ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

INFLUENCE OF WATER-CEMENT, POLYMER-CEMENT AND FIBER-CEMENT RATIOS ON PROPERTIES OF FIBER REINFORCED MORTARS

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Polymer Science and Technology Programme

DECEMBER 2016

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ABBREVIATIONS

PET	: Polyethylene terephtalate
Sp	: Superplasticizer
Sa	: Shrinkage Reducing Agent
W/C	: Water/Cement ratio
F/C	: Fiber/Cement ratio
P/C	: Polymer/Cement ratio
MPa	: Megapascal
GPa	: Gigapascal
MFFT	: Minimum film forming temperature

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INFLUENCE OF WATER-CEMENT, POLYMER-CEMENT AND FIBER-CEMENT RATIOS ON PROPERTIES OF FIBER REINFORCED MORTAR

SUMMARY

It is a frightening fact that the world population has been increasing very rapidly. This creates the reality of urbanism and a very urgent needs of architectural developments. Huge buildings, higher landscapes, longer bridges, wider highways, and so on...It is known very well that mortars are one of the very important construction materials for safe buildings and strong constructions. Because of this requirement and its wide usage, variety of technical researches are being done in this area. Consequently, scientists and civil engineering firms have been taking place in those experimental researches as well universities. There is also needs for further modification and analysis of mortars to develop this material for future applications and according to needs of humans.

The aim of this study is examining the affection of different ratios of water-cement, polymer-cement, fiber-cement ratios and hybrid fibers on mortars. It has been observed mechanical, viscosity and processability properties of polymer-modified mortars during experimental period. In experiments, polymeric additives such as acrylic-styrene resin, polycarboxlate eter based superplasticizer and shrinkage reducing agent, fibers such as 12 mm, 3 mm glass fibers, 6 mm surface treated glass fiber, polypropylene and polyamide fibers have been used. Because of different materials and variables used in experiments, a mathematical model has been evaluated which is based on surface response model.

For determination design of experiments, central composite design has been used. Out of mathematical model, some of the hybrid fibered groups are produced to evaluate their effect on mechanical properties when fibers are used together simultaneously. In this thesis, as mechanical tests: flexural and compression tests have been performed. Flow tests have given important information about the viscosity of the fresh mortars. In addition, weigh changes of specimens have been recorded in every stage to calculate weigh loss of mortars.

In the route of production of mortar specimens, first solid formed ingredients such as cement, calcite, fibers, sands and cellulose have been mixed and 70% of required water have been added. This premixture has been mixed at low speed around 1.5 minute. At the same time, in different bottles, 30% of required water and superplasticizer, polymeric cement modifier and shrinkage reducing agents have been prepared. After 1.5 minute premix, the whole ingredients have been mixed at high speed around 1.5 minute in cement mixtures again. After completing the mixing pover, flow tests have been performed rapidly and the results were recorded. And the mortar specimens were moulded. After 24 hours of production, the mortar specimens were removed from moulds and they were cured 2 days in water pools. After waiting for 60 days, their mechanical tests were performed.

Styrene-Acrylic resin was used as polymeric cement modifier. It is known that polymeric cement modifiers generate a phase in mortar structure. Simultaneously

cement hydration occurs and both of these phases increase binding effect of aggregates in structure. This situation can provide superior properties to mortars and concretes. To be able to see this situation, the proof tests were done. 6.6%, 10%, 15%, 20% and 23.4% of resin were added to mixtures one by one. It was found that there was a critical value of usage polymeric cement modifiers in mortars. The best results were obtained in the mixtures which had 15% and 10% polymer/cement ratios. It was observed that when polymer/cement ratios increased from 15% to 20%, flexural and compressive strength decreased. Increasing p/c ratios from 20% to 23.4%, decreased mechanical strength dramatically. According to weigh loss results, mixtures which had high polymer content, lost their weigh more at the end of 60 days. These results also explain the decreasing of flexural and compressive strength with increasing polymer content in mortars. According to results of flow tests, increasing polymer content provides getting increased flow value of fresh mortar. It is clear that, the conclusion of experiments define the relation between increasing polymer content and workability in mortars.

One of the important ingredients was Polycarboxlate eter based superplasticizer. Because fine ingredients were used in experiments, the superplasticizer had critical role to increase workability. It is known that superplasticizers increase workability of product and enables to decrease water content. Normally, Decreasing water content without loss in workability makes possible to achieve higher results in compression and flexural tests. In every mixture, constant 0.01% superplasticizer (5 gram) was added. Although a quality superplasticizer was used in experiments, decrease of workability in some of mixtures, which had low water/cement ratios, caused heterogeneous distribution of ingredients and decrease of mechanical strength.

Shrinkage reducing agent was other polymeric ingredients, which were used in experiments. It is known that shrinkage reducing agent not only decreases shrinkage of mortars and concretes but also makes more durable them in wet environments. This polymeric additive was important because moulded mortars were cured 2 days in water pools. And there is a problem about the curing of polymer-modified mortars and concretes to generate polymeric phase in structure. If the specimens are waited too long in water cure or if they aren't enough durable in wet environments, polymeric phase may not be generated properly.

Hydroxyethyl cellulose was used in experiments to increase binding effect of fluid content of mixtures such as styrene-acrylic resin, polycarboxylate eter based superplasticizer, shrinkage reducing agent and water with solid ingredients. In the very early stages of experiments, it was seen that, the whole polymeric ingredients were insufficient to bind aggregates and other solid formed ingredients of mixtures. But using small amount of hydroxyethyl cellulose (2gr) in powder form, better mixtures and results were obtained.

According to experimental design, 15 different mixtures were prepared with 12 mm glass fiber in different ratios. One mixture was prepared by 6 mm surface treated glass fibers. And also three different mixtures with hybrid fibers were prepared. 0.5%, 0.9%, 1.5%, 2.1% and 2.5% fiber/cement ratios were examined. According to flexural and compression test results, increasing fiber ratio from 0.9% to 2.1% and increasing fiber ratio from 1.5% to 2.5% decreased their strength. Decreasing workability with increasing fiber content may cause this result. And also it may be the reason of balling effect of fibers in mortars. Increasing fiber content decreases flow test results as it is expected. Above all, the highest flexural and compression test results were achieved

in mixtures with 6mm surface treated glass fibers. This mixture had also higher flow value than other mixtures with 12 mm glass fibers, which had higher polymer or water content. This is important that treated surface of 6mm fibers not only increases strength with better fiber-matrix interaction, but also contributes positive to flow test results.

The hybrid fibers are polypropylene and 12 mm glass fibers, polyamide and 12 mm glass fibers, 12 mm and 3 mm glass fibers. So, 1% of 12 mm glass fiber and 1% one of the other fibers, totally 2% of fibers were added in every mixture. According to flexural test results, the highest flexural strength was achieved with 12 mm and 3 mm glass fiber. The results of 12 mm glass fiber-polypropylene fiber and 12 mm glass fiber-polyamide fiber mixtures follow the highest results. The contribution of polyproylene fibers and polyamide fibers are relatively close but polypropylene fibers increase flexural strength a bit more than polyamide fibers. The same situation was observed in flow tests. The flexural test results of hybrid fibered mixtures are higher than even the strengthest single 12mm glass fibered mixture. Therefore, it can be said that hybrid fibers can be used for obtaining higher results in flexural strength. According to compression test results, any positive effect of hybrid fibers were observed.

In conclusion in this summary, it's been mentioned the different materials which were used in the experiments and their effects and additives as results briefly.

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ÖZET

Harçlar çok uzun zamandır kullanılan yapı malzemeleridir. Güvenli binalar, köprüler, yollar ve barajların yapımı için kaliteli ve dayanıklı harç ve beton malzemeleri gerekmektedir. Harçlar çok kullanıldıkları için ve kullanıldıkları ürünlerdeki işlenebilirlik, viskozite ve mekanik özelliklere önemli katkıda bulunmalarından dolayı, firmalarda ve akademik çevrelerde sıklıkla araştırılmaktadır. Her nekadar eski bir yapı malzemesi olsa da, insanlığın ve sanayinin yeni ihtiyaçları ve gelecek uygulamalara adaptasyon için harçların geliştirilmeleri gerekmektedir.

Bu tez çalışması harçların farklı değişkenlerle özelliklerinin nasıl değiştiğini incelemek üzerine yapılmıştır. Su-çimento bilindiği üzere harçlar ve betonlar için en önemli dayanım parametrelerinden birini oluşturmaktadır. Su her nekadar çimentoyu hidrate edip, harç içindeki fazların bağlanmasını sağlayarak harçların mekanik özellik kazanmasını sağlasa da, ileriki süreçte çimento hidrate olduktan sonra buharlaşarak uçmaktadır. Bu buharlaşma hadisesi zaman içerisinde gelişip iki sebepten dolayı harçların ve betonların mekanik özelliklerini düşürmektedir. Birincisi buharlaşırken yapı içerisinden yüzeye doğru ilerleme mekanizmaları, ikincisi ise buharlaşıtıktan sonra harç ve betonların yapısında bıraktıkları boşluklardır. Harçlar ve betonlar nekadar boşluklu yapıya sahip olurlarsa dayanımlarının o ölçüde düşük olacağı söylenebilir. Bu nedenle yüksek su-çimento oranına sahip beton ve harçlar daha düşük mekanik dayanıma sahip olmaktadırlar. Bu tezde üzerinde çalışılan parametrelerden biri su-çimento oranıdır.

Diğer ve en önemli değişkenlerden biri harçlara ve çimentolara polimerik katkılardır. Bu tezdeki temel amaçlardan biri harçlara yapılan polimer katkısının hangi oranlarda ve harç özelliklerine nasıl etki ettiğinin araştırılmasıdır. Polimerler harçlara ve betonlara farklı özellikler kazandırabilmektedirler. Harçlara polimer malzemeler katılması 20. Yüzyılın ortalarından itibaren ilgi çeken bir konu olmuştur. Özellikle malzeme teknolojisinde olan yeni gelişmeler ve yeni polimerik harç ve beton katkılarının senteziyle su-çimento oranı hiç olmadığı kadar düşük seviyelere çekilebilmiş ve daha dayanıklı harç ve betonlar üretilmiştir.

Polimer modifikasyonun harçlara kattığı özellikler, genel olarak çimentonun yanında ikinci bir bağlayıcı faz oluşturmak şeklinde özetlenebilir. İç yapıda oluşan polimer filmi, agrega, çimento bağını arttırarak harçların daha yüksek mekanik dayanımlara ulaşamasını sağlayabilir. Polimer modifikasyonu harçlara su geçirmez özellik katar. Süperplastikleştirici olarak kullanılarak harçların veya betonların akışkan özellik sağlayarak işlenebilirliğini ve kalıp tutabilirliğini arttırabilirler. Ayrıca ince kesitte üretilen harç veya beton panellerde rötre çatlaklarının engellenmesinde kullanılabilirler. Bu geniş kullanım alanı ve polimerlerin harçları modifikasyon yeteneği bu tezin konusu olmuştur. Fiberler günümüzde kompozit malzemelerde sıklıkla kullanılan takviye elemanlarıdır. Çimento matrisli kompozit malzemeler olan harçlar ve betonlarda da sıklıkla kullanılan fiberlerin mekanik ve rötre özelliklerine oldukça önemli etkileri bulunmaktadır. Bu sebeplerden dolayı bu tezde temel olarak su-çimento, polimerçimento ve fiber-çimento oranlarının etkileri araştırılmıştır.

