite bar profiles and plates by pultrusion and heated compression molding, respectively. A prototype pultrusion line (Fig. 5) [13] and a 400 kN Moore hot platen press were used to all these fiber reinforced thermoplastic matrix pre-impregnated products.

2.3.1 Pultrusion

Our own developed 10 kN pultrusion equipment, schematic depicted in Fig.6, consists in five main parts: i) an initial towpreg bobbins holding cabinet; ii) guiding system; iii) pultrusion head, that includes a pre-heating furnace and the pressurization/consolidation and cooling dies; iv) pulling system and, v) the final profile cutting system.

To produce composite profiles, the pre-impregnated materials are guided into the pre-heating furnace to be heated up to the required temperature. Then, they enter in the pultrusion die to be heated up and consolidated to the required size in its first zone and, after cooled down in order to solidify. The pultruded material is then cut into specified lengths. The pre-heating furnace may reach a temperature of 1000 ºC and was designed to allow processing almost every type of fiber/thermoplastic-based pre-impregnated materials.

A rectangular 20 ×2 (mm) die was used in the present work to produce a tape-shaped thermoplastic matrix composite profile.

Twenty pre-impregnated towpreg rovings were used to process the rectangular 20 ×2 (mm) composite pultruded profiles from the towpregs. To determine the best processing window, the main processing conditions were varied following ranges by maintaining the cooling die at 25 ºC:

- pre-heating temperature (ºC): 170 - 180
- press./consolidation die temperature (ºC): 240 - 300
- linear pultrusion speed (m/min): 0.2 - 0.4

Results have shown that was not possible to produce in steady conditions pultruded profiles from towpregs at pultrusion speeds and pressurization/consolidation die temperatures higher than 0.3 m/min and 280 ºC, respectively.

By using higher values in these two parameters the process became unsteady mainly due to high level of fiber breakage between dies and reflux and accumulation of the thermoplastic polymer at entrances of the pressurization/consolidation and cooling dies, respectively (see Fig. 7).The same processing problems occurred when temperatures below 270º C were used in the pressurization/consolidation die and, because of that, it was decided maintaining constant the temperature of 280 ºC in this die.

By maintaining constant the temperatures in the cooling and pressurization/consolidation dies at 25 ºC and 280 ºC, respectively, composite profiles pultruded in different processing conditions were submitted to the flexural tests, as described in next paragraph 2.4, for optimizing the above mentioned processing variables in order to obtain the profiles presenting best mechanical performance. As may be seen from the obtained results summarized in Table 5, very similar values of flexural moduli and strengths were found by using pre-heating furnace temperatures and linear pultrusion pulling speeds in the ranges of 170 - 180 (ºC) and 0.2 - 0.3 m/min, respectively. While the slower pultrusion pulling speed of 0.2 m/min seemed to generate profiles with higher absolute values, this was not confirmed by the flexural properties divided by the determined fiber volume fraction depicted in two last the columns of Table 5. On the other hand, higher flexural strength values, both in absolute and relative terms, were obtained at the higher temperature of 180 ºC in pre-heating furnace.

Thus, it was concluded to use as optimal pultrusion operating window the following one:

- pre-heating temperature (ºC): 170 - 180
- press./consolidation die temperature (ºC): 280
- cooling die temperature (ºC): 25
- linear pultrusion speed (m/min): 0.2 - 0.3

The same above mentioned processing window was used to process, without major difficulties, rectangular 20 ×2 (mm) composite pultruded profiles from the both other thermoplastic matrix pre-impregnated materials studied in this work: the GF/PP tapes and Twintex® commingled fibers.

2.3.1 Heated Compression Molding

In the present work, all the three different GF/PP thermoplastic fiber reinforced pre-impregnated products studied were also processed into rectangular 180 × 180 × 2 (mm) composite plates.

After having been cut and weighted all pre-impregnated were introduced in a 180 × 180 (mm) cavity placed between the heated platen of a 400 kN

Moore press. After a 10 min delay at press platen temperature, the press was closed until reaching the maximum compression force of 200 kN. One minute after reaching the maximum force, the press platen were cooled down maintaining constant the press closing force. When the temperature of 30 ºC was reached, the press platen were opened and the final composite plate finally removed from the mold. Thus, the unidirectional fiber reinforced composite plates were produce by using the following processing conditions:

- press platen temperature (ºC): 250
- pre-heating time (min): 10
- press closing force (kN): 200
- delay at maximum closing force (min): 1.0
- opening platen temperature (ºC): 30

2.4 Composites Testing

The final manufactured composites were tested to determine their glass fiber mass content and flexural, tensile and interlaminar mechanical properties. Their cross-sections were also analyzed under optical microscopy to evaluate the fiber distribution and fiber/matrix adhesion.

2.4.1 Testing Procedures

Glass fiber mass content in the composites was determined by using calcination tests according to the EN ISO 1172 standard. After calcining the composite sample inside a crucible in a furnace at 600 ºC, the glass fiber mass fraction, ωf, was obtained by:

$$\omega_f = \frac{m_3 - m_1}{m_2 - m_{1_t}} \qquad (2)$$

where m_1, m_2 and m_3 are the measured crucible and composite sample plus crucible initial weights and the final measure weight of crucible plus residue.

Furthermore, by knowing the fiber and polymer densities, ρ_f and ρ_p, respectively, the fiber mass fraction (ω_f) may be converted in fiber volume fraction (v_f) by:

$$v_f = \frac{\omega_f/\rho_f}{\omega_f/\rho_f - (1-\omega_f)/\rho_{f_t}} \qquad (3)$$

Tensile tests were conducted according to the ISO 527 standard in a 100 kN Shimadzu universal testing machine at the crosshead speed of 2 mm/min using a 50 mm Shimadzu strain gauge. Well-known Eq. 4 was used to determine composite stress, σ, as:

$$\sigma = \frac{F}{S} \qquad (4)$$

where F and S are the measured force and sample cross section area, respectively.

The tensile modulus, E, was determined from the slope of the initial linear portion of the experimental stress/strain curve acquired from the tensile test.

Three-point flexural tests were also conducted on five 110 × 15 × 2 (mm) composite specimens, using 100 kN Shimadzu universal testing machine and a distance between supports of 80 mm, according to ISO 14125 standard at the crosshead speed of 1 mm/min. The flexure stress, σ_f, was determined from Eq. 5:

$$\sigma_f = \frac{3 \cdot F \cdot L}{2 \cdot l \cdot h^2} \qquad (5)$$

where F, L, l and h are the applied force, distance between supports and sample width and thickness, respectively.

The flexure modulus, E_f, was also determined by:

$$E_f = \frac{L^3 \cdot m_d}{4 \cdot l \cdot h^3} \qquad (6)$$

where m_d is the initial linear slope of the force versus displacement acquired from the flexural test.

Samples with dimensions of 20 × 15 × 2 (mm) cut from the compression molded composites plates were submitted to interlaminar shear tests according to ASTM D2344 standard. The tests were conducted in a 50 kN Shimadzu universal testing machine by using an initial pre-charge of 1 N at the crosshead speed of 1 mm/min and a 10 mm span between supports. The interlaminar shear strength, F_{SBS}, has been determined as:

$$F_{SBS} = 0.75 \cdot \frac{P_m}{b \cdot h} \qquad (7)$$

where P_m, b and h are the maximum failure force and the sample width and thickness, respectively.

2.4.2 Discussion of Results

Table 6 summarizes all results obtained from the unidirectional composites processed by pultrusion and compression molding from the pre-impregnated products under study. The high strength of unidirectional composite specimens didn´t permit break them in the tensile tests made in fiber direction due to grip slippage and, due to that, their respective tensile strengths are not shown in the table.

To better evaluate and compare the mechanical properties obtained on the composites processed from the different pre-impregnated products studied, Table 6 also presents theoretical expected values and relative values of those properties divided by the obtained fiber volume fraction, from which they are supposed to be linearly dependents.

The theoretical values of moduli, E, and strengths, σ_{ult}, were directly obtained from the rule of mixtures by using the raw-materials properties presented in Table 1 as can be seen in the following Eqs. 8 and 9:

$$E = E_f \cdot v_f + E_p \cdot (1 - v_f) \qquad (8)$$

$$\sigma_{ult} = \sigma_{fult} \cdot v_f + \sigma_{pult} \cdot (1 - v_f) \qquad (9)$$

where, E_f, E_p, σ_{fult}, σ_{pult} are the fiber modulus, polymer modulus and fiber and polymer matrix tensile strengths, respectively.

As the raw-materials presented in Table 1 were not used to manufacture the commingle fibers Twintex® and PCTs, the theoretical predictions for properties of the composites made from these materials may present more important deviations from the real values obtained.

Obtained results allow concluding that all the pre-impregnated products studied in this work presented enough good properties for being employed in the major commercial engineering structural applications.

From results in Table 6 is possible concluding that commingled fibers Twintex® presented, in general, better properties and had also shown to be more adjusted to commercial application demands and adapted for being easily processed into final composites by the currently used manufacturing methods, probably because they have already been available for longer time in the market.

Nevertheless, the GF/PP pre-impregnated products produced in our laboratories (towpregs and PCTs) have already demonstrated to have very good mechanical behavior, namely, in terms of stiffness. In fact, the composites manufactured from these products presented experimental moduli values very nearby the theoretical expected ones. While composites processed from the PCTs demonstrated to have better mechanical strength, those produced from towpregs presented higher moduli. As mechanical strength values are plus affected by small defects than those from moduli, the composites manufactured from PCTs seem to profit from the pre-consolidate state already presented by this product before final processing.

As Fig. 8 shows, under optical microcopy still was possible distinguish important discontinuities on the cross section of composites pultruded from towpregs, where it may be seen zones very rich in polymer contrasting with others with much greater quantity of fibers.

Finally, it may be noted that any of composites made from the towpregs and PCTs reached failure in the interlaminar shear tests. This fact reveals the high degree of ductility exhibited by these materials which may be relevant for many applications. Thus, the interlaminar shear strength results shown in Table 6 correspond to maximum force applied in the test. It must be also referred that values of interlaminar shear strength for composites processed from the commingled fibers Twintex® don´t appear on Table 6 because such composites were not submitted to interlaminar shear tests.

3 Conclusions

Three different commercial promising glass fiber reinforced thermoplastic matrix pre-impregnated materials were easily processed by pultrusion and compression molding in the present work: a commercial available GF/PP commingled fibers product and also GF/PP towpregs and tapes manufactured in our own laboratories.

The production of and processing of GF/PP towpregs and tapes were optimized.

The mechanical properties of the composites processed from all those three GF/PP pre-impregnated were determined and evaluated. All of them demonstrated to have mechanical properties compatible with the requirements of the major current structural engineering applications. In general, commingled fibers Twintex® presented slight better mechanical properties and have shown to be more adjusted for composite processing than the other pre-impregnated products due to be already for longer time in the market.

More research must be done to try increasing the processing speeds of GF/PP towpregs and tapes and improve the uniformity and dispersion of raw-materials in the composites made from the towpregs.