Bahsi geçen etkilerin geniş bir çerçevede araştırılması için yüzey yanıt metodu adı verilen bir yöntem kullanılarak matematiksel bir model oluşturulmuştur. Bu modelin oluşturulmasında ve deney düzeneklerinin hazırlanmasında merkezi kompozit tasarımından yararlanılmıştır. Bu tasarım doğrultusunda su-çimento, polimer-çimento ve fiber-çimento değerleri, deneysel optimizasyon ve dizayn kısmında bulunan değer aralıklarında kodlanmış ve deney düzeneği bu kodlu aralıkta oluşturulmuştur. Bu yöntemin en önemli yararlarından bir tanesi deney sonuçlarının denklemler halinde matematiksel olarak ifade edilmesi ve seçilen deney aralığı dâhilindeki tüm değerler test edilmese bile sonuçlarının tahmin edilebilmesidir.

Bu tezde üç farklı polimer katkısı kullanılmıştır. Birincisi akrilik-stiren kopolimerdir ve iç yapıda oluşturduğu film ile mekanik özelliklere katkısı incelenmiştir. İkinci olarak polikarboksilat eter bazlı süperplastikleştirici kullanılmıştır. Bu made düşük suçimento oranlarında bile harcın iyi akışkanlık gösterip iyi kalıp tutmasını sağlayarak harca katkıda bulunur. Üçüncüsü rötre ajanıdır. Deneyde incelenen bileşimlerin ince kesitte üretilmesi halinde çatlamaması için kullanılmıştır. Akrilik-stiren reçinesi farklı oranlarda kullanılırken, süperplastikleştirici ve rötre ajanı sabit oranlarda katılmışlardır.

Deneysel çalışmalar sırasında farklı tip fiberler kullanılmıştır. Bunlar 12mm ve 3mm cam fiberler, 6mm yüzey işlemi görmüş cam fiber, polipropilen ve poliamid fiberlerdir. Matematiksel model dâhilinde yapılan deneylerde fiber tipi olarak sadece 12mm cam fiber kullanılmış ve farklı oranlarda bileşime olan etkisi incelenmiştir. Bunun yanında 3 tane karışık fiberli üretim yapılmıştır bu karışımlar: 12 mm cam fiber-polipropilen fiber, 12 mm cam fiber-poliamid fiber ve 3mm cam fiber-12 mm cam fiber karışımlarıdır. Ayrıca bir grupta da 6mm lik yüzey işlemi görmüş fiber katkısı denenmiştir.

Deney numuneleri 40x40x160 mm³'lük numuneler halinde üretilmiştir. Harç numuneleri öncelikle 1,5 dakika yavaş karıştırılıp 1 dakika beklendikten sonra 1,5 dakika hızlı olarak tekrar karıştırılır. Harç karışımları üretilirken öncelikle katı birleşenler olan; kum, çimento, kalsit, fiber ve selüloz karıştırılmış ve üzerine eklenmesi gereken suyun yüzde 70 i eklenmiştir. Geriye kalan yüzde 30 oranındaki su süperplastikleştiriciye eklenip ayrı bir kapta bekletilirken rötre ajanı da başka bir kaba alınır. Yavaş hızdaki ilk karıştırmadan sonra süperplastikleştirici-su karışımı, rötre ajanı ve akrilik-stiren reçinesi eklenerek yüksek hızda tekrar karıştırılır. Bu prosesin sonunda gerekli harç karışımı üretilmiş olur.

Taze harca ilk olarak çökme deneyi uygulanmıştır. Çökme deneyi üretilen harcın viskozitesi ve işlenebilirliği ile ilgili fikir vermektedir. Daha sonra numuneler tartılarak 2 gün boyunca su havuzunda tutulmuştur. Kür sürelerini daha uzun tutmak, harç numunelerinin polimer içerikleri nedeniyle mümkün değildir. Aksi takdirde yapı içerisinde istenen polimerik film oluşmayabilir. Kürden alındıktan sonra tekrar tartım değerleri alınmış ve 60 gün beklemeye bırakılmıştır. Bu sürenin sonunda numunelerin son tartımları alınarak, numunelere eğme ve basma testleri yapılmıştır. Ayrıca bu süreç üretim sonrasında, kür sonrasında ve deney öncesinde ağırlık ölçümleri alınarak numunelerin zamana bağlı kütle kaybı sonuçları elde edilmiştir.

Deney sonuçlarına bakıldığı zaman en yüksek eğme testi değeri 6mm'lik yüzey işlemi görmüş cam fiberli grupta elde edilmiştir. Bu grubun eğme ve basma sonuçları kendinden daha düşük su çimento oranına sahip başka gruplardan bile yüksek çıkmıştır. Bunun sebebi yüzey işlemi görmüş cam fiberin matrise daha iyi tutunup daha yüksek mekanik özellikler sağlaması olabilir. 12 mm'lik cam fiberli grupta 0.54 su çimento, %10 polimer çimento ve yüzde 0,9 fiber çimento bileşimine sahip grupta en yüksek eğme ve basma değerleri elde edilmiştir. Diğer değerler sabitken polimer oranı % 20 ye çıkarıldığında mekanik dayanımın düştüğü görülmüştür. Bunun sebebi harçlara polimer katkısında kritik bir değerin varlığıdır. Belirli bir miktar katkıdan sonra polimer katkısı harçların mekanik özelliklerine negatif etkide bulunmaktadır. Eğme sonuçlarında karışık fiberli grupların, 12mm'lik cam fiber kullanılmış olan gruplara üstünlüğü bulunmaktadır. Ancak bu üstünlük basma sonuçlarında eğme sonuçlarında olduğu kadar açık olarak görülememektedir. Bu durum 3mm lik cam fiberin ve polimerik fiberlerin mekanik özellikleriyle alakalıdır.

1. INTRODUCTION

The structural materials are being developed according the new techniques and new industrial needs. Mortar is very important but old material. Although, mortars are well known and they are widely studied in universities as well as in research centres, trend of world is making always bigger, higher and stronger. To make higher buildings, to make bigger bridges, it is always needed new development of the structural materials and mortar is the one of the key material in structural engineering.

Today, different properties can be achieved due to using polymeric additives. Polymeric resins are generated a film at inner side of mortar and enhance the binding effect of cement and aggregate. Some polymers give waterproof properties to mortars. They have wide application areas in underwater applications. Also polymeric additives make it very low water-cement ratios possible.

Water is very essential additive of mortars. It hydrates the cement and initiate the binding effect on mortars. But there is a disadvantage of water in mortars and concretes. Water evaporates after mortar is produced. This cause high porosity. If there is added a little water to mortar mixture, the workability would be very low. But invention of superplasticizers makes it possible to achieve low water/cement ratios due to decreasing viscosity in mortar mixture. Shrinkage reducing agents are another example of polymers used in mortar mixture. Mortars are produced as precast component in thin cross-section. To prevent crack occurrence in this kind of thin materials, polymeric additives are used. These are some of the examples explains the usage of polymeric modifiers in mortars.

Fibers became one of the important component of the composite materials. The usage of fibers in cement matrix composites are quite high. Fibers improve the shrinkage reducing effects of polymeric additives in precast components and they make high contribution to mechanical properties of mortars and concretes. According to available literature review, most of the fiber types are added already to composites. But there are countless combinations of fibers possible. There may be new possibilities to improve properties of composite materials due to using different fibers together.

1.1 Definition of Mortars

Mortar is very important structural material that includes water, fine aggregates and cement. It can be said that, there is only one diffrence between mortars and concretes. There is no coarse aggregate in the mixture of mortar. In composition of mortar there is no coarse aggregate. Hence, it is possible to say that building mortar is a fine aggregate concrete.

Generally building mortar is used for these purposes:

In structural engineering, it is used for binder material of stone, brick, blocks and it can also be used for filling the gaps in brick walls and the joints in large wall panels and various components,

For decorative purposes; structural beams and columns, brick walls, floors can be plastered by mortar,

Natural stones, ceramic tiles, mosaic tiles and artificial stones can be inlayed [1].

1.2 Mortars Classification

Construction mortars can be categoreized in five grops: joint mortars and pavement smoothing mortars (screeds), rendering mortars, cement-glues, masonry bedding mortars [2].

1.2.1 Functional classification

- Watertightness coatings— it is possible to guarantee watertightness of the wall against rainwater by using special mortars. Even If the wall is damaged or cracked, theoretically this type of coating can hinder water entry to the inside (non-absolute criterion, e.g.: It is up to damage level of the wall)
- Waterproofing coatings— they make a serious contribution to the watertightness of the wall. But this contribution doesn't ensure by themselves that watertightness alone. It should use another additive to ensure watertightness.
- Thermal insulation coatings— The first aim of this type of coating is ensuring thermal insulation, instead of watertightness,

Finishing mortars—their first aim is to finish the walls, their contribution to watertightness properties is very few (e.g. water-based paints) [3].

Interior coatings types can be classified in four categories [5]:

- ✓ Smoothing coatings— it provides the wall planeness, verticality and surface regularity.
- ✓ Finishing coatings—they provide the wall a smoothing complement. In most cases a pleasant visual aspect can be provided too.
- ✓ Water-resistant coatings—it is the finishing coat of the walls. It is applied where water is present frequently or cleaning is wet.
- ✓ Decorative coatings—they can provide the new look willing by the users in terms of visual comfort [5].

1.2.2 Classification according to the binder type

Different type of binders can be added to mortars. The mortar classification is given according to their binder type.

- Slaked air lime and sand mortars— they have very slow hardening, high ultimate deformation, friable structure and low shrinkage in rehabilitation works.
- Natural hydraulic lime and sand mortars— they have intermediate characteristics between slaked lime-sand mortars and cement- sand mortars.
- Artificial hydraulic lime and sand mortars—they have with similar properties to natural hydraulic lime mortars. Also they have less ultimate deformation.
- Gypsum mortars—this type of mortars are used only in interiors. They have weak mechanical strength and sensitive to humidity.
- Cement and sand mortars—they have good mechanical properties such as: high stiffness, high strength and also they have high shrinkage and great propensity to cracking properties.
- Cement, lime and sand (mixed-binder) mortars—in comparison of cement and sand mortars, they have better workability and lesser cracking propensity. It is mostly the cement that confers strength and the initial mechanical characteristics.
- Mixed-binder mortars, made with mineral and synthetic binder (e.g. polymer) in a
 proportion over 2.5 %— they have generally good characteristics of adherence,
 waterproofing capacity and tensile strength. There is a big interest for this type of
 mortars in walls coatings (repair renders, exterior thermal insulation systems).

1.2.3 Classification according to the production site

The classification of mortars according to their production site are divided mainly into three groups:

- Industrial mortars—they are "in powder" form. They require only water to be added on construction site or "in paste" form. They are ready to apply.
- Semi-finished industrial mortars—They get ready to available on-site, such as:
 - Pre-dosed mortars— they get available on-site when they are mixed to conditions of manufacturer. (e.g. multi-chamber silo). Their components are dosed at the factory.
 - Premixed mortars—their components are mixed at the factory, they get available on-site, when other components that the manufacturer specifies or provides (e.g. cement) are also added.
- Made on-site or traditional mortars—these mortars are mixed and dosed on-site. They are only composed by primary constituents (e.g. binders, aggregates and water).

1.3 The Composition of Mortar

To produce quality mortar, components in the composition of must meet some technical requirements.

1.3.1 Cementing Materials

There are diffrent types of cement materials that are added to mortar mixture. Slag cement, fly-ash cement and ordinary cement are some of the examples of them. The selection of cement is very important. The cements must be chosen according to application area of the construction. There is also another factor that is important to choose correct cement for application. This is strength grade. In design, cement must have at least 5 times higher strength grade than that of mortars. In some cases, strength grade of cement can be very high. In these cases, it is appropriate to use some kind of mixture materials such as fly ash. Addition of fly ash can decrease the consumption of cement and save money. It is recommended that strength grades of cements which will be used in mortars should be in range of 32.5 [1].

1.3.2 Fine aggregate

Aggregates are very important for mortars and concretes and the particle diameter of aggregates which will be used in mortars should be very small. Application areas of mortars are defined according to their particle size. For example, in brickwork the diameter of used sand must be in range of 2.5 mm. For jointing applications, the diameter should be finer and it must be limited with 1.2 mm [2].