Acknowledgments

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Tables

Table 1. Properties of GF/PP Towpregs raw-materials

Property	**PP powder** (ICORENE 9184B P®)		**Glass fiber** (305E-TYPE 30®)	
	Manufacturer datasheet	Experimental	Manufacturer datasheet	Experimental
Linear density (Tex)	-	-	2400	-
Specific gravity (Mg/m^3)	910	910	2650	-
Tensile strength (MPa)	30[1]	19[1]	3500	1657
Young Modulus (GPa)	1.3	0.98	76	62.5
Poisson´s ratio	-	0.21	-	0.26
Average powder particle size (μm)	440	163	-	-
Average fiber diameter (μm)	-	-	17	13.7

[1] Yield Strength

Table 2. Properties of the raw-materials used to produce GF/PP tapes accordingly to manufacturers datasheets

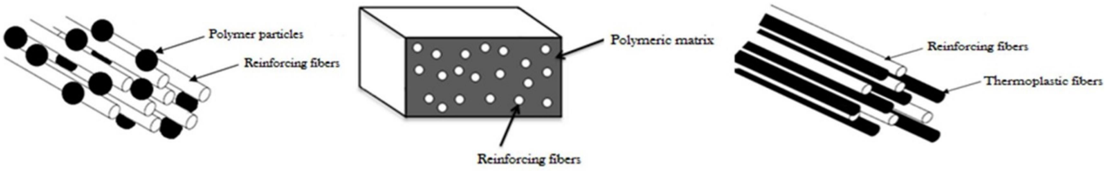
Property	**PP granules** (Moplen RP348U® from Basell)	**Type E Glass fiber roving** (TufRov 4599® from PPG)
Linear density (Tex)	-	2400
Specific gravity (Mg/m3)	900	2540-2600[2]
Tensile strength (MPa)	30[a]	1900-2400[2]
Young Modulus (GPa)	1.1	69-76[b]
Average fiber diameter (μm)	-	17

[a] Yield Strength
[b] Typical properties

Table 3. Twintex® R PP 60 B 1870 FU from Owens Corning

Property	**Values**
Linear density (Tex)	1870
Tensile strength (MPa)	760
Young Modulus (GPa)	29.5
Fiber mass content (%)	60

Figures



a) towpregs b) Pre-consolidate tapes (PCTs) c) Commingled fibers

Figure 1. GF/PP pre-impregnated products under studied

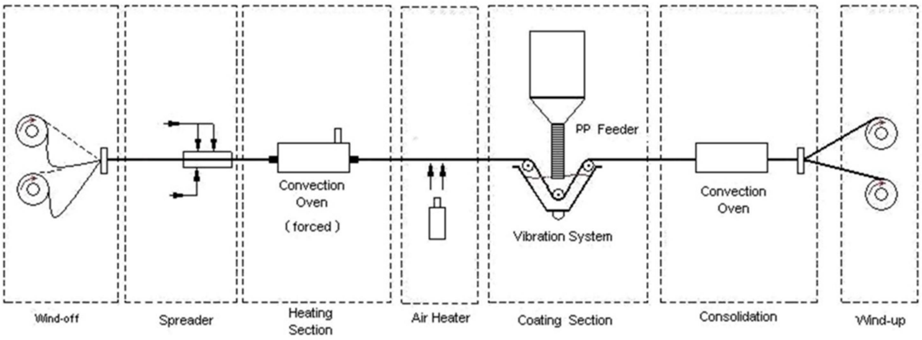


Figure 2. Powder coating line setup.

Figure 3. Prototype coating line equipment used to produce towpregs

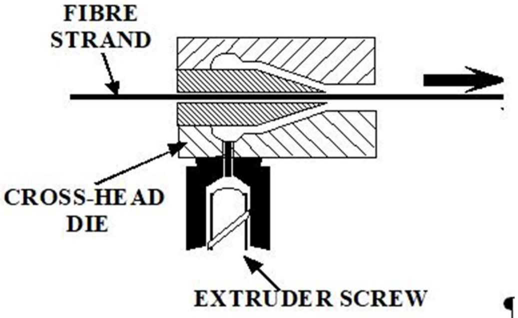


Figure 4. Cross-head extrusion die

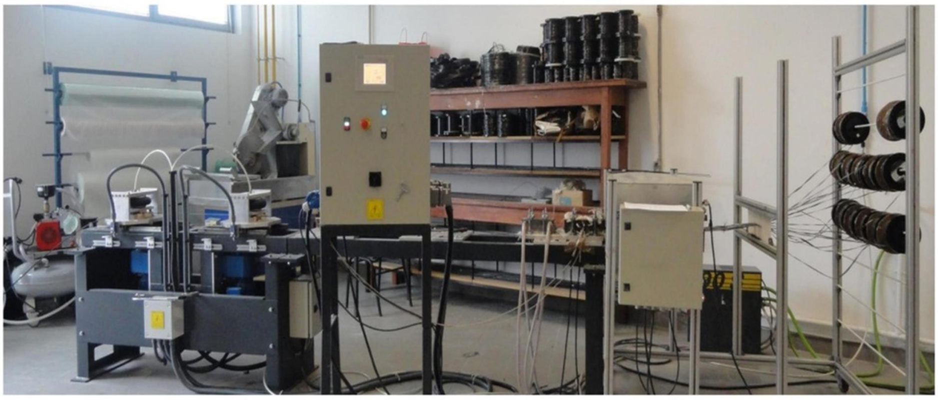


Figure 5. Developed prototype pultrusion line

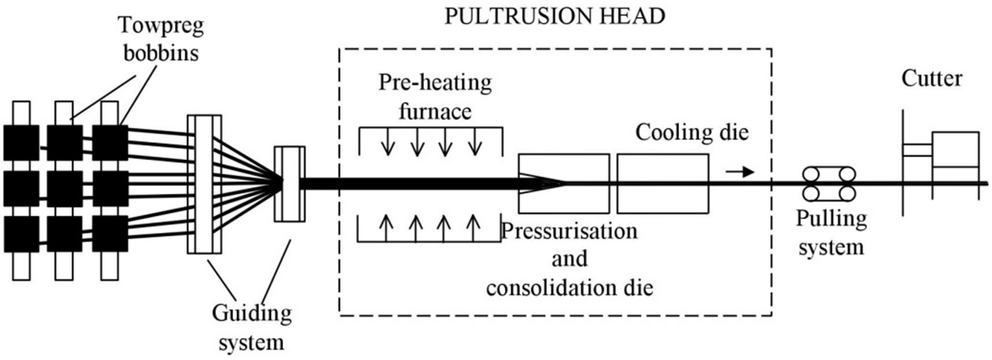
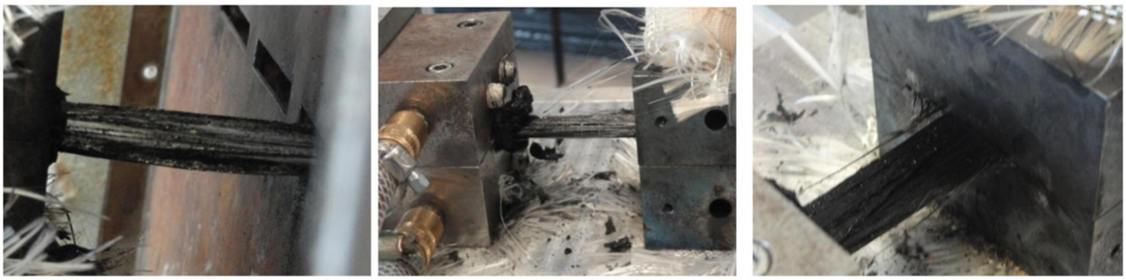


Figure 6. Schematic diagram of the pultrusion line.



a) polymer reflux at the entrance of pressurization/consolidation die

b) polymer accumulation at the entrance of cooling die

c) fiber breakage

Figure 7. Major pultrusion problems

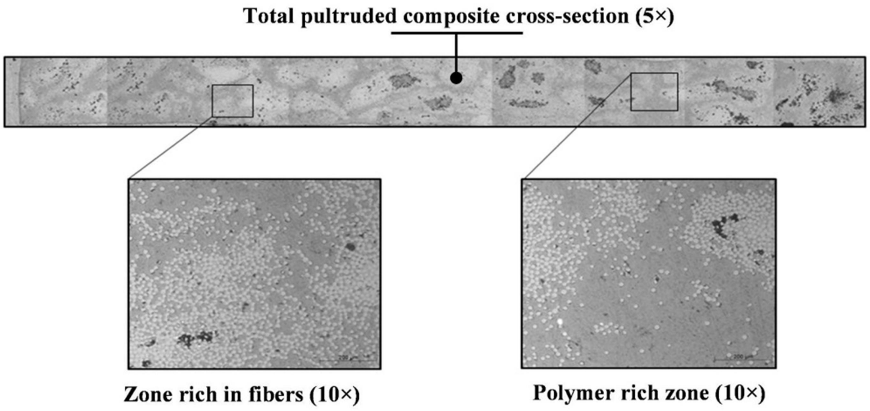


Figure 8. Cross-section of profile pultruded from towpregs observe under optical microscope

6.3. Paper 2

ECCM17 - 17th European Conference on Composite Materials
Munich, Germany, 26-30th June 2016

PROCESSING OF CARBON REINFORCED THERMOPLASTIC PRE-IMPREGNATED MATERIALS

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Keywords: carbon fibre, thermoplastic, towpreg, pultrusion, compression moulding

Abstract

The aim of this work is to produce and optimize the processing of carbon fibres thermoplastic matrix pre-impregnated materials (towpregs and PCT´s). Pultrusion and heated compression moulding were the selected manufacturing methods for processing all carbon fibres thermoplastic matrix pre-impregnated materials into composite parts.

The optimization of those processes was made by studying the influence of the most relevant processing parameters in the final properties of the produced carbon fibres thermoplastic matrix pre-impregnated materials and composites. The method of Taguchi / DOE (Design of Experiments) was used to achieve this aim as it allowed making more rational choices of processing windows.

The composite relevant mechanical properties were determined and studied. The final composites were also submitted to SEM microscopy analysis.

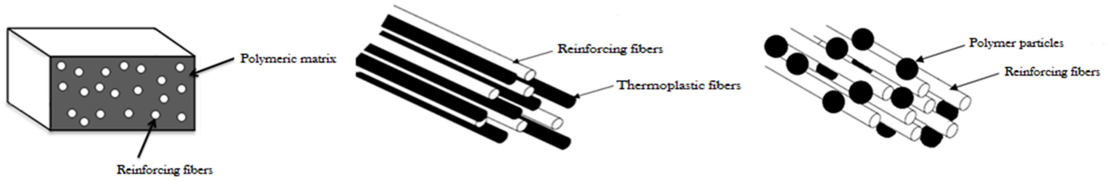
1. Introduction

Historically, thermoset resins have dominated the composite industry but thermosets start to be replaced by thermoplastics. Composites with thermoplastic matrices offer increased fracture toughness, higher damage tolerance, short processing cycle times and excellent environmental stability. They are recyclable, post-formable and can be joined by welding. The use of long/continuous fibre reinforced thermoplastic matrix composites involves, however, great technological and scientific challenges since thermoplastics present much higher viscosity than thermosettings, which makes much difficult and complex the impregnation of reinforcements and consolidation tasks [1-6].

Today, two major technologies are being used to allow wet reinforcing fibres with thermoplastic polymers: i) the direct melting of the polymer and, ii) the intimate fibre/matrix contact prior to final composite fabrication. Continuous fibre reinforced thermoplastic matrix pre-impregnated tapes (PCT´s) are, for example, produced by direct melting processes. Alternatively, intimate contact processes allow producing cheap and promising pre-impregnated materials, such as, commingled fibres and powder coated towpregs (Figure 1).

Different raw-materials were used in the production of thermoplastic matrix pre-impregnated materials: those to be used in parts for highly demanding markets were based on carbon fibres and Primospire® and those for more commercial composites on carbon fibres and polypropylene.

Heated compression moulding and pultrusion were the processing methods used to obtain final composite parts. Thus, the efficient processing windows allowing producing continuously the thermoplastic matrix towpregs and PCT´s and also transform them into composites were established.



a) Pre-consolidate tapes (PCTs) b) Commingled fibres c) towpregs

Figure 1. Pre-impregnated products under study.

2. Experimental

2.1. Raw Materials

The following raw materials were used to produce CF/PP pre-impregnated materials for this work: i) a PP powder ICORENE 9184B P® and carbon fibre roving M30 SC® from the ICO Polymers and TORAY, respectively, were used to produce the CF/PP towpregs, ii) PP powder Moplen RP348U® from Basell and the carbon fibre roving already mentioned were used to manufacture the CF/PP PCT tapes. On other hand, composite parts for highly demanding advanced markets were processed from towpregs manufactured by using a highly aromatic amorphous thermoplastic polymer in powder form, the PRIMOSPIRE® PR 120 from Solvay Advanced Polymers, and 760 Tex M30SC carbon fibre tows TORAY.

Tables 1 and 2 summarise relevant properties of the polypropylene, Primospire® and carbon fibres used in present work to produce pre-impregnated raw materials (towpregs and PCT´s).

Table 1. Properties of Towpregs and PCT powders raw-materials

Property	**PP powder** (ICORENE 9184B P®)		**Primospire®**		**PP granules** (Moplen RP348U ®)
	Manufacturer datasheet	Experimental	Manufacturer datasheet	Experimental	Manufacturer datasheet
Specific gravity (Mg/m^3)	0.91	0.91	1.21	-	0.90
Tensile strength (MPa)	Yield Strength 30	Yield Strength 19	207	104	Yield Strength 30
Young Modulus (GPa)	1.3	0.98	8.3	8.0	1.1
Poisson´s ratio	-	0.21	-		-
Average powder particle size (μm)	440	163	-	139	-
Glass transition temperature (T_g)	Typical value 0-20	-	158	156	Typical value 0-20
Melting temperature (T_m)	Typical value 170	166	-	-	Typical value 170

Table 2. Properties of Towpregs and PCT fibre raw-materials.

Property	**Carbon fibre** (TORAY M30 SC®)	
	Manufacturer datasheet	Experimental
Linear density (Tex)	760	-
Specific gravity (Mg/m^3)	1.73	-
Tensile strength (MPa)	5490	2731
Young Modulus (GPa)	294	194.5
Average fibre diameter	5	7.37

2.2 Production of Thermoplastic Matrix Pre-Impregnated Products

The dry powder coating equipment used to produce fibre reinforced towpregs is schematically depicted in Figure 2 [7-10].

The pre-consolidated tapes (PCT´s) used in this work were produced in a cross-head extrusion equipment (see Figure 3) from our own laboratories [10].

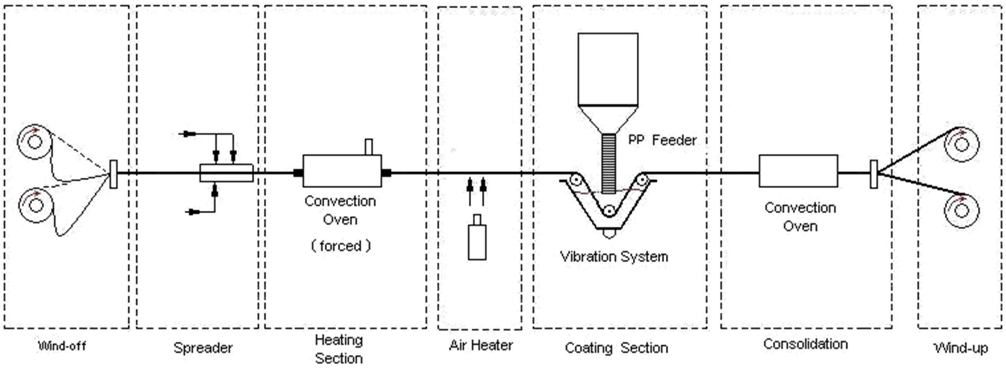


Figure 2. Powder coating line setup.

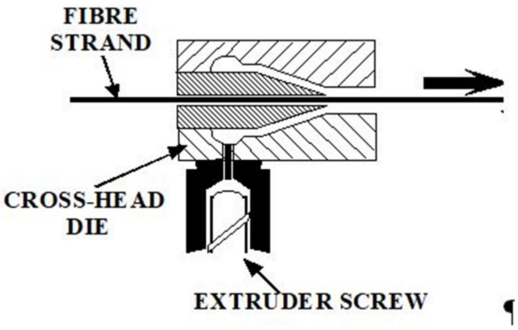


Figure 3. Cross-head extrusion die.

2.2.1. CF/PP and CF/Primospire® towpregs production

In order to optimize the production of CF/PP powder coated towpregs, different processing variables combinations were experimented and the number of trials optimized using the Taguchi approach. The studied operational parameters were:

- heating oven temperature (600, 650 and 700 ºC); consolidation oven temperature (350, 400 and 450 ºC); linear pull speed (4, 6 and 8 m/min).

The Taguchi approach was applied to the towpregs production process in order to obtain the condition that maximizes polymer powder content.

The polymer mass fraction in the towpregs was determined by weighting towpreg strips produced in those different conditions.

The optimal condition obtained from Taguchi method application led to the following operating parameters selection: heating oven temperature and consolidation oven temperatures of 700 ºC and 400ºC respectively, and a linear pulling speed of 6 m/min. Using this optimal operative condition, the amount of polymer should increase up to 45.6%. However, it was found that the average polymer content in continuous towpreg production was only 40.0%.

In order to produce CF/Primospire towpregs, the powder coating equipment was operated at different following woven temperatures and fibre linear pull speeds:

- heating oven temperature (700 ºC); consolidation oven temperature (500 - 550 ºC); linear pull speed (4 and 6 m/min). From such work the best values of the operational variables, which allow simultaneously producing towpregs in good and stable circumstances and having the maximum polymer powder content were:
- heating oven temperature - 700 ºC; consolidation oven temperature - 525 ºC and linear pull speed - 6 m/min. Using those conditions towpregs with a polymer mass content of approx. 40% were produced.

2.3 Pultrusion of pre-impregnated materials

The towpregs and PCT's were processed into composite bar profiles using the laboratorial pultrusion line, Figure 4 [7-10].

To produce composite profiles, the pre-impregnated materials are guided into the pre-heating furnace to be heated up to the required temperature. Then, they enter in the pultrusion heated die to be heated and consolidated to the required size and, after cooled down in the cooling die to solidify.

In this work, it was designed and manufactured a die to allow producing a 20×2 mm2 bar-shaped profile.

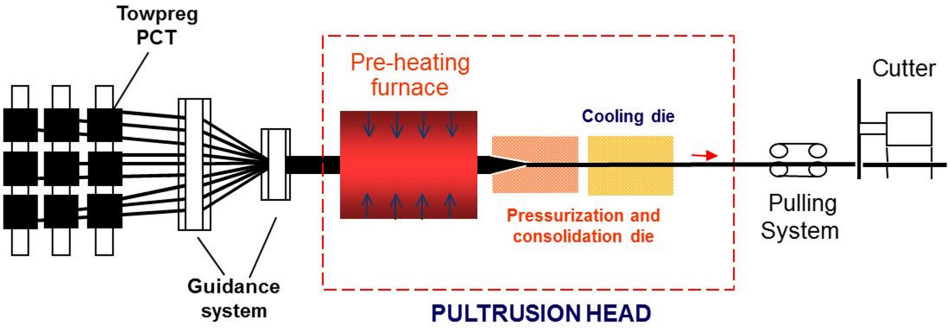


Figure 4. Schematic diagram of the pultrusion line.

Those profiles were manufactured from different pre-impregnated materials, using operating conditions in order to optimize the processing.

2.3.1 Towpreg processing

CF/PP towpregs were manufactured by pultrusion into composite bar profiles using the most relevant operating conditions. The Taguchi´s/DOE method was applied, maintaining the cooling die at 25 ºC, in order to optimize the processing parameters:

i) furnace temperature (160 or180 ºC); ii) heating die temperature (240 or 260 ºC); iii) linear pull-speed (0.2 or 0.3 m/min).

Results have shown that was not possible to produce, in steady, conditions pultruded profiles from towpregs at pultrusion speeds and consolidation die temperatures higher than 0.4 m/min and 260 ºC, respectively. By using higher values of these two parameters, the process became unsteady, mainly due to reflux and accumulation of the thermoplastic polymer at the entrances of the consolidation and cooling dies.

The found optimal operating conditions that maximize mechanical properties were: furnace and heated die oven temperatures of 160 ºC and 260ºC respectively, and a linear pulling speed of 0.2 m/min.

The CF/Primospire pultruded bars were produced in this work with the following operational conditions: i) furnace temperature (380 - 400 ºC); ii) heating die temperature (420 - 475 ºC); iii) linear pull-speed of 0.2 m/min.

2.3.2 Pre-consolidate tapes (PCT´s) processing

PCT´s were processed into rectangular 20×2 (mm2) bar using the already mentioned pultrusion equipment being operating conditions shown in Table 3.

Table 3. Pultrusion processing parameters for PCT´s.

Raw-material	Heated die temperature (ºC)	Cooled die temperature (ºC)	Furnace temperature (ºC)	Pulling speed (m/min)
CF/PP PCT	230	50	160	0.2

2.4. Compression moulding of CF/Primospire® towpregs

A technique described elsewhere [11] was used to produce unidirectional fibre reinforced laminate plates with 100×100×4 mm directly from the towpregs. First, the towpreg were wound over a plate with appropriate dimensions and the resultant pre-form then conveniently placed in the cavity of a heated mould. A 400 kN SATIM hot platen press was used to obtain the desired consolidation pressure. After heating the cavity, pressure was applied and, finally, the mould was cooled down to room temperature and the final composite laminate plate removed.

Table 4 shows the compression moulding conditions used to process composites from CF/Primospire® towpregs.

Table 4. Conditions used to process composites by compression moulding by using the towpregs.

Variable	Units	Values
		CF/Primospire® towpregs
Platen temperature	ºC	320
Compression pressure	MPa	20
Compression time	min	20
Final cooling temperature (at press opening)	ºC	30

2.4 Testing

2.4.1 Microscopy analysis

CF/PP and CF/Primospire® towpregs samples were characterized by scanning electron microscopy (SEM) to evaluate the adhesion of the polymer powder to the fibres and its distribution.

2.4.2 Mechanical testing

Bar samples were submitted to flexural, tensile and interlaminar testing according to the ISO standards 14125, 527 and 14130, respectively.

The mechanical properties were compared to the theoretical ones predicted by using the Rule of Mixtures (ROM).

Tensile tests were conducted, according to ISO 527, in a 100 kN universal testing machine at the crosshead speed of 2 mm/min using 180×20×2 mm^3 rectangular samples obtained from pultrusion.

The tensile modulus was determined from the slope of the initial linear portion of the experimental stress/strain curve. A SG Shimadzu® 50 mm length strain-gauge was used up to 0.3% strain, for accurate determination of the tensile modulus.

Three-point flexural tests were also conducted on five 100 × 20 × 2 mm^3 pultruded profiles specimens and 100 × 15 × 4 mm^3 for the compression moulded samples, using 100 kN universal testing machine and a distance between supports of 80 mm, according to ISO 14125, at a crosshead speed of 1 mm/min.

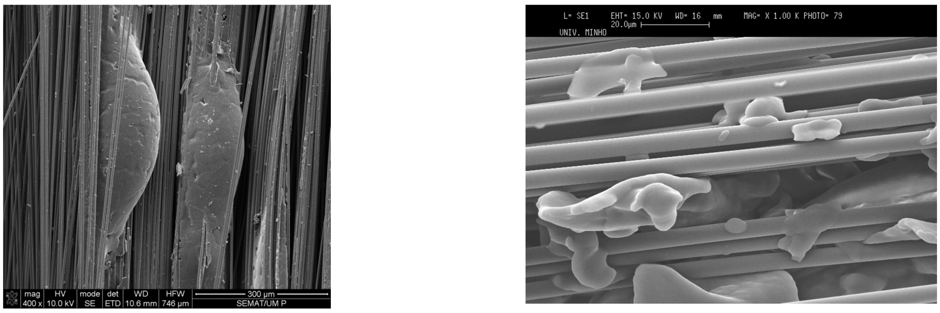
Samples with dimensions of 20 × 20 × 2 (mm3), cut from composites processed from each pre-impregnated raw material, were submitted to interlaminar shear tests according to ISO 14130. The tests were conducted in a 50 kN universal testing machine by using an initial pre-load of 1 N at the crosshead speed of 1 mm/min and a 10 mm span between supports.

2.4.3 Calcination testing

CF/PP composites fibre mass content was determined by using calcination tests according to the EN ISO 1172. Composite samples, weighting approximately 2 g, were submitted to calcination inside a crucible in a muffle furnace during 10 min at 625º C.

3. Results and Discussion

Figure 5 show representative SEM micrographs of the studied CF/PP and CF/Primospire® towpregs.



CF/PP towpreg (magnification 400×). CF/Primospire® towpreg (magnification 1000×).

Figure 5 - Micrographs of Carbon/Primospire® towpreg under SEM.

As may be seen, most of the polymer particles exhibit bigger size than the fibre diameter and, even after heating, the polymer particles present an irregular shape. It is also possible to observe that some degree of adhesion between fibres and polymer powder was achieved, especially in the case of CF/PP towpregs.