1.3.3 Water

The used water in mortars must be clean as much as possible. If there are lots of impruties in used water, it can decrease the mechanical properties of mortars.

1.3.4 Mixtures and additives

Some inorganic fine additives can be added to improve some of the properties of mortars. There is also another benefit that inorganic additives enhance cement saving. Lime paste, clay paste and fly ash are some of the examples for this kind of additives. To improve effect of additives, fly ash should be ground and lime should precipitate.

1) When quick lime ages to lime paste, it should be screened by sustainable aperture and the maximum aging time should not be less than 7 days. The aging time of the ground quick lime should not be less than 2 days. The lime paste must be waited in sedimentation tank. And it must be protected against undesirable conditions such as drying, freezing and polluting [1].

2) Clay or mild clay should be mixed with water and it should be screened by the sieve with aperture in the size of 3 mm X 3 mm. The organic compounds of clays are checked by colourimetry. Their colour should be paler than the standard colour.

3) The carbide slag used for carbide plaster should be screened by the sieve with the aperture in the size of 3 mm X 3 mm, and it should be heated to 70°C for 20min. It can only be used without the odour of acetylene [8].

4) In masonry mortar, hydrated lime powder can not be used directly

5) In preparation, consistency of lime paste, clay plaster and carbide plaster should be 120 mm x 5 mm.

6) The quality of fly ash must meet the requirements of Fly Ash Used in Cement and Concrete (GB 1596-9 I). The other important standard is Building Quick Lime Powder (JC/T480-92) for that of ground quick lime [8].

If it is needed, micro foam agent can be added. This agent improves the workability of mortar. Pyrolytic polymer is one of the very common micro foam agent. It is added 0.005%- 0.01% of the mass of cement. Additives have positive on construction properties and workability of mortar. The physical properties and mixing amount of additives should be tested [1].

1.3.5 Fibers

Fibers are characterized by their long and thin shape. This shape enhances flexibility and high strength to fibers. Fibers can be produced by organic, inorganic or metal substances. But the material must have small cross-sectional diameter in comparison with its length. Fibrous materials are one of the important materials of industry as well as our lives. Because fibrous materials sustain flexibility and strength. They are demanded by huge area from textile industry to aerospace industry. Commercial fibrous materials can be divided into two categories: natural fibers and chemical fibers. Natural fibers are classified as plant fibers (hemp, pineapple fibers and cotton), animal fibers (silk, wool, mohair) and mineral fibers (asbestos). Chemical fibers are classified as rayon, semi-synthetic fibers (acetate), synthetic fibers (organic fibers of nylon, acrylonitrile, polyester), (inorganic fibers as glass fibers, metal fibers and carbon fibers) [9]. Generally, the fibers are produced by spinning drawing and other processing methods and the performance of fibers depend on these processing methods. For example, polyester fibers are used in very huge area e.g in cloths as well as in automotive tyres. For textile industry, polyesters should have good hand and easy dyeability. For tyre cords, polyesters must have high modulus, toughness and thermal stability. The technology of fiber production is sophisticated to rule the fibers and process characteristics to meet the design requirements [10].

The other classification of fibers can be made as apparel and nonapparel fibers. It is up to the final use of fibrous materials. Synthetic fibers such as nylon, polyester, spandex, and natural fibers such as cotton, jute, sisal, ramie, silk etc are included to apparel fibers. Aramid, polyethylene, steel, copper, carbon, glass, silicon carbide, and alumina are examples of nonapparel fibers. It is possible to use nonapparel fibers for making cords and ropes, geotextiles and structural applications such as fiber reinforcements of composites [11].

The fibers can be also classified in terms of fiber length, continuous or staple fiber [12]. Staple fibers have short lengths. Continuous fibers have an infinite length. It is possible spinning into yarn for staple fibers, like continuous fibers. The staple fibers would be excellent choice for providing bulkinnes for filling, filtration, etc [11].

Another suitable classification can be made in the matter of natural and synthetic fibers. Their chemical structure has very important of fibers. For example, both of vegetable based and animal based fibers are polymeric. But natural fibers in the form of minerals correspond with crystalline ceramics [11]. Properties of most commonly used fibers in composite materials are given in Table 1.1.

	•	• •	-	
	Density	Elastic	Tensile	Axial
Fibers	g.cm ⁻³	Modulus	Strength	CTE/C°
		(GPa)	(MPa)	
E-Glass	2.6	72	1.7×10^3	5.0x10 ⁻⁶
S-Glass	2.5	87	2.5×10^3	5.6x10 ⁻⁶
PAN based C-fiber	1.7-1.9	230-370	1.8×10^3	-0.5x10 ⁻⁶
Pitch based C-fiber	1.6-1.8	41-140	1.4×10^3	-0.9x10 ⁻⁶
Single-crystal	2.25	1000	20.6×10^3	-
graphite				
Kevlar-49	1.44	131	3.8×10^3	-
Kevlar-149	1.47	186	3.4×10^3	-
Spectra(polyethylene)	0.97	117	2.6×10^3	-
Boron	2.5	400	2.8×10^3	4.9x10 ⁻⁶
FP (alumina)	3.9	379	1.38×10^{3}	6.7x10 ⁻⁶
SiC particles	3.3	430	3.5×10^3	4.9x10 ⁻⁶
SiC whiskers	3.5	580	8.0×10^3	4.9×10^{-6}
SiC fibers	2.6-3.3	180-430	$2.0-3.5 \times 10^3$	4.9x10 ⁻⁶
Stainless Steel	8.0	198	$0.7 - 1.0 \times 10^3$	18.0x10 ⁻⁶
Tungsten	19.3	360	3.8×10^3	11.6x10 ⁻⁶

Table 1.1 Properties of typical fibers used in composite materials.

1.3.5.1 Polymeric fibers

Natural polymeric fibers

Natural polymeric fibers are classified into two main groups [15]: Animal fibers group such as silk fiber, wool fiber etc and vegetable fiber such as cotton fiber, jute fiber, and rayon fiber etc. Properties of some vegetable fibers are given in Table 1.2.

Silk

Silk fiber is a product of some insects and spiders. Their mechanical properties depend on the type of insect or spider the fiber has been produced. The cocoon silk of the silk worm can be good example of excellent textile material. However, its mechanical properties are modest then spiders web silk. This is directly related with the fact that the cocoons don't need superior mechanical characteristics. But in spiders orb-web silk must absorb impact of the falling spider. Therefore, it is needed superior mechanical properties. As a material, silk fiber is a good electrical insulator. Their density is about 1.25 gcm⁻³. And the elastic modulus of silk fiber which is produced from spiders are about 10 GPa [11].

Cotton

Cotton fibers are one of the most important fibers in general. The cross section of cotton is flat because its lumens, internal space of a cell collapse when it is harvested. The composition of cotton includes mostly crystalline cellulose with varying amounts of pectin, fat and wax. Cotton fiber is biodegradable and takes colour easily. Therefore, they are very versatile fibers. Also their durability in different environment is very good. Their density is about 1.5 g.cm⁻³.

Jute

Jute fibers are produced mainly in Bangladesh, Brazil, and India. Their main application areas are generally making cords, coarse cloth and sacks. Their colour may be from lustrous yellow to brown. Individual jute fibers which are commercially obtained as strands are cemented together by using natural gums. It can be observed that the cross section of a jute fiber shows polygonal cells when they are observed in an optical microscope. These cells have thick walls and they are about 2.5 mm long. Their density is about 1.5 g.cm⁻³ and their strain to fracture is about 1.7%.

Fiber	Density (gcm ⁻³)	Strength (GPa)	Young's Modulus	Specific strength ^a	Specific modulus ^a
Jute	1.50	0.85	(GPa) 64	0.57	43
Ramie	1.50	0.83	59	0.62	43 39
Hemp	1.50	0.90	69	0.60	46
Flax	1.50	1.08	100	0.71	67

Table 1.2: Properties of some vegetable based fibers.

Note: ^a Specific strength and modulus are strength/density and modulus/density, respectively.

Synthetic polymeric fibers

Nylon

Nylon is a common name when a long chain polyamide thermoplastic contains more than 85% aliphatic groups in the main chain. It should be known that nylon and polyamide are accepted common names for the identical group of fibers. The term polyamide is more common in Europe while the term nylon is commonly accepted in North America and UK. Nylon 66 and Nylon 6 are most well-known polyamides which are produced by polycondensation of (hexamethylene diamine) and (adipic acid), or ring-opening polymerization of lactam (ϵ -caprolactam). They have similar characteristics, even their melting point is similar. Nylon 610, Nylon 11, and Nylon 12 are some examples of other commercially available polyamides which are used in industrial field mostly [11].

Polyester fibers

Polyester fibers are other important family of fiber. Polyesters commonly known as Dacron in USA and Terylene in UK. There are thermoplastic and thermoset polyesters but Polyethylene terephthalate (PET) is one of the most important polyester fiber and PET became synonym with polyester. PET is composed of ester links of aliphatic and aromatic groups. The nylon or polyethylene structure is tiny than that of polyester. These factors affect the flexibility and crystallization rate of PET. The crystallization rate of nylon or polyethylene is faster than PET and because of polyesters rather bulky structure, polyester is less flexible [11].

Polyolefin fibers

The two most well-known polyolefin fibers are polyethylene and polypropylene fibers. Chemical structure of polyethylene contains only of methyl groups. High density polyethylene and Low density polyethylene are very well known types of polyethylene. New developed ultra-high molecular weight polyethylene has very good properties. Especially UHMWPE fibers have high strength and high modulus. Polypropylene fibers don't have very high modulus. Every ethylene group of polypropylene has methyl side groups. There is steric repulsion between these methyl side groups and therefore the trans-gauche transformation is prevented. This effect cause that the Young's modulus of polypropylene is lower than that of polyethylene and nylon [11].

1.3.5.2 Metallic fibers

Metals are one of the most common engineering materials used in structural industry. Their reasonable cost and combination of their excellent mechanical and physical properties make them very important. One of the reason why metals have so important position between engineering materials is their ability of plastic deformation. This allows producing them in simple and giving them complex shapes and forms. Metallic fibers have been being used for a long time. Some of the common examples of metallic fibers: Tungsten filaments for lamps, steel cables for structural industry and also strings for musical instrument.

1.3.5.3 Ceramic fibers

Ceramics are generally crystalline structure but silica-based glasses as a sub-category of ceramics are non-crystalline. And mostly ceramics have ionic bonding. In ionic bonding, it occurs electron transfer between atoms and that makes the compound. As a result of ionic interaction between ceramic atoms, high strength and brittleness can be observed. In ceramic materials generally intrinsic lattice resistance to dislocation motion is very high. There are two main subclasses of ceramic fibers: Natural ceramic fibers and Synthetic ceramic fibers.

Natural ceramic fibers

Naturally occurring ceramics are lesser than natural polymer fibers, however there are two well-known types of ceramic fibers: Asbestos fibers and Basalt fibers.

Asbestos term is used for some natural silicate based ceramic minerals in fibrous form. It has an important advantage that it is resistant to heat, acids, alkalis, and other chemicals. The structure of asbestos fiber is crystalline. They have low strength but although asbestos is natural, they are not attacked by insects or micro-organisms as on conduction with vegetable fibers. The use of asbestos is restricted because it cause lung cancer if inhaled.

Basalt is a volcanic rock found especially in North America and Eastern Europe. The composition of basalt fibers is very depended of the native basalt rock. The fiber diameter is generally between 10 and 15 μ m and it can be changed with melt temperature and speed of pulling.

Synthetic ceramic fibers

There are two main category of synthetic ceramic fibers: oxide and nonoxides. An important example can be given for oxide fibers is alumina and for the nonoxides is silicon carbide. The melting point of ceramics are very high. Therefore, to produce synthetic ceramic fibers, sintering or low firing must be chosen. Due to these methods will result in a small grain size but residual porosity must be in control. Too high level of residual porosity is unacceptable. An important sub-category of oxide fibers is silica based glass fibers.