Tables 5 and 6 summarize all experimentally results obtained from the CF/PP and CF/Primospire® composites processed by pultrusion from the pre-impregnated products under study. To better evaluate and compare the mechanical properties obtained on the composites processed from the different pre-impregnated products studied the tables also present theoretical expected values and relative values of specific properties.

As can be seen from Tables 5 the experimental moduli obtained from de CF/PP composites are in good agreement with the predicted theoretical ones. Some experimental values are even higher than the theoretical expected ones. This can be explained considering that the volume fraction content of some samples can be higher than the determined by the calcination tests.

Analysing Table 5, one can conclude that composites processed from the CF/PP PCT´s demonstrated to have better flexural and interlaminar shear strengths than those produced from CF/PP towpregs. Concerning the interlaminar shear tests, the CF/Primospire® composites shown a much higher value than CF/PP probably due to the better mechanical properties that the Primospire® matrix exhibits. As it may be seen and expected, the CF/Primospire® towpregs required the use of much higher temperatures than the CF/PP ones in pre-heating furnace and pressurization/consolidation die. Due to such higher temperatures, tests still continue being done to optimise the operational conditions and, consequently, the obtained mechanical properties.

Finally, it may be noted that any of composites made from pre-impregnated materials under study reached failure in the interlaminar shear tests. This fact reveals the high degree of ductility exhibited by these materials which may be relevant for many applications. Thus, the interlaminar shear strength results shown in Tables 5 and 6 correspond to maximum force applied in the test.

As may be seen from Table 7, flexural properties compatible with the applications envisaged for the composites processed by compression moulding from the produced towpregs were obtained in this work.

Table 5. CF/PP composite mechanical test results.

Test Type	**Property**		***Pultrusion***	
			Towpreg	***PCT***
Flexural	Flexure Modulus (GPa)	Experimental	90.1±0.4	37.7±2.2
		Theoretical	98.9	62.7
	Flexure Modulus / Fibre volume fraction (GPa)		178.1±0.8	118.2±6.9
	Flexure Strength (MPa)	Experimental	241.2±1.6	158.7±4.2
	Flexure Strength / Fibre volume fraction (MPa)		476.7±3.2	497.5±13.2
Tensile	Tensile Modulus (GPa)	Experimental	110.6±5.9	63.5±4.3
		Theoretical	98.9	62.7
	Tensile Modulus / Fibre volume fraction (GPa)		218.6±11.7	199.1±13.5
	Tensile Strength (MPa)	Experimental	1060.8±43.1	636.9±38.4
	Tensile Strength / Fibre volume fraction (MPa)		2096.4±85.2	1996.6±120.4
Inter-laminar Shear	Interlaminar Shear Strength (MPa)		12.3±0.3	14.0±0.2
Fibre volume fraction (%)			50.6	31.9

Table 6. Test results on the processed CF/Primospire® composites.

Test Type	**Property**	**Pultrusion**
		CF/Primospire® towpreg
Flexural	Flexure Modulus (GPa)	56.1±2.9
	Flexure Strength (MPa)	253.6±16.1
Tensile	Tensile Modulus (GPa)	92.2±5.6
	Tensile Strength (MPa)	839.2±28.7
Inter-laminar Shear	Interlaminar Shear Strength (MPa)	25.4±2.1
Fibre volume fraction (%)		~ 45%

Table 7. Properties of composite plates made by compression moulding from the CF/Primospire® towpregs.

Property	**Units**	**Compression moulding CF/Primospire®**
Flexural strength	MPa	124.3±15.0
Flexural modulus	GPa	30.0±5.0
Fibre mass fraction	%	59.7±0.3

4. Conclusions

The tests made using a proprietary pultrusion equipment already allow to conclude that is possible to produce, in good conditions, profiles from almost all available thermoplastic matrix pre-impregnated raw-materials using pull speeds of 0.3 m/min.

Existing powder-coating equipment was shown to be suitable to produce CF/PP and CF/Primospire® towpregs that could be adequately processed into pultruded profiles. From the tests made, the towpregs can be easily and continuously produced at industrial production speeds between 2 a 8 m/min.

It was possible to optimize the production of CF/PP pultruded profiles and CF/PP towpregs, through the use of Taguchi/DOE method, achieving optimal conditions.

In particular, for CF/PP pultruded profiles, very good agreement was found between the experimental moduli values of all composites produced and the theoretical ones.

More research must be done in order to increase the processing speeds of CF/PP and CF/Primospire® towpregs as well as PCT's and to improve the impregnation, uniformity and dispersion of raw-materials in the composites.

CF/Primospire® composites obtained by pultrusion showed a higher value for the interlaminar strength than all other ones. Due to higher processing temperatures, further tests should be done to optimise the operational conditions and further improve the obtained composite mechanical properties.

The mechanical properties obtained in all pultruded composites allow predicting their adequate use either in general or structural engineering applications.

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6.4. Paper 3

ECCM18 - 18th European Conference on Composite Materials
Athens, Greece, 24-28th June 2018

COMPRESSION MOLDING OF PULTRUDED CARBON REINFORCED THERMOPLASTIC COMPOSITES

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Keywords: carbon fiber; thermoplastic towpreg; pultrusion; compression molding; composite

ABSTRACT

Historically, thermoset resins have dominated the composite industry but they start to be replaced by thermoplastics. In this study two different thermoplastic matrix carbon reinforced pre-impregnated materials were used, one produced in our laboratories (towpreg) and another obtained from co-extrusion process (PCT). Carbon fibre and two different thermoplastic matrices (polypropylene and PRIMOSPIRE®) were selected for the production of the pre-impregnated materials.

Heated compression moulding and pultrusion were the two manufacturing technologies used to obtain composite plates and profiles for study. The optimization of those processes was made by studying the influence of the most relevant processing parameters in the final properties of the produced carbon fibres thermoplastic matrix pre-impregnated materials and composites.

The composite relevant mechanical properties were determined and the final composites were submitted to Dynamic Mechanical Analysis (DMA), Scanning Electron Microscope (SEM), optical microscopy and calcination tests.

The determination of the fiber volume fraction of all studied composite was obtained comparing the results of thermogravimetric analysis (TGA), SEM and calcination tests.

1. Introduction

Composites with thermoplastic matrices offer increased fracture toughness, higher damage tolerance, short processing cycle times and excellent environmental stability. They are recyclable, post-formable and can be joined by welding. The use of long/continuous fibre reinforced thermoplastic matrix composites involves, however, great technological and scientific challenges since thermoplastics present much higher viscosity than thermosettings, which makes much difficult and complex the impregnation of reinforcements and consolidation tasks [1-4].

Today, two major technologies are being used to allow wet reinforcing fibres with thermoplastic polymers [5]: i) the direct melting of the polymer and, ii) the intimate fibre/matrix contact prior to final composite fabrication. Continuous fibre reinforced thermoplastic matrix pre-impregnated tapes (PCT´s) are, for example, produced by direct melting processes. Alternatively, intimate contact processes allow producing cheap and promising pre-impregnated materials, such as, commingled fibres and powder coated towpregs.

Pultrusion was the selected manufacturing method for processing all these pre-impregnated materials into composite parts. It is a versatile continuous high speed production technology, allowing the production of fibre reinforced complex profiles. The optimization of the pultrusion process was made by studying the influence of the most relevant processing parameters in the final properties of the produced pre-impregnated materials and composites [5-8].

The produced profiles were then processed by heated compression moulding into composite plates that can be used for manufacturing complex shapes.

The final composite parts were also submitted to interlaminar and flexural tests, as well as calcination, optical microscopy and SEM. The experimental results were compared with theoretical ones that can be predicted by using the ROM (Rule Of Mixtures).

The determination of the fibre volume fraction of a composite with a high melting temperature thermoplastic polymer used as matrix was obtained comparing the results of thermogravimetric analysis (TGA) with the calcination tests.

2. Experimental

2.1. Raw Materials

The following raw materials were used to produce CF/PP pre-impregnated materials for this work: i) a PP powder ICORENE 9184B P® and carbon fibre roving M30 SC® from the ICO Polymers and TORAY, respectively, were used to produce the CF/PP towpregs, ii) PP powder Moplen RP348U® from Basell and the carbon fibre roving already mentioned were used to manufacture the CF/PP PCT tapes. On other hand, composite parts for highly demanding advanced markets were processed from towpregs manufactured by using a highly aromatic amorphous thermoplastic polymer in powder form, the PRIMOSPIRE® PR 120 from Solvay Advanced Polymers, and 760 Tex M30SC carbon fibre tows TORAY.

2.2 Production of Thermoplastic Matrix Pre-Impregnated Products

A dry powder coating equipment was used to produce fibre reinforced towpregs [7-8].

The optimal condition obtained from Taguchi method application led to the following operating parameters selection for the production of CF/PP towpregs: heating oven temperature and consolidation oven temperatures of 700 ºC and 400ºC respectively, and a linear pulling speed of 6 m/min. Using this optimal operative condition, the amount of polymer should increase up to 45.6%. However, it was found that the average polymer content in continuous towpreg production was only 40.0%.

In order to produce CF/PRIMOSPIRE® towpregs, the powder coating equipment was operated at the following processing conditions: 700 ºC for the heating oven temperature, 525 ºC for the consolidation oven temperature and a linear pull speed of 6 m/min. Using those conditions towpregs with a polymer mass content of approx. 40% were produced.

The pre-consolidated tapes (PCT´s) used in this work were produced in a cross-head extrusion equipment from our own laboratories [7-8].

2.3 Pultrusion of pre-impregnated materials

The towpregs and PCT’s were processed into composite bar profiles using the laboratorial pultrusion line [7-8].

To produce composite profiles, the pre-impregnated materials are guided into the pre-heating furnace to be heated up to the required temperature. Then, they enter in the pultrusion heated die to be heated and consolidated to the required size and, after cooled down in the cooling die to solidify.

In this work, it was designed and manufactured a die to allow producing a 20×2 mm^2 bar-shaped profile.

Those profiles were manufactured from different pre-impregnated materials, using operating conditions in order to optimize the processing.

2.3.1 Towpreg processing

CF/PP towpregs were manufactured by pultrusion into composite bar profiles using the most relevant operating conditions. The Taguchi´s/DOE method was applied in order to optimize the processing parameters. The found optimal operating conditions that maximize mechanical properties were: furnace and heated die oven temperatures of 160 ºC and 260ºC respectively, and a linear pulling speed of 0.2 m/min.

The CF/PRIMOSPIRE® pultruded bars were produced in this work with the following operational conditions: i) furnace temperature (380 - 400 ºC); ii) heating die temperature (420 - 475 ºC); iii) linear pull-speed of 0.2 m/min.

2.3.2 Pre-consolidate tapes (PCT´s) processing

PCT´s were processed into rectangular 20×2 (mm2) bar using the already mentioned pultrusion equipment being operating conditions shown in Table 1.

Raw-material	Heated die temperature (ºC)	Cooled die temperature (ºC)	Furnace temperature (ºC)	Pulling speed (m/min)
CF/PP PCT	230	50	160	0.2

Table 1. Pultrusion processing parameters for PCT´s

2.4 Heated compression moulding of pultrusion profiles

The different CF/PP and CF/PRIMOSPIRE thermoplastic fiber reinforced pre-impregnated profiles produced by pultrusion were also processed into rectangular 200×200×2 mm^3 composite plates.

The pultruded bars were introduced in a 200 × 200 (mm) cavity placed between the heated platen of a 200 kN GISLÓTICA S. A. heated plate press. For the production of CF/PP plates, after a 10 min delay at press platen temperature, the press was closed until reaching the maximum compression force of 200 kN. One minute after reaching the maximum force, the press platens were cooled down maintaining constant the press closing force. When the temperature of 30ºC was reached, the press platen was opened and the final composite plate finally removed from the mold. In the case of CF/PRIMOSPIRE plates, the mould was closed and heated until 315 ºC. Then pressure was applied during 10 minutes and after the cooling cycle was initiated. The mould was opened at 30 ºC. Heated compression moulding cycle variables are summarized in table 2.

Variable	Units	Values	
		CF/PP Towpregs and PCT	CF/PRIMOSPIRE® towpregs
Platen temperature	ºC	250	315
Compression force	kN	200	10
Compression time	min	1	10
Final cooling temperature (at press opening)	ºC	30	30

Table 2. Conditions used to process composites by compression moulding.

2.5 Testing

2.5.1 Microscopy analysis

To determine the impregnation quality and to evaluate the fibre distribution and fibre/matrix adhesion of the thermoplastic composites, their cross-sections were studied under optical microscopy (CF/PP) and under by SEM-scanning electron microscopy (CF/PRIMOSPIRE®).

2.5.2 Mechanical testing

Bar samples were submitted to flexural and interlaminar testing according to the ISO standards 14125 and 14130, respectively. The mechanical properties were compared to the theoretical ones predicted by using the Rule of Mixtures (ROM).

Three-point flexural tests were also conducted on 100×20×2 mm^3 using 100 kN universal testing machine and a distance between supports of 80 mm, according to ISO 14125, at a crosshead speed of 1 mm/min.

Samples with dimensions of 20×20×2 mm^3, cut from composites processed from each pre-impregnated raw material, were submitted to interlaminar shear tests. The tests were conducted in a 50 kN universal testing machine by using an initial pre-load of 1 N at the crosshead speed of 1 mm/min and a 10 mm span between supports.

2.5.3 TGA tests

The determination of mass fractions of composites made from carbon fibre and polymer with high temperature resistance like PRIMOSPIRE® is difficult and usually assessed by image processing techniques. Standard calcination tests are the mostly used with glass-reinforced plastics composites.

In this work, we used calcination tests for the evaluation of fibre mass fraction on carbon fibre and PRIMOSPIRE® composites, but since there's only a partial degradation of reinforcement and matrix, this method couldn't be applied directly as in the case of glass-reinforced plastics composites.

In order to obtain carbon fibre and PRIMOSPIRE® temperature degradation behaviour TGA test were carried out using a thermo-gravimetric balance TA Q500 under different atmospheres (inert, oxidative and air).

In tests made under inert (N_2), oxidative (O_2) and air atmospheres, carbon fibres and polymer samples were heated from 30/40/60ºC until 900ºC using a 10ºC/min constant heating rate.

Being air the atmosphere in the muffle furnace for calcination, TGA tests were also carried out under the same condition.

Polypropylene polymer matrix was also submitted to TGA tests with air as atmosphere to evaluate its degradation behaviour which is a relevant parameter to the determination of the processing conditions of composites that uses this polymer.

To avoid weight loss due to air flow, this was not used in all TGA tests performed with air atmosphere.

2.5.4 Calcination testing

Calcination tests were carried on the CF/PRIMOSPIRE® composites using results obtained from the TGA tests since this polymer matrix exhibits high temperature resistance and so is not fully eliminated on conventional calcination tests.

Initially, matrix (PRIMOSPIRE®) and reinforcement (CF) mass loss curves as a function of time resulting from the TGA tests were evaluated. This analysis concluded that the temperature 700 ºC was a good compromise between the end of PRIMOSPIRE® high degradation rate and the beginning of significant carbon fibre mass loss.

In order to simulate TGA behaviour calcination tests were performed on the constituents of the studied composite using the same thermal cycle (10° C/min) until the temperature of 700 ºC was reached. The initial mass of the samples, placed in a ceramic crucible, was approximately 2 g in accordance with the conventional standard.

CF/PP composites fibre mass content was determined by using calcination tests according to the EN ISO 1172. Composite samples, weighting approximately 2 g, were submitted to calcination inside a crucible in a muffle furnace during 10 min at 625ºC.

2.5.5 DMA tests

A Dynamic Mechanical Analysis Triton TRITEC 2000 was used to obtain the elasticity modulus dependence on temperature of the CF/PP PCT. The specimen, with 40×5×1 mm^3 , was used in the three point bending configuration having a span of 30 mm. Temperature was increased at a rate of 5 ºC per minute, from ambient until 155 ºC.

3. Results and Discussion

The cross-sections of the pultruded composites were studied under optical Microscopy and SEM. As can be seen from Figures 1 and 2, all CF/PP and CF/PRIMOSPIRE® composite profiles from towpregs and PCT´s have a reasonable distribution of the reinforcing fibres over the cross-sections. However, large differences in impregnation quality occur between the different samples that are likely to be related, directly, to the impregnation state of pre-impregnated materials used in pultrusion. It may be seen that the impregnation quality of the PCT composite samples is good, presenting almost all fibres completely surrounded (‘wet-out’) by the polymer. Only a few large dry spots were observed. This is most likely due to the good degree of impregnation already achieved in the PCT raw-material tape prior to the pultrusion step. In the case of PCT tape based composites, its outside layers exhibited richer polymer regions.

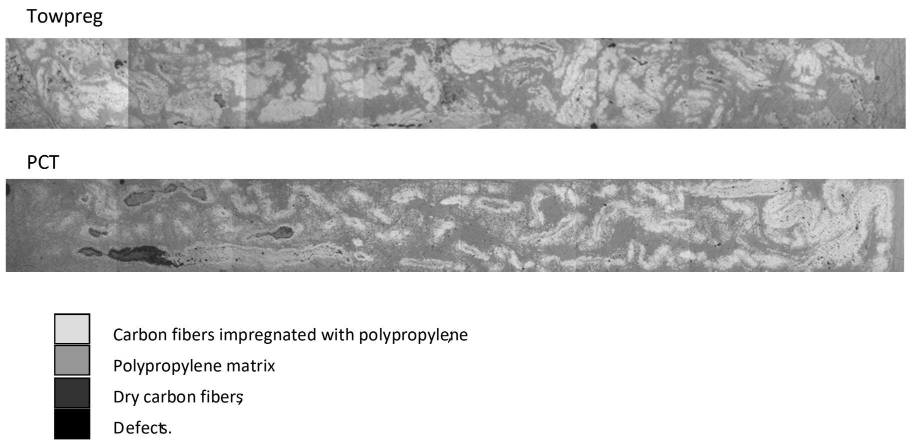

Figure 1. Optical micrographs of pultruded profiles cross-section (magnification of 8.75×)

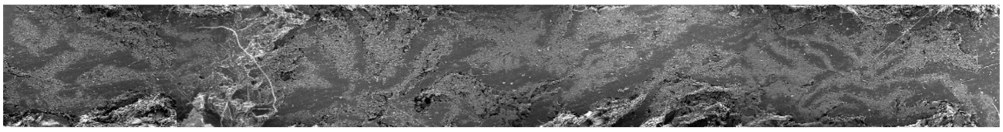

Figure 2. SEM image of CF/PRIMOSPIRE® pultruded profile cross-section sample (magnification of 40×)

The results obtained for carbon fibre and PRIMOSPIRE® TGA tests under air atmosphere (Figure 3) show that the degradation behaviour is between the one found for inert and oxidative atmospheres.

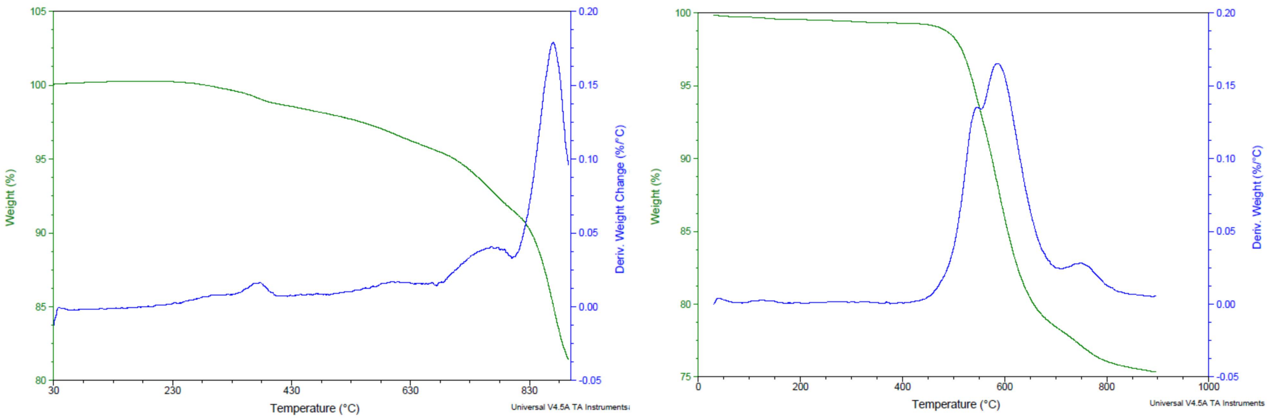

Figure 3. TGA results carried out on carbon fibres (left) and PRIMOSPIRE® (right) under air atmosphere

The results obtained in the calcination were similar to those of the TGA tests. The calcinations of PRIMOSPIRE® and carbon fibres at 700 ºC allowed establishing 25.9% and 7.2% as average mass losses, respectively, and as a consequence, the proportion of the remaining mass was 74.1% (*wp*) and 92.8% (*wf*) In TGA tests, the average mass loss of carbon fibre and PRIMOSPIRE® was 21.55% and 5.97%, respectively. Then, it was applied to the composite the same calcination parameters that were used for the testing of their constitutive materials.

After calcining the composite sample, the carbon fibre mass fraction, wfc, was obtained by:

$$wfc = 1 - \frac{mc_f - wf \cdot mc_i}{mc_i \cdot (wp - wf)} \qquad (1)$$

where mc_i and mc_f are the measured composite sample initial and final weights, respectively. Also, *wf* and *wp* are the carbon fibre and PRIMOSPIRE® remaining mass fractions, respectively.

Furthermore, by knowing the fibre and polymer densities, ρ_f and ρ_p, respectively, the fibre mass fraction (*wfc*) may be converted in fibre volume fraction (*vf*) by:

$$vf = \frac{\frac{wfc}{\rho f}}{\frac{wfc}{\rho f} + \frac{(1 - wfc)}{\rho p}} \qquad (2)$$

The composite calcination test obtained results allow determining the fibre mass fraction as 54.1% corresponding to a fibre volume fraction of 45.2%.

Those results were confirmed using the image processing software ImageJ. Using this software, the obtained fibre volume fraction was 44.7%.

Concerning polypropylene TGA tests, it was found that the degradation temperature was about 400 ºC.

Tables 3 and 4 summarize all experimentally results obtained from the CF/PP and CF/PRIMOSPIRE® composites processed by pultrusion and heated compression moulding from the pre-impregnated products under study. To better evaluate and compare the mechanical properties obtained on the composites processed from the different pre-impregnated products studied. The tables also present theoretical expected values and relative values of specific properties.

As can be seen from Table 3 the experimental moduli obtained from de CF/PP towpreg composites are in good agreement with the predicted theoretical ones.

The heated compression moulding results show an increasing of the mechanical strength properties when compared to the ones obtained by pultrusion, possibly due to a better consolidation. Also, the elastic modulus exhibits no significant variations.

Still analysing Table 3, one can conclude that composites processed from the CF/PP PCT´s demonstrated to have better flexural and interlaminar shear strengths than those produced from CF/PP towpregs.

Concerning the interlaminar shear tests in the pultrusion bars, the CF/PRIMOSPIRE® composites have shown a much higher value than CF/PP probably due to the better mechanical properties that the PRIMOSPIRE® matrix exhibits. As it may be seen and expected, the CF/PRIMOSPIRE® towpregs required the use of much higher temperatures than the CF/PP ones in pre-heating furnace and pressurization/consolidation die. Due to such higher temperatures, tests still continue being done to optimise the operational conditions and, consequently, the obtained mechanical properties.

Finally, it may be noted that any of composites made from pre-impregnated materials under study reached failure in the interlaminar shear tests. This fact reveals the high degree of ductility exhibited by these materials which may be relevant for many applications. Thus, the interlaminar shear strength results shown in Tables 3 and 4 correspond to maximum force applied in the test.