1.3.5.4 Glass fibers

"Glassy materials" term is used generally large family of materials which their structure is noncrystalline. Glass fibers have several application areas such as automotive, aerospace [13], marine, civil construction, insulation, sporting goods and electronical industries. One of the most important application area for glass gibers is composite materials. Especially they are being used so much with polymer matrix materials. Their diameter differs between 5 and 20 µm. Because they have fine diameter and low modulus, they are extremely flexible. Commonly used glass fibers in market have different chemical compositions. But most of them are silica based which means their 50% or 60% of composition is SiO₂. They also contain other oxides of Ca, B, Na, Al, Fe etc. The most well-known types of glass fibers in the marke are E-glass, S-glass, C-glass and Cemfil. Table 1.3 gives their chemical compositions. Eglass is a good electrical insulator. It has high strength and reasonable Young's modulus. C-glass is developed for corrosion resistance. It has a better resistance to corrosion then that of others. S-glass has high silica content. They can tolerate higher temperatures than others. Cemfil is a special class of glass fiber. It is noted that more than 90% of the produced glass fibers are E-glass.

Compound	E-glass	C-glass	S-glass	Cemfil
SiO ₂	55.2	65.0	65.0	71.0
Al ₂ O ₃	8.0	4.0	25.0	1.0
CaO	18.7	14.0	-	-
	1.5	2.0	10.0	
MgO	4.6	3.0	10.0	-
No O	0.2	05	0.2	No. O I
Na ₂ O	0.3	8.5	0.3	Na ₂ O+
K ₂ O	0.2	_		11
K 2 O	0.2	-	-	11
Li ₂ O	7.3	5.0	_	<1.0
		5.0		~1.0

Table 1.3: Chemical composition of some of the common glass fibers.

The density of silica-based glasses is mostly very low. Their strength is absolutely high. But their elastic modulus is not very high. Therefore, their strength to weight ratio is really high. Because of moderate elastic modulus, their modulus to weight ratio is also moderate. Effect of fibers to structural materials are represented in Figure 1.1.

1.3.5.5 Carbon fibers

Carbon fibers are very important fibers used in high-performance composite materials. As an element carbon is very light. Its theoretical density is 2.27gcm⁻³. It can be found in a variety of forms, amorphous, glassy and diamond. Carbon fibers are produced by pyrolysis of organic fiber precursors. Some of the most well-known precursors are Rayon, Polyacrylonitrile (PAN) and Pitch. The Modulus and strength of carbon fibers highly depend on the precursor type and processing. Yielding percentage (wt %) is very important to select of precursor. For example, as a precursor fiber, polyacrylonitrile (PAN) fibers are more important than Rayon fibers. But PAN fibers are chosen more, because their higher yield is higher than Rayon fibers. As a raw material, pitch is very cheap. Therfore, Pitch-based carbon fibers are also very popular. Carbon fiber is commonly used for reinforcing low modulus polymeric materials. Some applications of this kind of composites are range from aerospace to sporting goods. Carbon fibers are also used for reinforcing cement based materials. This

improve tensile strength, flexural strength, impact strength, dimensional stability etc.

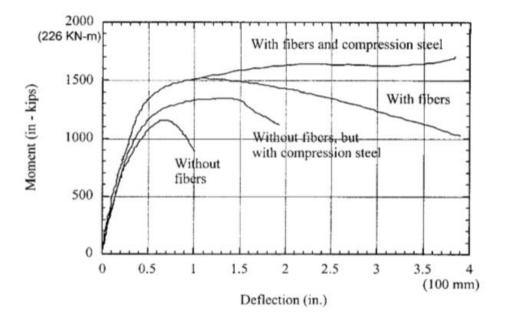


Figure 1.1: Enhancement of structural ductility in R/C FRC beam.

1.3.6 Polymers and monomers for cement modifiers

1.3.6.1 Brief history of invention of the polymers and monomers for cement modifiers

Polymer modified mortars and concretes are famous structural material since they were developed 170 years ago. In 1923, Cresson had the first patent about a polymer-hydraulic cement system [18]. After that in 1924, another important invent about the polymer latex-modified systems was succeed by Lefebure [19]. Chloroprene rubber (Neoprene) latexes [20] and polyacrylic latexes [21] were invented in the 1940's. In 1960's, Styrene-butadiene rubber [22], polyacrylic ester [23] and poly(vinylidene chloride- vinyl chloride) were begun to use in structural applications.

Dikeou, Steinberg, et al developed other systems in 1971[24]. Donnelly [25] and Duffi [26] were invented and patented systems based on epoxy resins in 1965 and 1973 respectively. A system modified with urethane prepolymer was invented and patented in 1959 [27].

As a water-soluble polymeric cement modifier, methyl cellulose has been widely used in the adhesive polymer-modified mortars area since the beginning of 1960's [28]. The effect of hydroxyethyl cellulose and polyvinyl alcohol for the water-soluble polymermodified mortars were shown by Shibazaki [29]. Riley and Razl. were summarized review of the polymer modified systems in 1974 [30]. At present, polymeric cement modifiers are used often as a construction material in advanced countries.

1.3.6.1 Classification of the polymers and monomers for cement modifiers

They can be produced by mixing, a polymer or monomer in a liquid, powdery or dispersed form with fresh mortar or concrete. If it is needed, the monomer in the concrete or mortar can be polymerized in situ.

There are several types of polymer-modified concretes and mortars. These are latexredispersible polymer powder, water soluble polymer, liquid resin and monomermodified concretes and mortars are some of the examples of polymer-modified concretes and mortars. These are shown in Figure 1.2. The most commonly preferred cement modifiers are latex-modified concrete and mortar.

As it is stated that polymers and monomers can be used in form of latexes, liquid resins, monomers and water-soluble polymers in mortars and in concretes. But there is very important point about usage of such modifiers. Both of polymer phase generation and cement hydration must continue well to create a monolithic matrix phase with a network structure in which the hydrated cement phase and polymer phase interpenetrate. Aggregates are bounded in polymer-modified mortars or concretes by such a co-matrix phase. Superior properties of polymer-modified mortars and concretes are a result of this process.

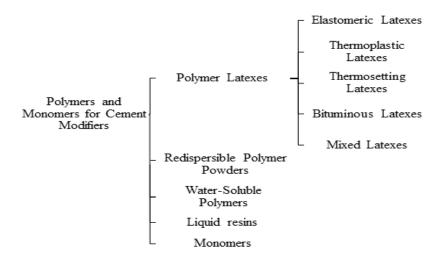


Figure 1.2: Polymers and monomers for cement modifiers.

1.4 Principles of Polymer Modification for Mortars and Concretes

1.4.1 Modification with latex

Hydration and polymeric film formation processes control the latex modification of mortar and concrete. Generally, the polymer formation process follows the cement hydration process [31]. There are two important points about latex modification of mortars and concretes. These are mechanism of polymer-cement co-matrix formation and influence of latex modification on physical and mechanical properties of mortars and concretes.

1.4.1.1 Mechanism of polymer-cement co-matrix formation

Co-matrix phase is composed of polymer films and cement gel. This co-matrix phase is formed according to three steps. Figure 1.3 [32-33] illustrates these forming steps. It is examined composite mechanisms of latex modified mortars. The result shows that interfacial layer of cement hydrates with a large amount of polymer particles on the aggregates and cement particles. Thus, it is understood that generation of polymeric film and the dispersion of polymeric particles are both required for description of composite mechanism of latex modified systems.

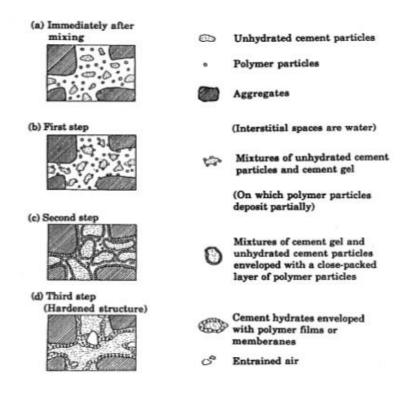


Figure 1.3: Simplified model of formation of polymer-cement co-matrix.

Polymer film generation on the cement hydrates is illustrated in Figure 1.4.

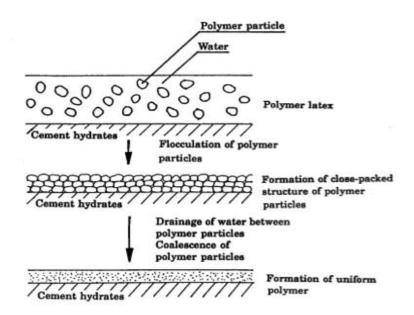


Figure 1.4: Simplified model of process of polymer film generation on cement hydrates [32].

Step 1 When polymer latexes and fresh cement concrete or mortar come together, the polymer particles are dispersed in the cement phase. Due to cement hydration and the saturation of water with calcium hydroxide generated along the hydration, the cement gel is generated gradually in polymer-cement paste. This resembles reaction of calcium hydroxide in the water phase with a silica surface of the aggregates. In the end of this reaction calcium, silicate layer is generated [34]. It is known that the generation of the ettringite and calcium hydroxide in the contact area of the aggregates and cement hydrates is related with their bond between them [35-36]. It is found that, calcium hydroxide [Ca(OH)₂] crystals are generated at the interfacial zone between granite or limestone and cement hydrates in the presence of polymer latexes [39-40]. Also it is important that properties of latex modified mortars are affected by morphology or behaviour of calcium hydroxide crystals [39-40].

Step 2 In the capillary pores, the polymer particles are encircled step by step, due to generation of the cement gel structure. On the surfaces of the mixture of cement- gelunhydrated cement particles, the polymer particles get together and create floccules to generate a continuous close-packed layer of polymer particles, during the cement hydration continues and capillary water is reduced. Simultaneously the particles stick to the mixtures and silicate layer of the aggregates. The adhesive polymer particles fill the larger pores in the mixture. This case can be described by the differences of the size of the pores in the cement paste. The range of the pore size of cement paste is from a few hundred picometres to several hundred nanometres. In typical latex, it ranges from 50 to 500 nanometres. Between the particle surface of reactive polymers and calcium ions (Ca⁺⁺), calcium hydroxide [Ca(OH)₂] silicate surfaces or crystal surfaces over the aggregates, some chemical reactions can occur. Poly (styrene-acrylic ester) (SAE), polyacrylic esters (PAE) are some of the examples for reactive polymers which are reacted [41-44]. The mechanism of the reactions is illustrated in Figure 1.5. It is supposed that the bond between aggregates and cement hydrates, the polymer-cement co-matrixes are improved by this chemical reaction. But chemical bonds have not important effect to improve the properties of the latex-modified mortars and concretes. Because the effect of the chemical bond of the properties of this type of mortars are controlled by their volume fraction.

Step 3 The close-packed polymer particles on the cement unit inti continuous films by cement hydration. Finally, Monolithic network is generated when the continuous films or membranes are bound together. In this network structure, throughout the cement hydrate phase interpenetrates polymer phase. This kind of structure become matrix phase of latex-modified concrete and mortar. The aggregates are bounded by this matrix phase to the hardened mortar and concrete [45].

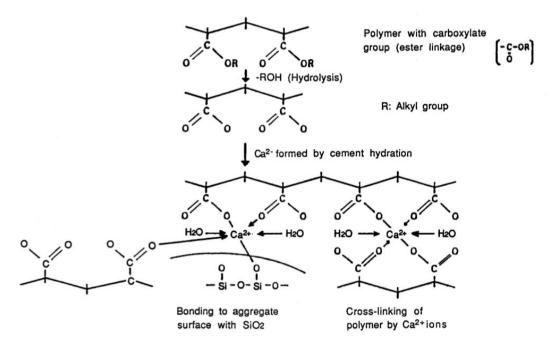


Figure 1.5: Schematic representation of reaction between polymer with carboxlate groupe (ester linkage), ordinary portland cement and aggregate.