Test Type	**Property**		***Pultrusion***		***Compression***	
			CF/PP Towpreg	***CF/PP PCT***	***CF/PP Towpreg***	***CF/PP PCT***
Flexural	Flexure Modulus (GPa)	Experimental	90.1±0.4	37.7±2.2	88.7±1.4	42.9±3.2
		Theoretical	98.9	62.7	99.3	79.0
	Flexure Modulus / Fibre volume fraction (GPa)		178.1±0.8	118.2±6.9	174.6±2.8	106.2±7.9
	Flexure Strength (MPa)	Experimental	241.2±1.6	158.7±4.2	267.4±21.4	226.4±20.0
	Flexure Strength / Fibre volume fraction (MPa)		476.7±3.2	497.5±13.2	526.4±42.1	560.4±49.5
Inter-laminar Shear	Interlaminar Shear Strength (MPa)		12.3±0.3	14.0±0.2	13.3±0.2	15.9±0.4
Fibre volume fraction (%)			50.6	31.9	50.8	31.6

Table 3. CF/PP composite mechanical test results

Test Type	**Property**	**CF/PRIMOSPIRE® towpreg**	
		Pultrusion	**Compression**
Flexural	Flexure Modulus (GPa)	56.1±2.9	39.8±3.3
	Flexure Strength (MPa)	253.6±16.1	142.0±9.4
Inter-laminar Shear	Interlaminar Shear Strength (MPa)	25.4±2.1	19.6±4.2
Calcination	Fibre volume fraction (%)	45.2±5.3	37.7±5.9

Table 4. Test results on the processed CF/PRIMOSPIRE® composites

As can be seen in table 4, the flexural properties of the compression moulding plates are considerable lower than those obtained in the pultruded profiles. This is probably explained by the use of a mixture of different manufacturing conditions profiles and to a non-optimized heated compression moulding processing cycle variables.

The theoretical values of moduli, using the pultrusion results, were directly obtained from the rule of mixtures. In the case of CF/PRIMOSPIRE® composites, it was possible to estimate the fibre volume fraction as approximately 45%. This result is in good agreement whit the one obtained from calcination test (45.2).

As can be seen in figure 4, the elastic modulus at room temperature is in accordance with the one obtained from flexural tests. Also, as it would be expected, the elastic modulus decreases gradually with temperature.

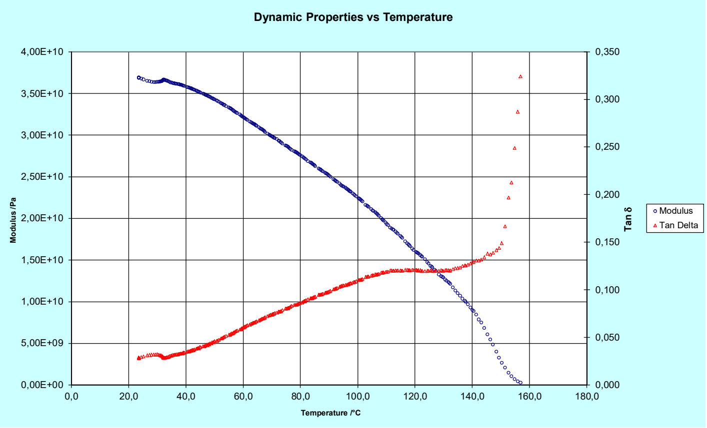

Figure 4. DMA test results for CF/PP PCT.

4. Conclusions

The tests made using proprietary pultrusion equipment already allow to conclude that it is possible to produce, in good conditions, profiles from almost all available thermoplastic matrix pre-impregnated raw-materials using pull speeds of 0.3 m/min.

In particular, for CF/PP pultruded profiles, very good agreement was found between the experimental moduli values of all composites produced and the theoretical ones.

The compression moulding results obtained in CF/PRIMOSPIRE composites need to be further studied in order to achieve better mechanical properties. In the case of CF/PP composites produced by heated compression moulding, they reveal good mechanical properties and can be applied for the manufacture of complex shapes.

More research must be done in order to increase the processing speeds of CF/PP and CF/PRIMOSPIRE® towpregs as well as PCT's and to improve the impregnation, uniformity and dispersion of raw-materials in the composites.

CF/PRIMOSPIRE® composites obtained by pultrusion showed a higher value for the interlaminar strength than all other ones. Further tests should be done to optimise the operational conditions and to improve the obtained composite mechanical properties.

The calcination tests based on the results obtained from TGA tests reveal to be a very interesting method to experimentally determine composite mass fractions in the case of temperature resistant materials used as matrix and reinforcement.

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6.5. Paper 4

ACM4 - 4th Fourth International Symposium on
Automated Composites Manufacturing
Montreal, Canada, 25-26th June 2019

PULTRUSION AND COMPRESSION MOULDING OF THERMOPLASTIC PRE-IMPREGNATED MATERIALS REINFORCED BY CONTINUOUS GLASS FIBRES

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ABSTRACT

Four different pre-impregnated materials were used in this study: towpregs and tapes (PCT´s), both produced in our manufacturing lines and commingled fibres (TWINTEX®) and tapes (CompTape®) supplied by external companies. The laboratory made pre-impregnated materials consisted of carbon and glass fibres and a polypropylene thermoplastic matrix.
Pultrusion and heated compression moulding processes were used to obtain composite profiles and plates and were described in this paper. The optimization of those processes was made by studying the influence of the most relevant processing parameters – preheating, heating and cooling inside the die and speed for the pultrusion, and heating temperature, pressure and time for compression moulding - in the final properties of the produced carbon and glass fibres thermoplastic matrix pre-impregnated materials and composites. One interesting target to be achieved was the increase of pultrusion speeds to meet the industrial needs. This was possible particularly with the thermoplastic composite Tape due to its consistency. The composite relevant mechanical properties were determined and the final composites had optical microscopy and calcination tests.

KEYWORDS

Thermoplastic composites; towpreg; pultrusion; compression molding; composite tape

1. INTRODUCTION

Two major technologies were used to allow wet reinforcing fibres with thermoplastic polymers [1, 2-4]: i) the direct melting of the polymer and, ii) the intimate fibre/matrix contact prior to final composite fabrication. Continuous fibre reinforced thermoplastic matrix Tapes and PCT´s are, for example, produced by direct melting processes using a cross-head extrusion technique [5]. Intimate contact processes allow producing commingled fibres and powder-coated towpregs. Sometimes, thermoplastic compatibilizers are added to the matrices to improve their adhesion and facilitate impregnation to reinforcements [6].

The processability of different pre-impregnated materials produced by each one of the above mentioned impregnation techniques into final composites was studied. Pultrusion and heated compression moulding were the selected manufacturing methods for processing. The pultrusion optimization was made by studying the influence of the most relevant processing parameters in the final properties of the produced pre-impregnated materials and composites, using the Taguchi method. A similar methodology was used to process pultruded rectangular profiles into composite plates by heated compression moulding [7-9].

2. EXPERIMENTAL

2.1. Raw Materials

Table 1 – TWINTEX® R PP 60 B 1870 FU from Owens Corning (W_f 60%)

Property	Values
Linear density (Tex)	1870
Tensile strength (MPa)	760
Young Modulus (GPa)	29.5

For GF/PP pre-impregnated materials, i) a PP powder ICORENE 9184B P®/E glass fiber rovings 305E-TYPE 30®, were used for the GF/PP towpregs, ii) PP Moplen RP348U® and E glass fiber roving TufRov 4599® were used for the GF/PP Tapes and PCT's. Twintex® R PP 60 B 1870 FU was the commingled fibers used (Table 1).

Table 2 – Properties of polymer raw-materials

Property	PP powder (ICORENE 9184B P®)		PP powder (ICORENE 4014®)	PP granules (Moplen RP348U ®)
	Manufacturer	Experimental	Manufacturer	Manufacturer
Specific gravity (Mg/m^3)	0.91	0.91	0.9	0.90
Tensile strength (MPa)	Yield Strength 30	Yield Strength 19	Yield Strength 24	Yield Strength 30
Young Modulus (GPa)	1.3	0.98	1.15	1.1
Poisson´s ratio	-	0.21	0.21	-
Average powder particle size (µm)	440	163	400	-
Glass transition temperature (T_g)	Typical value 0-20	-	Typical value 0-20	Typical value 0-20

For CF/PP pre-impregnated materials, i) PP powder ICORENE 9184B P® and CF roving M30 SC® and PP powder ICORENE 4014® and CF roving SIGRAFIL® C30 T050 TP1 were used to produce the CF/PP towpregs, ii) PP powder Moplen RP348U® and the CF roving already mentioned were used for the CF/PP PCT tapes (Table 2). [10]

Table 3 – Properties of fibres raw-materials

Property	Glass fibre			Carbon fibre		
	305E-TYPE 30®		TufRov 4599®	TORAY M30 SC®		SIGRAFIL® C30 T050 TP1
	Manufacturer	Experimental	Manufacturer	Manufacturer	Experimental	Manufacturer
Linear density (Tex)	2400	-	2400	760	-	3280
Specific gravity (Mg/m^3)	2.65	-	2.54-2.6	1.73	-	1.8
Tensile strength (MPa)	3500	1657	1900-2400	5490	2731	4000
Young Modulus (GPa)	76	62.5	69-76	294	194.5	240
Average fibre diameter	17	13.7	17	5	7.37	7

2.2 Transformation of thermoplastic pre-impregnated materials by pultrusion and the pultruded profiles by heated compression moulding

2.2.1 Processing GF pre-impregnated materials

Tapes were processed by pultrusion and heated compression moulding. The set-up parameters in pultrusion were: i) pre-heating oven temperature: 160 °C; ii) heated die temperature: 200 °C; iii) Cooling die temperature: 25 °C; - Pulling Speed: 0.2 – 0.7 (m/min).

At the beginning of the processing, a range of temperatures was tested to determine what could be the maximum and minimum temperature of the consolidation and pressurization die. It was determined that the maximum set-point was 210°C and minimum of 190°C. When using temperatures higher than the maximum referred, reflux problems in the consolidation die occurred, and lower temperatures would create problems in the first die.

The processing by pultrusion of the other GF/PP pre-impregnated materials can be found in [10].

The GF/PP Tape and the pultruded profiles from this type of pre-impregnated material were also processed into rectangular 290 × 200 × 2 (mm^3) composite plates. To manufacture a plate from GF/PP Tape, a weaving technique was also performed. Each weaved prepreg tape consisted in a ply, and a lay-up was done with four layers. In this case because of the rigidity of the GF/PP Tape the same number of fibres was not possible to achieve, being the number of fibres in one direction higher than in the other direction. With that in mind, the plate was produced in a symmetrical lay-up, using a 200 kN Hot Plate Press. A temperature of 230°C for processing was selected to ensure the uniformity of the laminate, allowing the melting polymer to migrate to all areas inside the mould (Table 4).

Table 4 – Heated Compression Moulding steps for weaved prepreg

Step	Stage	Temperature (°C)	Pressure (MPa)	Time (min)
1	Heating	230	0	25
2	Consolidation	230	0	10
3	Compression	230	2.0	1
4	Cooling	50	2.0	25

GF/PP Tape pultruded profiles were also processed by heated compression moulding, using the same setup, only varying the heating, consolidation and compression temperatures from 230 to 250 ºC.

2.2.2 Processing CF pre-impregnated materials

Different processing variables and combinations were tested with a dry powder coating equipment for fibre reinforced towpregs [7-8] and the process was optimized by the Taguchi approach. The optimal parameters for CF/PP towpregs were: i) convection oven: 700°C for 760 Tex and 650ºC for 3280 Tex carbon fibre; ii) onsolidation oven: 400°C; iii) linear pull speed: 6 m/min. The best conditions for processing the towpregs by pultrusion are presented in Table 5 and were established from processing window defined in previous works. For hot press moulding, the temperatures chosen to process the pultruded profiles on the plates were selected taking into account the temperatures used in the heated die of the pultrusion process.

Table 5 – Pultrusion and heated compression moulding process parameters

Condition	Carbon Fibre	Polypropylene	Pultrusion				Heated Compression
	Tex	Reference	Pre-heating oven (°C)	Heated die temperature (°C)	Cooled die temperature (°C)	Pull Speed (m/min)	Temperature (°C)
1	3280	*ICORENE®* 4014	160	250	25	0,2	-
2							200
3							250
4	760		70	200			-
5							200
6							250
7						0,3	-
8							200
9		*ICORENE®* 9184B P [12]	160 [12]	240 [12]		0,2 [12]	-
10							250

Heated compression moulding was carried out in a 200 kN Gislotica heated plate press installed in ISEP to manufacture a composite laminate. The pultruded composites were placed in a frame and a PTFE based releasing film was used. Two processing temperatures were employed: 200 and 250°C. In Figure 3 the assembly for heated compression moulding can be seen. To manufacture the laminate, the pultruded material was heated up to 250°C and maintained that temperature for 10 minutes to ensure the uniformity of temperature in all areas inside the mould. Then, a compression force was done to consolidate the laminate. Finally, it was cooled down and the laminate was taken out of the mould. The main stages and processing conditions of the heated compression moulding process are described in Table 6.