1.4.1.2 Influence of latex modification on physical and mechanical properties

The properties of cement concrete and mortar are usuallu improved very much with modification of latex. Polymer-cement co-matrix formation which has great influence on the properties of cement mortar and concrete is illustrated in Figure 1.6 [46]. Usually it is expected that, agglomerated calcium hydroxide and calcium silicate hydrates are main structure of hardened cement paste. This agglomerated structure is bound together by weak van der Waals forces. Because of this weak bond, microcracks can occur easily under stress. This cause poor mechanical properties on cement mortar and concretes such as poor tensile strength and poor fracture toughness. But the microcracks are connected by the polymer membranes or films in latex-modified mortar and concrete. Due to bridging microcraks by polymeric membranes or films, crack propagation is prevented and the bond between cement hydrate-aggregate is improved.

Due this positive effect, increase in the polymer-cement ratio of modified cement mortar and concretes increases tensile strength and fracture toughness.

(Polymer cement ratio is the weight of total solids in a polymer latex to cement in a concrete or mortar). But some discontinuities can occur in generated monolithic network structure by air entrainment and polymer inclusion. Despite some chemical reactions continue effectively, strength is reduced in this case. Due to polymer membrane or film generation in the modified mortar and concrete, increase in some properties can be observed. Improved waterproofness, watertightness, moisture transmission, chemical resistance, resistance to chloride properties can be given as example for some advantages of using latex modifiers. This kind of effect is advanced with increasing polymer-cement ratio.

The hydration product of Portland cement is called cement gel. This gel has a high specific surface area. The surface area of cement gel can be a thousand times large than surface area of the unhydrated cement. Degree of hydration is a measure of formation of the surface area. According the studies, addition of the latex at the beginning stage can affect the rate of cement hydration depending on their chemical nature. But the compare the specific surface area, 28-day for curing must be waited. It is not possible to observe polymer modification before 28-day cure period [45].

Polymer-cement ratio and the type of polymer in the latex affect the pore structure of latex-modified systems. Generally, pore volume or total porosity is depended on the polymer-cement ratio. They decrease with increasing polymer-cement ratio. This improves the impermeability, freeze-thaw durability and resistance to carbonation of the latex-modified cement mortar and concrete. Latex modified cement mortar and polymeric film can be seen in Figure 1.7 [47]. In Figure 1.8, interface between Portland cement paste and VA copolymer is shown [48].

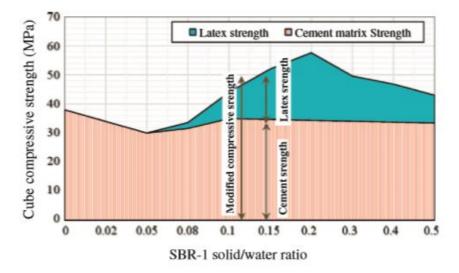


Figure 1.6: Effect of SBR latex solid/water ratios on latex netweork and cement matrix compressive strength at 28 days for cement paste co-matrix subjected to dry curing.

1.4.2 Redispersible polymer powders

Except the addition of redispersible polymer powders, it is nearly the same general modification principles of redispersible polymer powders with general modification principles of latex of cement mortar and concrete. Frequently there are two steps of modification with redispersible polymer powders. Generally, first the dry mixing is implemented for redispersible polymer powders and premix of concrete or mortars. Wet mixing with water follows the dry mixing. In the modified concrete and mortar, the redispersible polymer powders are re-emulsified at the wet mixing stage. Thus, redispersible polymer powders have same behaviour in the same way with latex modifiers after addition of water to redispersible powders with premix of concretes and mortars.

1.4.3 Water-soluble polymers

During mixing of the water-soluble polymers e.g. cellulose derivatives, and polyvinyl alcohol with cement concrete or mortar, small amount of the polymer powders is added into mortar or concrete in form of powder or aqueous solution. Modification with water-soluble polymers are improved workability of modified mortars and concretes. Main reason of the improving of workability is about the surface activity of the water-soluble polymers and this kind of modification prevents the 'dry-out' phenomena. The explanation of the prevention of 'dry-out' is the viscosity increase in the water phase of modified cement concrete or mortar and in them a blocking effect by the generation of very thin and water-impervious film. Because of this phenomena, generally, it is hard to observe the contribution of water-soluble polymers to an improvement in the mechanical properties of modified cement concretes or mortars.

1.4.4 Liquid resins

The principle of modification with liquid thermosetting resin is addition of big amount of prepolymers or low-molecular weight polymers which can be polymerized to cement concrete or mortar during mixing. Generally, the latex modified systems have lower polymer content than liquid thermosetting resin modified mortars and concretes. In this modification, simultaneously the cement hydration occurs and polymerization initiated with addition of water to generate a polymer phase. Co-matrix is generated with a cement hydrated phase and network of polymer. In conclusion due to this occurrence, aggregates are bound strongly. The mechanical properties of modified cement concretes and mortars by liquid thermosetting resins are improved in same mechanism with latex-modified systems.

1.4.5 Monomers

The main principles of modification of mortars and concretes with monomers resemble the modification of latex-modified systems. In this type of modification, the monomers are added to premix of cement composites. In latex-modified systems, the polymer latex is added. This is the main difference between two systems. In modification with monomers system, cement hydration and polymerization of monomers occur simultaneously after mixing of considerable amount of monomers with cement concrete and mortar. After curing, monolithic matrix occurs and this matrix binds the aggregates. Usually, this type of modification can not succeed. The first problem is hindrance of cement hydration. Mortars and concretes are alkaline due to cement. The second problem is bad effect of alkaline environment on the monomers. The monomers are degraded in such environment. The last problem is the difficulties dispersing the monomers and other components uniformly during mixing.

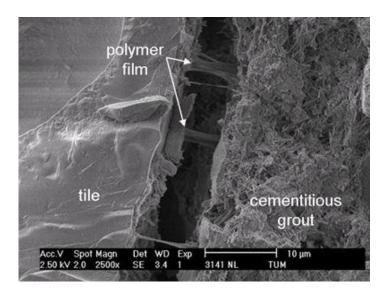


Figure 1.7: Adhesion of a sintered tile on cement mortar by latex film bridging (SEM recording- hardening: 28 days).

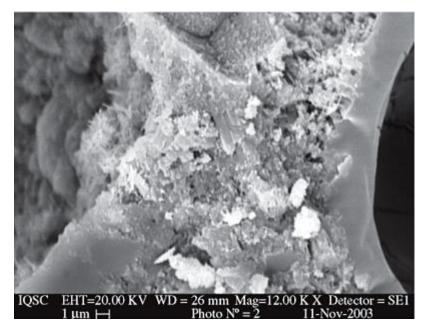


Figure 1.8: Interface between VA copolymer and Portland cement paste.

2. EXPERIMENTAL DESIGN AND OPTIMIZATION

2.1 Response Surface Method

Response surface methodology (RSM) is combination of statistical and mathematical techniques. It is used for building an empirical model. The response is affected by lots of independent variable. An experiment consists of series of tests. It is called runs. The change about runs are done in the input variables to describe the reasons for changes in the output response.

In 1987, RSM is first developed by Box and Draper for model experimental responses. After the first development of RSM, the method is further developed for modelling of numerical experiments. The type of error which is made by response, is main difference between them.

Some of the errors in physical experiments are measurement errors in computer experiments, incomplete convergence of iterative processes, discrete representation of extended physical phenomena or round-off errors. The errors are expected random in response surface method [49].

RSM is practical in three different techniques:

- 1) Techniques of regression modelling,
- 2) Statistical experimental design,
- 3) Optimization methods.

Industrial, Biological and Clinical Science, Social Science, Food Science, and Physical and Engineering Sciences are some of the application areas which are RSM most commonly used. The first aim of the using response surface method is obtained the optimum response. It is important to obtain the compromise optimum response, if there is more than one response. If design data has constraints, the experimental design must be adjusted to meet requirements of the constraints. The second aim is investigation response changes due to controlling design variables. It is needed an implicit or explicit functional relationship between input parameters and output response for the probabilistic analysis. Except the simple cases, this is very difficult. Sometimes establishing functional relationship can be also very complicated to perform probabilistic analysis. In this kind of situations, it is suggested using the concept of response surface methodology (RSM). Three dimensional response surface is illustrated in Figure 2.1.

For example, Engineers want to investigate properties of calcination of the Roman cement. Therefore, they have used response surface method for optimization. X_1 represents the levels of temperature and X_2 represents the time. In this optimization, the aim of the engineers is finding the levels of temperature, time and they want to maximize the early age strength of the cement (y).

$$y = f(x_1, x_2) + \epsilon \tag{2.1}$$

In Equation 2.1, ϵ symbolizes the error observed in the response y. $f(x_1, x_2)$ represents the surface, which is called response surface. The response can be illustrated either as contour plots or in 3-D space. Constant response of curves are contours. Contours fix the all other variables. Height of the response surfaces can be matched with contours.

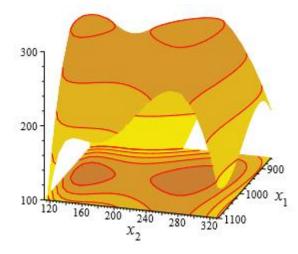


Figure 2.1 : Three-dimensional response surface and the corresponding contour plot for the early age strength of Roman cement where x1 is the calcination temperature (°C) and x2 is the residence time (mins).

2.2 Design of Experiments

Design of experiment is important part of RSM. Usually, this topic is symbolized with 'DoE' abbreviation. These experiment strategies can be fitted in models of either physical experiments, or numerical experiments. The aim of DoE is choosing points where the response should be evaluated. The principles of optimal design for

experiments are related with the mathematical model of the process. Usually, these mathematical models are based on polynomials. They have unknown structures. Therefore, conformed experiments are performed only for every particular problem. Accuracy of the approximation and the cost of the making response surface are very depended on the selection of the design of experiments.

In the recent steps of the process, screening experiments are implemented, when some of the design variables have little or no effect on the response. The aim is identifying the design variables. Because there are large influence identifying the design variables for further investigations. Box and Draper (1987), Myers and Montgomery (1995) and some other researchers are described design of experiments in detail.

As it is introduced before, runs defines an experimental design and levels are potential settings of each independent variable in the N-dimensional space.

2.2.1 Full factorial design (FFD)

In a full factorial design, it is necessary to examine all possible combinations to build an approximation for investigating interactions between N design variables. The strategy of factorial experiment is about design variables. In factorial experiments, design variables are changed together, instead of one at a time.

In the optimization of lower and upper bounds of N design variables, some problems can occur. These problems must be defined. 2^{N} full factorial is an experimental design which of the variables described at only the lower and upper bounds. In 3^{N} full factorial design, the midpoints are also included. Midpoints are the only difference between them. In Figure 2.2, a 3^{3} full factorial design is represented.

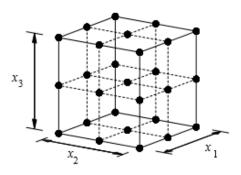


Figure 2.2: A 3³ Full factorial design.

Second-order models can be fitted by factorial designs. Second-order models increase greatly the optimization process than the first-order model. Second-order models are defined in Equation. 2.2:

$$y = a_0 + \sum_{i=1}^n a_i x_i + \sum_{i=1}^n a_{ii} x_i^2 + \sum_{i=1}^n \sum_{i=1}^n a_{ij} x_i x_j \ (i < j)$$
(2.2)

In this model the tuning parameter is represented with the design parameters are represented as x_i and x_j .

For development of a quadratic response surface in N variables, it is needed the estimation of the tuning parameters. So (N+1) (N+2)/2 evaluations must be done at least. Generally, full factorial designs are constructed if there are five or fewer variables are considered. Because for more variables, it must be made more experiment and the number of experiments are increased exponentially with increasing number of variables (3^N) . Fractional factorial design is used for such circumstances. In this design, only the important design variables are used for screening. (3^{N-p}) is used for fractional factorial design. For example, if p=1is for 3^3 design, it results 3^{3-1} . This situation is represented in Figure 2.3.

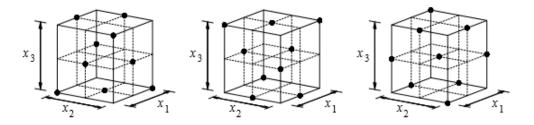


Figure 2.3: An example of fractional factorial design.

2.2.2 Central composite design (CCD)

Central composite design is a suitable model for creating second-order models. CCD are developed by axial points which help to estimation of tuning parameters of second-order model and additional centre [53]. Central composite design for 3 variables are illustrated in Figure 2.4.

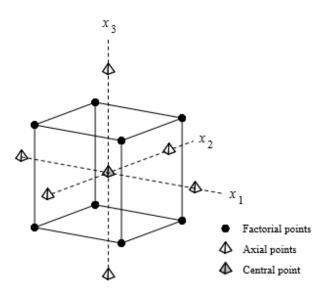


Figure 2.4: CCD for 3 variables at 2 levels.

In central composite design, there are 3 different type of design points. These are 2 levelled full-factorial or fractional factorial points, star (axial) points and centre points. The total number of experiment is illustrated by Equation 2.3.

Total number of experiments =
$$2^{k}+2k+1$$
 (2.3)

At this equation, factorial points are represented with (2^k) . (-1) and (+1) are the minimum and maximum values of the factors. For example, if there are only 2 factors considered, it means that, there are 4 factorial design points. Star (axial) points are represented with (2k). The levels are represented with $\pm \alpha$. (α) is different from minimum and maximum values and it is generally larger than 1. The value of α represents the positions of the star points. (α) is calculated with $\pm \sqrt[4]{2^k}$. The last term of this equation is 1. It represents the central points. The central points are the points which level is 0. Level 0 is calculated by mean of minimum and maximum points [50].

2.2.3 D-optimal designs

The D-optimality criterion makes possible to create useful quadratic models. The aim of this method is choosing P design points.

$$Y = X * B + e \tag{2.4}$$

In Equation 2.4, Y represents a vector of observations, e represents a vector of errors, B represents the vector of tuning parameters and X represents matrix of the design

variables of design variables at plan points. Using the least-square method B can be calculated by Equation 2.5.

$$B = (X^T * X)^{-1} X^T Y$$
(2.5)

In the experiments, the best set of points make the determinant $|X^TX|$ maximum according to D-optimality criterion. "D" symbolizes the determinant of X^TX . By using D-optimal design is created response surface model with maximum variance of the estimated response is minimized which means the points of the experiment minimizes the error in the predicted coefficients of the response model. Some of the advantages using of this methods are: It is possible to use irregular shapes and it is also possible to include extra design points due to this method. In computer-developed design of experiments, D-optimality method is one of the most commonly used criteria.

2.2.4 Taguchi's contribution to experimental design

Taguchi's contribution is called orthogonal arrays which is a study of the parameter space based on the fractional factorial arrangement from design of experiments. Taguchi brings something different about a system of tabulated designs. This development of a system of tabulated designs get decrease the number of experiments in comparison with that of full factorial design. He discusses that the consideration of interaction between two design variables is not needed. The ability to process discrete variables is an advantage of this method. And the ignorance of the parameter interaction can be given as a disadvantage.

2.2.5 Latin hypercube design

Latin hypercube design is an N-dimensional improved variant of the traditional Latin square design. Only one point is located on each level of every design. The number of levels and runs are the same. The levels are attached to runs randomly. The first advantage of this method is guaranteeing of the representation of every level, no matter if the response is managed by only few ones. The number of points to be analysed can be easily determined. This is another advantage of this method.

2.2.6 Audze-Eglais' approach

Audze and Eglais have developed a novel elaboration of plans of experiments in 1977. This is similar to the Latin hypercube design. The number of experiments (K) and the number of factors (N) are the only parameters of the input data for the elaboration of the plan. Space-filling property is one of the important advantage of this method. However, it is not possible to add extra points to the initial set after the definition of the design. This a serious disadvantage of this methods. Rikards has been used this method to design composite materials. The comparison of CCD, latin hypercube and audze-eglais methods are represented in Figure 2.5.

The main principles of this methods are:

- The number of experiments is equal to the number of levels of factors. (This is one of the similarity with Latin hypercube design.)
- 2) The points of experiments are distributed uniformly as much as possible. A physical correlation is considered with the potential energy of repulsive forces for points of unit mass, if the distance between the points and the magnitude of the repulsive forces are proportional, the situation is represented in Equation 2.6.

 $\sum_{p=1}^{p}\sum_{q=p+1}^{p}\frac{1}{L_{nq^2}} \rightarrow min$

(2.6)

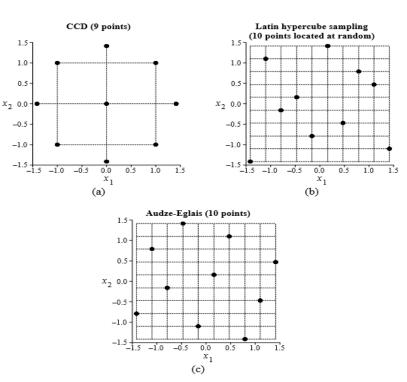


Figure 2.5: Comparison of Audze-Eglais (c), CCD (a) and Latin hypercube design (b)

3. EXPERIMENTAL PART

Specific surface

Mechanical Properties

Compressive Strength (2 days)

Compressive Strength (28 days)

Initial set

3.1 Materials

3.1.1 Cement

The type of cement, which is used in the specimen, is Çimsa 52.5 R White. Some physical, chemical and mechanical properties of this cement is given in Table 3.1.

experiments.		
Chemical Properties		
SO ₃	3.65%	
Dissolved Chromium Cr ⁻⁶	0.50 ppm	
MgO	0.87%	
Cl ⁻	0.0137%	
Insoluble matter	0.06%	
Loss of ignition	3.68%	
Physical Properties		
Specific weight	3.06 g/cm ³	
Whiteness	85.3%	
Sieve fraction (0.045 mm)	1.1%	

4835 cm²/gr

110 minute

40.6 MPa

62.4 MPa

Table 3.1: Some chemical, physical and mechanical properties of used cement in experiments.

3.1.2 Sand

60-70 Silica sand has been in experiments. Results of sieve analysis and some physical properties of used sand are given in Table 3.2 and in Table 3.3.

Mesh	Oversize grain	Multiplication	Percentage
2.0			
1.6			
1.0			
0.710			
0.500	0.016	4.0	0.32
0.355	1.41	49.35	2.86
0.250	9.18	413.1	18.63
0.180	20.93	1255.8	42.47
0.125	13.69	1108.89	27.78
0.090	3.22	379.96	6.53
0.063	0.65	106.6	1.32
Pan	0.04	11	0.08
Sum	49.28	3328.7	100
AFS	67.55		
Average size, µm	209.15		

Table 3.2: Results of sieve analysis of 60-70 sands.

Analysis	Acceptable Criteria		Results
	Min	Max	
AFS	-2	+2	67.55
% Humidity	3	8	
% Clay	0.1	0.5	0.30
% SiO ₂	98	99	98.10
% Fe ₂ O ₃	0.16	0.40	0.16
% Al ₂ O ₃	0.5	1.2	1.08
Sintering	1500 °C	1750 ⁰ C	>1500 °C
Temperature			
Temperature	-4	+4	
Loss of ignition	0.02		

Table 3.3: Some physical properties of sands.

3.1.3 Calcite

 $30 \ \mu m$ calcite has been used in experiments. Some details about the used calcite are given in Table 3.4.

Analyse name	Range	Results
Colour	96.0-98.0	97.18
CaCO ₃	min 98%	98.14
MgCO ₃	max 2%	1.47
Dissolved in HCL	max 0.5%	0.39
Humidity	max 0.20%	0.09
Top cut (D 97)	160-240 μm	210.83 µm
Average (D 50)	32-40 µm	37.25 μm

 Table 3.4: Some properties of Calcite used in experiments.

3.1.4 Cellulose

Tylose H300 P2 cellulose has been used in experiments. Some detailed information about cellulose used in experiments are given in Table 3.5.

Constitution	Hydroxyethyl cellulose
Appearance	white powder
Etherification	standard etherification
Particle size	powder
Delayed solubility	yes
Level of viscosity	300 mPa.s
Product Specification	
Moisture	$\leq 89\%$
Bulk density	ca. 450 g/l
Etherification (MS)	ca. 2.00
Particle size	< 63 µm; ca. 35%

 Table 3.5: Some properties of cellulose used in experiments.

Product Properties

3.1.5 Fibers

Four types of fibers have been used in experiments. These are 12 mm glass fiber, 6 mm surface treated glass fiber, polyamide fiber and polypropylene fiber. Some details about fibers used in experiments are given in Tables (3.6 - 3.8).

Composition	%100 Virgin polypropylene
Туре	Multifilament
Cross Section	Round
Fiber Length	3 mm
Tenacity	6.5-7.0 grams/denier- High Tenacity
Tensile Strength	600-700 MPa
Young's Modulus	3000-3500 MPa
Elongation	20-25%
Specific Density	0.91g/cm ³
Softening Point	150 °C
Melting Point	160 ⁰ C

Table 3.6: Technical details about polypropylene fibers used in experiments.

Fiber Length3 mmFilament Diameter14 μmLoss on ignition55%Specific Gravity2.68 g/cm³Modulus of Elasticity72 GPaTensile Strength1,700 MPaMoisture0.3% max	Cem-FIL Anti-Crack AR-Glass fibers	
Loss on ignition55%Specific Gravity2.68 g/cm³Modulus of Elasticity72 GPaTensile Strength1,700 MPa	Fiber Length	3 mm
Specific Gravity2.68 g/cm3Modulus of Elasticity72 GPaTensile Strength1,700 MPa	Filament Diameter	14 µm
Modulus of Elasticity72 GPaTensile Strength1,700 MPa	Loss on ignition	55%
Tensile Strength1,700 MPa	Specific Gravity	2.68 g/cm ³
	Modulus of Elasticity	72 GPa
Moisture 0.3% max	Tensile Strength	1,700 MPa
	Moisture	0.3% max

Table 3.7: Technical details about 3 mm glass fibers used in experiments.

Table 3.8: Technical details about 12 mm glass fibers used in experiments.

Technical Characteristics of Anti Crack HP 12		
Material	Alkali resistant glass	
Fiber Length	12 mm	
Aspect Ratio (length/diameter)	58	
Filament Diameter	$17 \ \mu m \ / \ 0.00067$	
Loss on ignition (%)	1.00	
Moisture (%)	0.50 max	
Specific Gravity	2.68 g/cm^3	
Modulus of Elasticity	72 GPa	
Tensile Strength	1000-1700 MPa	
Softening Point	860 ⁰ C	

3.1.6 Polymeric cement modifier

BASF Acronal S400 styrene-acrylic copolymer has been used in experiments. This is aqueous plasticizer-free of an acrylic acid ester and styrene. Some technical details about this resin are given in Table 3.9.

Type of dispersion	anionic
Solids content	approx. 57%
pH	approx. 7-9
Viscosity	140-200 mPa.s
Glass transition temperature	approx8 ⁰ C
MFFT	approx. 0 ⁰ C

Table 3.9: Some properties of polymeric resin used in experiments.

3.1.7 Superplasticizer

Sika ViscoCrete Hi-Tech 3051 type superplasticizer has been used in experiments. This is a polycarboxylate ether based polymer. Some technical information about this superplasticizer are given in Table 3.10.