Table 6 – Heated Compression Moulding process parameters

Process		Temperature (°C)	Force (ton)	Pressure (MPa)	Time (min)
1	Heating	200 / 250	0	0	20 / 25
2	Temperature maintenance	200 / 250	0	0	10
3	Compression	200 / 250	20	2,0	1
4	Cooling	50	20	2,0	25 / 30

The processing by pultrusion and heated compression moulding of the other CF/PP pre-impregnated materials can be found in [11, 13].

2.3 Testing and Results

2.3.1 Testing GF composites

The flexural properties of the pultruded profiles were determined by doing a series of three-point flexure tests according to ISO 14125. The dimensions of the specimens were 20 mm x 2 mm. The outer span was 80 millimetres and testing speed 2 mm/min. The flexural mechanical properties of the pultruded profiles were determined and presented in Table 7.

Table 7 - Mechanical properties of pultruded profiles

Condition	Pulling Speed (m/min)	Flexural Strength (MPa)[a]	Flexural Modulus (GPa)	Fibre Volume Fraction (%)	Specific Strength (MPa)	Specific Modulus (GPa)
1	0.2	416.6±13.0	20.9±0.9	36.28	1148.3	57.6
2	0.3	351.8±14.2	19.3±1.4	35.11	1001.9	54.9
3	0.4	324.1±24.0	18.2±1.1	35.51	912.6	51.1
4	0.5	320.0±11.4	18.5±0.8	34.99	914.6	53.0
5	0.6	300.8±31.4	17.5±0.3	35.08	857.4	50.0
6	0.7	271.0±16.6	17.4±0.8	34.51	785.2	50.4

[a] with the large-deflections correction

Analysing Table 6 it's possible to verify that the condition with the highest flexure strength and a relatively low standard deviation is condition 1. This condition was produced with a constant temperature of 200°C in the consolidation and pressurization die with the lowest pulling speed improving impregnation of the polymer in the fibres, enhancing the consolidation of the composite and reducing the amount of voids. It is also important to note that in condition 1, the deviation of the strength and modulus is relatively low, meaning the process is in control. Mechanical properties were expected to decrease with higher processing speeds. Higher pulling speeds make impregnation harder due to the reduced exposure time of the prepregs to temperature and pressure inside of heated die. Increasing the speed by 3.5 times lowers the flexural strength by 33.7% and the modulus by 16.7%.

Microscopy (Figures 1 to 4) of the transverse section of condition 1 and 6 was done to see how the fibres and the polymer are arranged after pultrusion at different processing speeds.

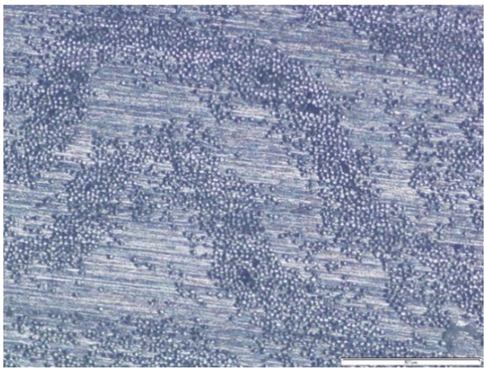

Figure 1 – Microscopy in pultrusion composites Condition 6 (0.7 m/min) (50x zoom)

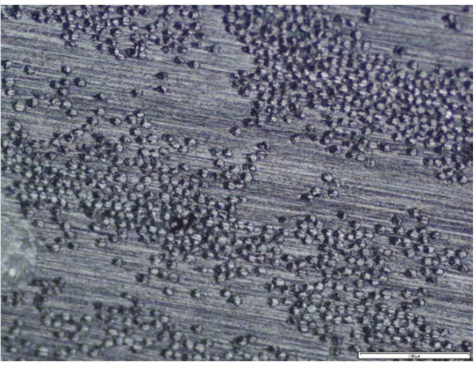

Figure 2 – Microscopy in pultrusion composites Condition 6 (0.7 m/min) (100x zoom)

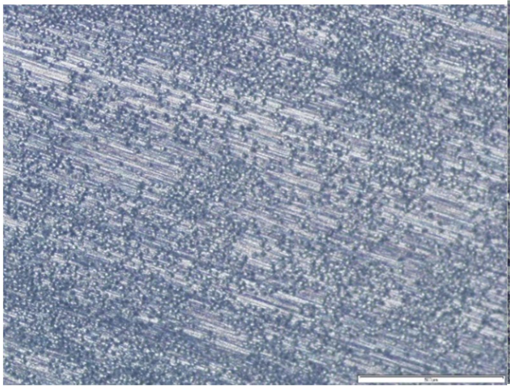

Figure 3 – Microscopy in pultrusion composites Condition 1 (0.2 m/min) (50x zoom)

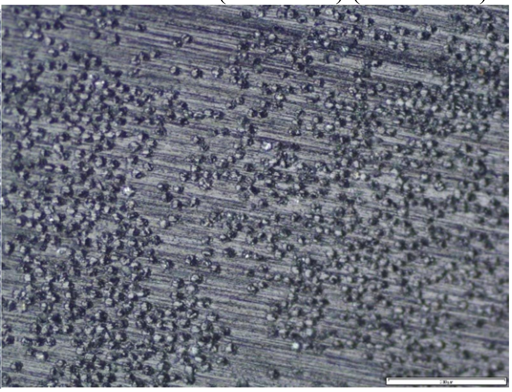

Figure 4 – Microscopy in pultrusion composites Condition 1 (0.2 m/min) (100x zoom)

Seeing condition 6 in Figure 1, a separation can be identified between fibres. The separation zone is filled with polymer and a very low quantity of fibres can be seen, meaning the impregnation during pultrusion was worst. If we zoom Figure 2, we can see separate areas in which there is a concentration of fibres with low polymer quantity around some of them. The distribution of the polymer and fibres through the area is very uneven. In the case of condition 1 (Figure 3), the dispersion of fibres and polymer is much equitable. The impregnation was more successful due to the parameters of processing. With lower speeds, it is expected that the polymer reaches a temperature high enough for processing and has time to migrate through the composite, improving impregnation and reducing the amount of voids. Observing Figure 4, we can see that even in the zones with fibre concentration, polymer is distributed around them. Table 8 summarizes the mechanical properties obtained.

Table 8 – Test results of pultrusion of processed GF/PP composites

Test Type	Property	Towpreg (V_f 52.1%)	Commingled Fibres (V_f 37.1%)	PCT (V_f 30.0%)	Tape (V_f 36.3%)
Bending	Flexure Modulus (GPa)	28.6±0.9	26.2±2.0	16.8±1.5	20.9±0.9
	Flexure Modulus/V_f (GPa)	54.9±1.7	70.6±5.4	56.0±5.0	57.6±2.4
	Flexure Strength (MPa)	158.0±12.3	595.0±24 [a]	329.0±30 [a]	416.6±13.0 [a]
	Flexure Strength/ V_f (GPa)	303.3±23.6	1603.8±64.7	1096.7±100	1148.3±35.8

[a] with the large-deflections correction

For the flexure modulus and strength, commingled fibres have best mechanical properties due to the quality of the impregnation. On the other hand, the flexure strengths per fibre volume fraction of the Tape and PCT are similar and much higher than Towpreg. These weaker results obtained can be due to the relatively high fibre volume fraction, making impregnation difficult and allowing the formation of voids in the composite. The flexure modulus per fibre volume fraction, Towpreg, PCT and Tape had relatively similar results.

Tensile properties of the produced thermoplastic cross-ply laminate by hot press moulding from GF/PP Tapes were determined - ISO 527-4 (Table 9).

Table 9 – Tensile test results of heated compression moulding processed GP/PP composites

Test Type	Property		Towpreg	Commingled Fibres	PCT	Tape (CPL)
Tensile	Tensile Modulus (GPa)	Experimental	37.0±1.3	27.7±0.4	21.2±4.0	15.6±0.3
		Theoretical	32.4	24.5	19.9	14.6
	Tensile Modulus / V_f (GPa)c		72.4±2.5	71.3±1.0	69.3±13.1	84.3±1.6
	Tensile Strength (MPa)		-[a]	-[a]	-[a]	296.3±1.4
Interlaminar Shear	Interlaminar Shear Strength (MPa)		12.0±0.7	28.6±0.3	27.2±0.9	16.4±0.8
	Interlaminar Shear Strength / V_f (MPa)d		23.5±1.4	74.7±0.8	88.9±2.9	88.7±4.3
Fibre Volume Fraction (%)			51.1	38.3	30.6	18.5[b]

[a] property not determined; [b] half value of fibre volume fraction

Table 10 shows the bending test results of heated compression moulding processed GP/PP from pultruded profiles processed in condition 1. GF/PP Tape composites presented, in general, better properties. Twintex® composites exhibits also very good mechanical behavior. GF/PP composites demonstrated similar relative flexure modulus. Towpreg composites present worse mechanical properties due to high fibre volume fraction and uneven distribution of the dry polymer powder.

Table 10 – Bending test results of heated compression moulding GP/PP composites

Test Type	Property	Towpreg (V_f 51.1)	Commingled Fibres (V_f 38.3)	PCT (V_f 30.6)	Tape (V_f 37.1)
Bending	Flexure Modulus (GPa)	34.4±3.4	25.5±1.0	20.1±1.0	23.4±0.7
	Flexure Modulus / V_f (GPa)[a]	67.3±6.5	66.6±2.6	65.7±3.3	63.1±1.9
	Flexure Strength (MPa)	184.0±19.1	666.5±53.9 [a]	456.0±32.1 [a]	733.4±78.7 [a]
	Flexure Strength / V_f (GPa)[b]	360.1±37.4	1740.2±140.7	1490.2±104.9	1976.8±212.1

[a] with the large-deflections correction

2.3.2 Testing CF composites

In Table 11, it is possible to see that increase in pultrusion speeds affects significantly the flexural strength of these composites. This is expected because a reduction in exposure time to temperature and pressure during processing, leads to a lower quality of impregnation. The percentage of voids is likely to be higher resulting in a less well-consolidated composite.

Table 11 – Mechanical properties of tested conditions

Condition	Flexural test				
	Flexure Strength (MPa)	Flexure Modulus (GPa)	Fibre volume fraction (%)	Specific Flexure Strength (MPa)	Specific Flexure Modulus (GPa)
1	89,4 (±7,4)	27,5 (±1,5)	58,1	153,8	47,3
2	133,8 (±28,8)	39,7 (±6,1)	60,0	223,0	66,2
3	207,6 (±16,5)	59,4 (±5,4)	58,2	356,8	102,0
4	211,2 (±18,8)	63,8 (±4,0)	46,4	455,2	137,6
5	242,6 (±16,7)	74,2 (±6,2)	46,8	518,4	158,5
6	265,7 (±11,9)	73,8 (±4,0)	47,2	562,9	156,3
7	134,9 (±14,7)	44,9 (±2,0)	47,1	286,4	95,3
8	209,4 (±8,8)	70,4 (±9,5)	47,0	445,6	149,9
9	229,0[2]	86,7[2]	49,9	458,9	173,7
10	267,4 (±21,4)	88,7 (±1,4)	50,8	526,4	174,7

The post processing by heated compression moulding improved the mechanical properties, especially for higher pultrusion speed. The improved impregnation due to the relatively higher exposure time to heat and pressure in the hot plate press allowed the polymer to migrate, filling the spaces between fibres and reducing voids. Fibre contents were similar due to polymer uniformization in the pultruded composites.

3. CONCLUSIONS

The main conclusions of the work carried out are the following:

- Existing powder-coating equipment is suitable to produce CF/PP and GF/PP towpregs that can be adequately processed into pultruded profiles.
- The tests made using a proprietary pultrusion equipment show that is possible to produce, in good conditions, profiles from almost all available thermoplastic matrix pre-impregnated raw materials using pull speeds from 0.2 to 0.7 m/min.
- A process window was established for the production of CF/PP towpregs with different Tex´s and pull speeds, for pultrusion of towpregs and Tapes and for heat compression moulding of GF/PP Tapes and pultruded profiles.
- More research must be done in order to increase the linear pull speed to processing by pultrusion of the towpregs as well as Tapes, and to improve the impregnation, uniformity and dispersion of raw-materials in the composites.
- The GF/PP composites processed by heated compression present better mechanical properties than those obtained by pultrusion.
- Mechanical properties of CF/PP pultruded profiles allowed to conclude that flexural strength and modulus are smaller with increasing pull speeds and carbon fibre Tex. The heated compression composites increased mechanical properties substantially in relation to the pultruded profiles, especially the ones pultruded at higher speeds and used carbon fibres with higher Tex.
- The mechanical properties obtained in all pultruded and compressed composites anticipate their adequate use either in general or in structural engineering applications.

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6.6. Conclusions

Four different commercial promising glass fibre reinforced thermoplastic matrix pre-impregnated materials were easily processed by pultrusion and compression molded: two commercial available GF/PP commingled fibres and tapes products and also GF/PP towpregs and PCT´s manufactured in our own laboratories. The production of GF/PP towpregs and the processing (pultrusion and heat compression moulding of GF/PP tapes and pultruded profiles) of commingled fibres, towpregs and tapes were optimized. The mechanical properties of the composites processed from all those four GF/PP pre-impregnated were determined and evaluated. All of them demonstrated to have mechanical properties compatible with the requirements of the major current structural engineering applications.

A process window was established for the production of towpregs with different Tex´s and pull speeds, for pultrusion of CF/PP towpregs and tapes and for heat compression moulding of CF/PP pultruded profiles. It was possible to optimize the production of CF/PP pultruded profiles and CF/PP towpregs, through the use of Taguchi/DOE method, achieving optimal conditions.

The tests made using a proprietary pultrusion equipment show that is possible to produce, in good conditions, profiles from almost all available thermoplastic matrix pre impregnated raw materials using pull speeds from 0.2 to 0.7 m/min.

The GF/PP composites processed by pultrusion followed by heat compression have better mechanical properties than those obtained by pultrusion only.

For CF/PP pultruded profiles, very good agreement was found between the experimental moduli values of all composites produced and the theoretical ones.

More research must be done in order to increase the processing speeds of CF/PP and CF/PRIMOSPIRE® towpregs as well as PCT's and to improve the impregnation, uniformity and dispersion of raw-materials in the composites.

The compression moulding results obtained in CF/PRIMOSPIRE® composites need to be further studied in order to achieve better mechanical properties. In the case of CF/PP composites produced by pultrusion followed by heat compression moulding, they revealed good mechanical properties and can be applied for the manufacture of complex shapes.

CF/PRIMOSPIRE® composites obtained by pultrusion showed a higher value for the interlaminar strength than all other ones. Due to higher processing temperatures, further tests should be done to optimise the operational conditions and further improve the obtained composite mechanical properties. The calcination tests based on the results obtained from TGA tests revealed to be a very interesting method to experimentally determining composite mass fractions, in the case of temperature resistant materials used as matrix and reinforcement.

Mechanical properties of CF/PP pultruded profiles allowed concluding that flexural strength and modulus are smaller with increasing pull speeds and carbon fibre Tex. The pultruded followed by heat compression composites increased mechanical properties substantially in relation to the pultruded profiles, especially the ones pultruded at higher speeds and used carbon fibres with higher Tex.

The towpreg-based composite with higher Tex carbon fibres present worst mechanical properties than with lower Tex mainly due to the difficulty of the penetration of the dry powder into the roving and also to its uneven distribution, prior to pultrusion (production of towpregs). Consequently, seems to be harder to bridge the large distances of dry fibre during pultrusion, which results on bigger unimpregnated zones and consequently larger dry zones in the pultruded composites.

Chapter 7

CONCLUSIONS

The main conclusions of the work carried out are the following:

- Existing powder-coating equipment was shown to be suitable to produce CF/PP, GF/PP and CF/PRIMOSPIRE® towpregs that could be adequately processed into pultruded profiles. From the tests made, the towpregs can be easily and continuously produced at industrial production speeds between 2 and 8 m/min.
- Obtained polymer mass fraction in the produced towpregs, in optimal conditions, vary from 0,30 to 0,40 which are acceptable for the manufacturing technologies that can use them.
- The average radius of the powder particles was much higher than the average radius of the fibres used in the production of towpregs, which made difficult the impregnation of fibres by the powder particules as well as its uniform distribution, reducing the polymer mass fraction obtained in the process.
- The tests made using a proprietary pultrusion equipment allow concluding that it is possible to produce, in good conditions, profiles from almost all available thermoplastic matrix pre-impregnated raw materials using pull speeds from 0.2 to 0.7 m/min. More research must be done in order to increase the processing speeds of pre-imprenated materials and to improve the impregnation, uniformity and dispersion of raw materials in the composites.
- A process window was established for the production of towpregs, for the pultrusion of towpregs, PCT's, tapes and commingled fibres and for heat compression molding of pultruded profiles.
- It was possible to optimize the production of CF/PP towpregs and CF/PP towpregs pultruded profiles and, through the use of Taguchi/DOE method, achieving optimal conditions.

- The addition of the compatibilizing agent (maleic anhydride) did not improve the polymer mass content in towpregs and the mechanical properties on the final composites.

- SEM micrographs of CF/PP and GF/PP towpregs samples show that a good degree of adhesion between both carbon and glass fibres and the polymer powder particles was obtained. Also, a reasonable polymer powder distribution on the fibres was achieved at the optimised operating conditions.

- The cross-sections of the pultruded composites were observed under optical Microscopy. All CF/PP and CF/PRIMOSPIRE® composite profiles from towpregs (with and without additive) and PCT´s have a reasonable distribution of the reinforcing fibres over the cross-sections. It may be seen that the impregnation quality of the PCT composite samples is good, presenting almost all fibres completely surrounded (‘wet-out’) by the polymer. Only a few large dry spots were observed. The samples from CF/PP towpreg with additive show a higher quantity of dry zones than the ones without additive.

- The microscopy images taken from the samples of the pultruded composites using GF/PP PCT, TWINTEX® and GF/PP towpreg, lead to a reasonable distribution of the reinforcing fibres over the cross-sections, although small improvements in fibre distribution can be observed going from PCT through TWINTEX® to towpreg composites. It may be seen that the impregnation quality of the PCT composite samples was excellent; hardly showing any dry spots in the pultruded samples. The TWINTEX® -based samples also show a very good impregnation of the fibre. However, at larger magnifications, some larger dry spots were observed between the glass fibres showing an overall poor impregnation quality when compared with the one observed in the PCT tape based pultruded composites. Finally, it was still possible to distinguish discontinuities on the cross section of pultruded composites from GF/PP towpregs, where it may be seen zones very rich in polymer contrasting with others with much higher quantity of fibres. The towpreg-based composite samples exhibit larger apparent dry zones.

- For GF/PP and CF/PP pultruded profiles, very good agreement was found between the experimental moduli values of all composites produced and the theoretical ones.

- The specific mechanical properties of the CF/PP towpregs pultruded profiles and its compressed plates are higher than the PCTs, particularly the flexure modulus, but lower in relation to flexure strength and ILSS. An increase in the specific flexure strength was noticed with heated compression of the pultruded profiles.
- Mechanical properties of the CF/PP profiles obtained by pultrusion process allowed us to conclude that flexural strength and modulus are going lower with increasing pull speeds and carbon fibre Tex. The composites transformed by heated compression moulding increased mechanical properties substantially in relation to the pultruded profiles that were used in this process, especially the ones pultruded at higher speeds and used carbon fibres with higher Tex.
- CF/PRIMOSPIRE® towpregs composites obtained by pultrusion showed a higher value for the interlaminar strength than all other ones and present a better bending strength and worst flexure modulus than CF/PP towpregs composites. Due to higher processing temperatures, further tests should be done to optimise the operational conditions and further improve the obtained composite mechanical properties.
- CF/PP cmposites produced by heated compression moulding reveal good mechanical properties and can be applied for the manufacture of complex shapes.
- The GF/PP composites processed by heated compression moulding present better mechanical properties than those obtained by pultrusion, mainly in GP/PP composites from towpregs and specially PCT´s and Tapes.
- The calcination tests based on the results obtained from TGA tests reveal to be a very interesting method to experimentally determine composite mass fractions in the case of temperature resistant materials used as matrix and reinforcement.
- In the case of CF/PRIMOSPIRE composites obtained by pultrusion, using the rule of mixtures and the experimental tensile moduli, it was possible to estimate the fibre volume fraction as approximately 45.0%. This result is in good agreement whit the one obtained from calcination test (45.2±5.3) and SEM image processing (44.2%).
- The mechanical properties obtained in all pultruded and compressed composites allow predicting their adequate use either in general or structural engineering applications;

- The already obtained mechanical properties on the pultrudes profiles and compressed moulded plates are compatible with other traditionally used engineering materials (or even surpass), especially if specif values were considered.

Chapter 8

SUGGESTIONS FOR FUTURE WORK

For a possible continuation of the work done, it is suggested the following studies and/or experimental work:

- Study and production new pre-imprenated materials using different combinations of fibres and thermoplastic matrices that are useful for certain applications.
- Study, in the production of towpregs process, the influence of other processing conditions in final properties of pre-impregnted materials (quality of adhesion of polymer on fibre, a good uniformity and distribution of polymer on the fibres, a desired level of mass fraction, towpreg flexibility/stiffness and no damaged/fractured fibres, etc). Namely, air pressure levels in the spreader and the type of fibre spread in the powder bath can be considered. Moreover, the exiting twist level of the tow, the particle size of the powder, the pre-heating of the powder, the polymer deposition type on fibre (avoid deposition only on the top of the fibre and promote its even distribution inside and outside), the powder quantity in the bath and the amount and the particle size during production should also be investigated. The residence time of the fibre in the powder bath (inclusion of cylindrical rollers assemblies) and its outlet angle, the tension of the tow and the environment conditions also should be evaluated.
- Design the spreading die in the towpregs machine according to each fibre Tex (the used spreader was designed for a 2400 fibre Tex).
- Use a new tape die in line with the towpregger equipment allowing the production of a new kind of tapes.
- Use other different additives to improve the adhesion of the thermoplastic matrix to the fibres.
- Study the use of fibres with a thermoplastic compatible sizing.
- Produce higher Tex towpregs with good quality, decreasing the number of needed towpregs and, therefore, facilitating its processing.

- Improve the design of the dies, increasing the isolation and the instrumentation of the pressurization and consolidation die allowing for pressure and temperature sensors closed to the profile, study and design a improved geometry (length and a die taper angle).
- Study, in the pultrusion process, the influence of other processing parameters in the final properties of puldruded profiles, namely fibre and polymer volume fractions, the expansion and contraction of the polymer at the exit of the hot die, the pressure in the consolidation die, the pull force, the the final cooling temperature at the at the end of the cooling die and the cooling rate (type and degree of crystallization).
- Increase the pultrusion linear pull speed to a value similar or better than thermosets (1-2 m/min), improving the impregnation of pre-impregnated materials, the geometry of the dies, the processes parameters, the dies distance and the cooling system between the pressurization and consolidation die and the cooling die.
- Apply different statistical techniques, such as the Design of Experiments, to improve the quality of the pre-impregnated materials and composites produced optimizing their processing.
- Produce pultruded profiles with more complex geometries and with different pre-impregnated materials (hybrids) and multi-layer or hybrid laminates by heated compression.
- Using towpregs, commingled yarns and tapes to produce braiding and fabrics as pre-impregnated materials to be processed by compression moulding.
- Determinate the distribution, orientation and volume fraction of the fibres in the composite produced through new techniques such as computational tomography.
- Determine other relevant mechanical and thermal properties using DMA, DSC and TGA tests.
- Study the polymer degradation using fluorescence technics.
- Study other properties of produced composites, in particular, mechanical (impact resistance, fatigue and creep, among others), geometric (product dimensional analysis, residual stresses and significant deformations), aesthetic and functional (superficial finish).