Technical details	
Chemical structure	Modified polycarboxylate ether based
	polymer
Density	1.07 kg/l- 1.11 kg/l at 20 0 C
рН	3-7
Freeze point	-9 °C
Percentage of Cl can be dissolved	
in water	Max 0.1% contains no Cl
Alkali value (%Na ₂ O)	Max 0.4%

Table 3.10: Technical details of superplasticizer used in experiments.

3.1.8 Shrinkage reducing agent

As a shrinkage reducing agent, Sika Control-40 has been used. This agent minimizes shrinkage also makes mortars and concretes durable in wet environments. Some technical information about this agent is given in Table 3.11.

Form	Liquid hydroxyl combinations
Colour	Clear/Red
Density (20 °C)	1.0 kg/lt approximately
pH (20 ⁰ C)	10.0 ± 1.0
Chloride content	No added chlorides
TEA content	Does not contain triethanolamine
Air entrainment	May have an effect on depending on mixing.
Effect on setting time	May retard concrete at lower temperatures.

Table 3.11: Technical details of shrinkage reducing admixture.

3.1.9 Water

Tap water has been used.

3.2 Mix Proportions and Preparations of Specimens

In this experiment, effect of different water-cement, polymer-cement, fiber-cement ratios and effect of different fibers, hybrid fibers of mortars have been investigated. Due to this aim, a mathematical model by using surface respond method has been evaluated. In this method 15 different mixture have been prepared. Mixture 1 has been produced 6 times because they are the control unit of the mathematical model. Out of mathematical model, 3 hybrid fibered mixtures have been produced. Their water-cement, fiber-cement and polymer-cement ratios are the same.

H1 is 12 mm glass fiber and polypropylene fiber mixture. H2 is 12 mm glass fiber and polyamide fiber mixture. In H3, surface treated glass fiber by Şişecam has been used. In H4, the same amout of 3 mm Cem-FIL glass fiber and 12 mm glass fiber have been used together.

To minimize the experimental errors, 3 specimens have been produced by each group. Totally 24 groups have been produced.

Mix proportions have been determined to response surface model. Design of experiment model is central composite model. Mathematical modelling makes it possible to obtain the resulted optimizations effect of every factor. The data from design of experiments has been evaluated by multiple regression analysis. The responses are defined as polynomial. The general equation is given in Equation 3.1.

$$\mathbf{y} = \mathbf{a}_0 + \sum_{i=1}^n \mathbf{a}_i \mathbf{x}_i + \sum_{i=1}^n \mathbf{a}_{ii} \mathbf{x}_i^2 + \sum_{i=1}^n \sum_{i=1}^n \mathbf{a}_{ij} \mathbf{x}_i \mathbf{x}_j \ (i < j)$$
(3.1)

Y represents the response, $x_1, x_2...x_k$ are the factors, $a_i...a_k$ are the coefficients which are evaluated by regression analysis, $a_{ij}x_ix_j$ represents the interaction between factors and $a_{ii}x^2$ represents the curvature of the model [50].

Central composite design (CCD) has been used for construction a mathematical model in this thesis. In the test program, 3 input factors have been used. These are listed in the Table 3.12. According to CCD:

- k=3 independent variables,
- 2^k=8 factorial points,
- 2k=6 star (axial) points,
- α is calculated by $\pm \sqrt[4]{2^k}$, for k=3 variables $\alpha = \pm 1.68$. α represents the position of star points.
- Total number of experiments is $2^{k}+2k+1 = 15$

To detect the experimental errors, it is suggested that, the experiment of the central point should be repeated at least 4 times [50]. Codified models of mathematic model are given in Table 3.12. Mixture proportions are prepared according to these factors. Mixture proportions are given in Table 3.13.

Factors	Coded Value						
	-1.68	-1	0	1	1.68		
X_1 = water/cement ratio	0.47	0.54	0.64	0.74	0.81		
X ₂ = polymer/cement ratio	6.6%	10%	15%	20%	23.4%		
X ₃ = fiber/cement ratio	0.5%	0.9%	1.5%	2.1%	2.5%		

Table 3.12: Factors, their ranges and codified values

Run	Mixture Proportions						
	X1 (w/c)	X ₂ (p/c)	X ₃ (f/c)				
1	0	0	0				
2	-1.68	0	0				
3	1	1	1				
4	1	-1	-1				
5	-1	-1	1				
6	0	1.68	0				
7	1.68	0	0				
8	0	-1.68	0				
9	0	0	-1.68				
10	-1	1	1				
11	-1	-1	-1				
12	1	-1	1				
13	0	0	1.68				
14	1	1	-1				
15	-1	1	-1				
16	0	0	0				
17	0	0	0				
18	0	0	0				
19	0	0	0				
20	0	0	0				

 Table 3.13:Mixture proportions in codified values

Each specimen is produced according to this process:

Step 1: 500 gr cement+ 600 gr Sand+ 100 gr Calcite + Fibers + 2 gr Cellulose are mixed.

Step 2: 30% of water and superplasticizer are mixed

Step 3: 70% of water are added to mixture of cement, sand, calcite, fibers and cellulose and they are mixed in cement mixture together.

Step 4: In the pause during transition to high speed mixing, shrinkage agent and watersuperplasticizer and polymeric resins are added to pre-mixture. The used cement moulds have been made of steel includes Cr and Ni. Their size is 40x40x160. A typical cement mould used in experiments is illustrated in Figure 3.1.



Figure 3.1: Cement mould used in experiments.



Figure 3.2: Moulded mortars after 24 hours.

After 24 hours of moulding, the mortar specimens were removed from moulds and they were cured in water pool for 2 days. Totally, 60 days were waited after production of specimens. The materials and amount of ingredients used in mixtures are given in Table 3.14. Moulded mortars are shown in Figure 3.2.

Run	w/c	p/c	f/c	60-70	Cement	Calcite	Cellulose	Fiber	Fiber	Fiber	Sp&Sa***
name			(%)	Silica				Glass	PP	PA	(%/%)
				Sand				(gr)	(gr)	(gr)	
Run 2	0.47	15%	1.5	600 g	500g	100g	2 gr	7.5			1/1.5
Run 5	0.54	10%	2.1	600 g	500g	100g	2 gr	10.5			1/1.5
Run 11	0.54	10%	0.9	600 g	500g	100g	2 gr	4.5			1/1.5
Run 10	0.54	20%	2.1	600 g	500g	100g	2 gr	10.5			1/1.5
Run 15	0.54	20%	0.9	600 g	500g	100g	2 gr	4.5			1/1.5
Run 8	0.64	6.6%	1.5	600 g	500g	100g	2 gr	7.5			1/1.5
Run 1	0.64	15%	1.5	600 g	500g	100g	2 gr	7.5			1/1.5
Run 9	0.64	15%	0.5	600 g	500g	100g	2 gr	2.5			1/1.5
Run 13	0.64	15%	2.5	600 g	500g	100g	2 gr	12.5			1/1.5
Run 6	0.64	23.4	1.5	600 g	500g	100g	2 gr	7.5			1/1.5
		%		-	-	_	-				
Run 4	0.74	10%	0.9	600 g	500g	100g	2 gr	4.5			1/1.5
Run 12	0.74	10%	2.1	600 g	500g	100g	2 gr	10.5			1/1.5
Run 14	0.74	20%	0.9	600 g	500g	100g	2 gr	4.5			1/1.5
Run 3	0.74	20%	2.1	600 g	500g	100g	2 gr	10.5			1/1.5
Run 7	0.81	15%	1.5	600 g	500g	100g	2gr	7.5			1/1.5
H1	0.64	15%	2	600 g	500g	100g	2 gr	5	5		1/1.5
H2	0.64	15%	2	600 g	500g	100g	2 gr	5		5	1/1.5
H3	0.64	15%	2	600 g	500g	100g	2 gr	10^*			1/1.5
H4	0.64	15%	2	600 g	500g	100g	2 gr	10^{**}			1/1.5

 Table 3.14: Experimental designs and amount of materials used in mixtures.

*H3 specimens have been produced with 6 mm surface treated glass fibers.

H4 specimens have been produced with 3.75g of 3 mm and 3.75 g of 12 mm fiber * Sp&Sa is the percent ratio of superplasticizer and shrinkage reducing agent.

3.3 Test Methods

3.3.1 Flow test

Flow test is performed to have knowledge about viscosity and processability of fresh mortar. In this test, fresh mortar has been placed in slump cone. During placing, fresh mortar has been fog in three degrees. After that, slump cone has been removed and fresh mortar has been flowed by its own weight.

EYL-C208 type flow table has been used in flow test. The diameter of the table has been 762 mm. Due to turning crank, table has been risen 12.7 mm and dropped. Typical flow table used in flow tests are illustrated in Figure 3.3.



Figure 3.3: Flow table used in experiments.

3.3.2 Three-point flexural test

Flexural tests of specimens have been performed in MTS Criterion 64.305 type of machine. Rated force capacity of this machine has been 300 kN. It has got 6 columns and it has been servo controlled hydraulic machine. Test machine is illustrated in Figure 3.4.



Figure 3.4: MTS Criterion 64.305 type test machine

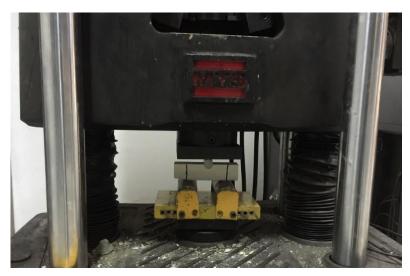


Figure 3.5: Specimen and machine during flexural tests.

The dimensions of specimens used in three-point flexural tests are 40x40x160 mm.A specimen during three-point flexural test is shown in Figure 3.5. The support span is 100 mm. All flexural tests have been performed at MTS Criterion 64.305 type of 300kN capacitated machine. In these tests, Load (N) to actuator (mm) graphs of each specimen have been drawn by computer. Load (N), deflection (mm), stress (MPa), strain (%) values have been obtained by these tests. Equation of flexural strength is given in Equation 3.2.

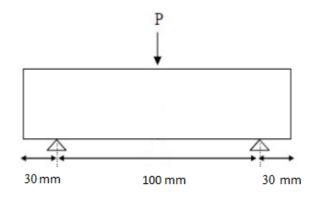
$$\sigma = \frac{3FL}{2bd^2} \tag{3.2}$$

In this equation,

F= load at a given point on the load deflection curve (N)

- L= Support span (mm)
- b= Width of test beam (mm)
- d= Depth or thickness of tested beam (mm)
- σ = Stress in outer fibers at midpoint (MPa)

For 40x40x160 specimens



L=100 mm

b=40 mm

d=40 mm

For these circumstances, flexural strength is calculated by Equation 3.3.

$$\sigma = \frac{1.5 \text{ F}}{640} \tag{3.3}$$

3.3.3 Compression test

Compression tests of specimens have been performed in MTS Criterion 64.305 type of machine. Rated force capacity of this machine has been 300 kN. It has got 6 columns and it has been servo controlled hydraulic machine. Load (N), deflection (mm), stress (MPa), strain (%) values of each specimen have been obtained in the end of compression tests. Equation of compressive strength is given in Equation 3.4.

$$\sigma = \frac{F}{A_0} \tag{3.4}$$

In this equation,

F= load at a given point on the load deflection curve (N)

A₀= Original specimen area

 σ = Stress in outer fibers at midpoint (MPa)

In these experiments modified compressive tests have been performed. The specimens have been the same with flexural test specimens.

For 40x40x160 specimen, the compressive strength is calculated by Equation 3.5. A=40x40=1600 mm²,

$$\sigma = \frac{F}{1600} \tag{3.5}$$

4. RESULTS AND DISCUSSION

4.1 Flow Test

According to Flow test results, fresh mortar has expanded more with increasing water/cement ratios and polymer/cement ratios as it is expected. Increasing fiber/cement ratio of 12 mm glass fibers, has been decreased the flow value of the specimens. Comparison of Run 5 and Run 11 can be given an example of this situation. Effect of polypropylene fibers and polyamide fibers have been almost the same. In spite of 2% high content of surface treated glass f/c ratio of H3, 27 cm flow value has been obtained. Different characteristic of surface treated glass fibers have caused different flow value from single fiber containing mixtures. The results of flow tests are given in Table 4.1.

Run	w/c	p/c	f/c	Flow (cm)
number				
Run2	0.47	15%	1.5%	14
Run5	0.54	10%	2.1%	20
Run 11	0.54	10%	0.9%	22.5
Run 10	0.54	20%	2.1%	22
Run 15	0.54	20%	0.9%	24
Run 8	0.64	6.6%	1.5%	22
Run 1	0.64	15%	1.5%	23.5
Run 16	0.64	15%	1.5%	22
Run 17	0.64	15%	1.5%	23
Run 9	0.64	15%	0.5%	27
Run 13	0.64	15%	2.5%	20
Run 6	0.64	23.4%	1.5%	24.5
Run 4	0.74	10%	0.9%	30
Run 12	0.74	10%	2.1%	24
Run 14	0.74	20%	0.9%	27
Run 3	0.74	20%	2.1%	25
Run 7	0.81	15%	1.5%	31
H1	0.64	15%	2%	23
H2	0.64	15%	2%	22.5
H3	0.64	15%	2%	27
H4	0.64	15%	2%	22.5

Table 4.1: Results of flow tests.

4.2 Three Point Flexural Test

According to flexural test results, the highest flexural strength in single fibered mixtures has been achieved in Run 11 (8.489 MPa). It has got 0.54 water/cement, 10% polymer/cement and 0.9% fiber/cement ratios. Comparing Run 11 and Run 5, it has been seen that flexural strength has been decreased, when fiber content increases from 0.9% to 2.1%. According to the literature [51], 0.9% fiber content is quite lower than fiber contents in other works. One of the reason of this situation might be balling effect of fibers in mortar specimens because of decreasing workability. In comparison of Run 11 and Run 15, it is clear that flexural strength has been decreased with increasing polymer/cement ratio from 10% to 20%. This phenomenon has been already reported by Majumdar et al [51]. Comparing Run 11 and Run 4, it has been seen that, if water/cement ratio increases, flexural strength has been decreased when polymer/cement ratio increases as well as when fiber/cement ratio increases. But flexural strength has been more sensitive to increasing polymer/cement ratio.

Above all, the H3 has been the strengthest mixture (10.28 MPa). Better surface properties of surface treated fibers have got positive effect on flexural strength. Although H1, H2 and H4 have got quite high water/cement ratios and even higher than some of the other mixtures, they have been more strength than single fibered mixtures. These results showed the importance of hybrid fibers. It is also important that polypropylene fibers have been more effective than polyamide fibers to improve flexural strength. The results of three point flexural tests and summary of regression analysis of flexural test results are given in Table 4.2 and Table 4.3. Flexural stress-deflection curves of specimens, which have 0.54 w/c, 0.64 w/c and 0.74 w/c ratios, are given in Figures (4.1-4.4).

Run	w/c	p/c	f/c	Flexural
number		(%)	(%)	Strength
				(MPa)
Run2	0.47	15	1.5	8.32
Run5	0.54	10	2.1	8.21
Run 11	0.54	10	0.9	8.49
Run 10	0.54	20	2.1	6.77
Run 15	0.54	20	0.9	7.91
Run 8	0.64	6.6	1.5	7.78
Run 1	0.64	15	1.5	7.64
Run 16	0.64	15	1.5	7.72
Run 17	0.64	15	1.5	7.31
Run 18	0.64	15	1.5	7.48
Run 9	0.64	15	0.5	8.29
Run 13	0.64	15	2.5	6.63
Run 6	0.64	23.4	1.5	7.03
Run 4	0.74	10	0.9	7.84
Run 12	0.74	10	2.1	7.47
Run 14	0.74	20	0.9	7.11
Run 3	0.74	20	2.1	6.73
Run 7	0.81	15	1.5	6.56
H1	0.64	15	2.0	9.48
H2	0.64	15	2.0	9.14
H3	0.64	15	2.0	10.28
H4	0.64	15	2.0	9.56

Table 4.2: Results of three point flexural tests.

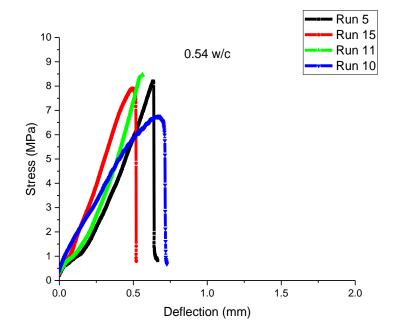


Figure 4.1: Flexural stress-deflection curve of 0.54 w/c ratio specimens.

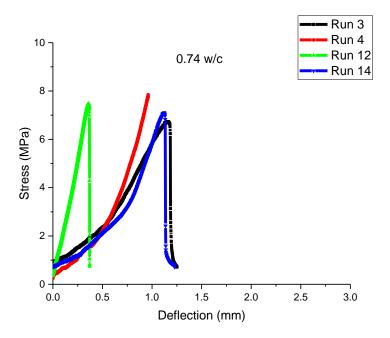


Figure 4.2: Flexural stress-deflection curve of 0.74 w/c ratio specimens.

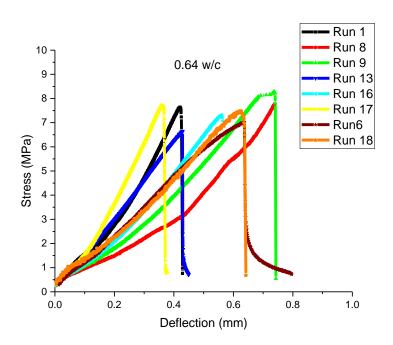


Figure 4.3: Flexural stress-deflection curve of 0.64 w/c ratio specimens.

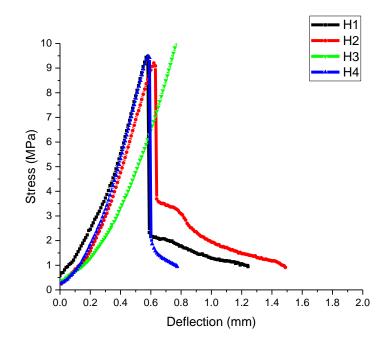


Figure 4.4: Flexural stress-deflection curve of hybrid fiber containing specimens.

Model Summar	ry				
S	R-sq	R-sq	- ·		
		(adjusted)			
118.367	87.92%	77.05%			
Coded Coeffici	ents				
Term	Coefficient	Se Coef.	T-Value	P-Value	VIF
Constant	3210.4	48.3	66.50	0.000	
W/C (X ₁)	-161.6	32.0	-5.04	0.001	1.00
P/C (X ₂)	-148.3	32.0	-4.63	0.001	1.00
F/C (X ₃)	-155.0	32.0	-4.84	0.001	1.00
W/C*W/C	-1.2	31.2	-0.04	0.971	1.00
(X_1^2)					
P/C*P/C	-6.6	31.2	-0.21	0.836	1.00
(X_2^2)					
F/C*F/C	2.6	31.2	0.08	0.936	1.00
(X_{3}^{2})					
W/C*P/C	28.6	41.8	0.68	0.510	1.00
W/C*F/C	36.1	41.8	0.86	0.408	1.00
P/C*F/C	-45.9	41.8	-1.10	0.299	1.00

Table 4.3: Summary of regression analysis of flexural test results

$$y = 3210.4 - 161.6X_1 - 148.3X_2 - 155X_3 - 1.2X_1^2 - 6.6X_2^2 + 2.6X_3^2 + 28.6X_1X_2 + 36.1X_1X_3 - 45.9X_2X_3$$
(4.1)

The general equation, which has been obtained by regression analysis for flexural strength, has been given in Equation 4.1. According to regression analysis of the flexural results, it has been seen that p values of w/c*w/c, p/c*p/c, f/c*f/c, w/c*p/c, w/c*f/c and p/c*f/c are higher than 0.05 and they have been insensitive. Therefore, the Equation 4.2 must be used.

$$y = 3210.4 - 161.6X_1 - 148.3X_2 - 155X_3 \tag{4.2}$$

The surface graphs of flexural tests are given in Figures (4.5-4.7).

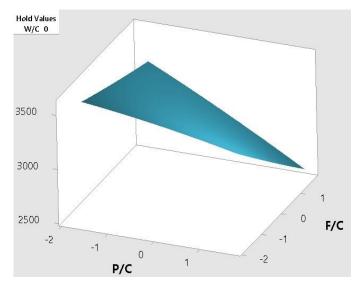


Figure 4.5: Surface graph of flexural tests where w/c is zero

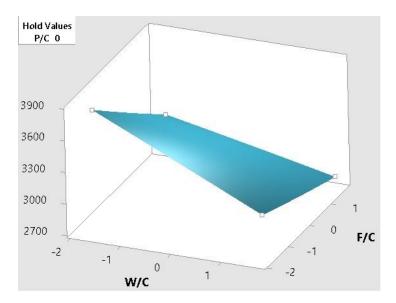


Figure 4.6: Surface graph of flexural tests where p/c is zero.

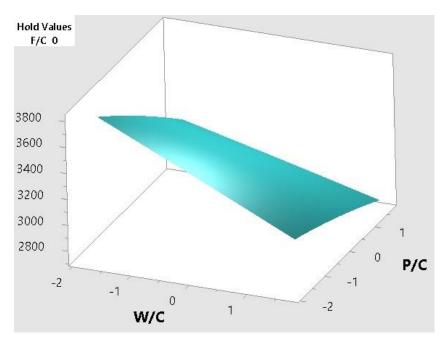


Figure 4.7: Surface graph of flexural tests where f/c is zero.

In the surface graphs of flexural tests, the coded values of w/c, p/c and f/c ratios are given in Table 3.12. The results of tests are represented with load(N). The contour graphs of flexural tests are given in Figures (4.8-4.10).

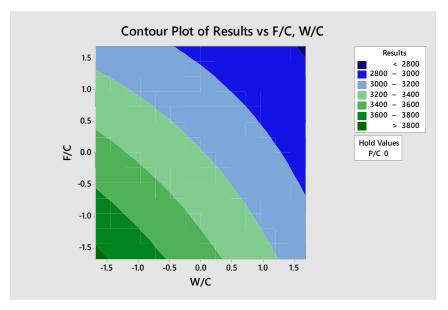


Figure 4.8:Contour graph of results of flexural test f/c vs w/c.

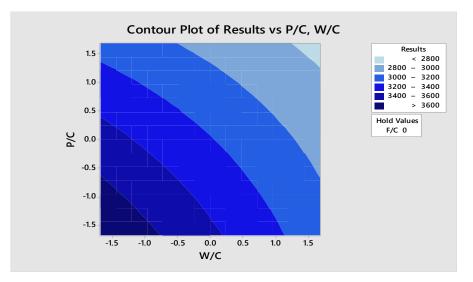


Figure 4.9:Contour graph of results of flexural test p/c vs w/c.

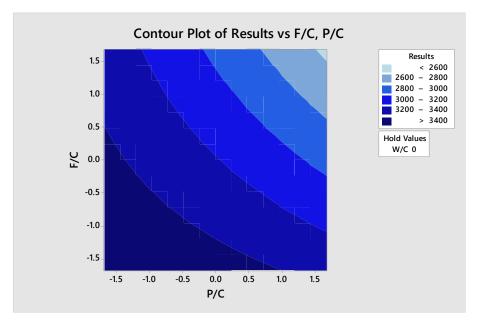


Figure 4.10:Contour graph of results of flexural test f/c vs p/c.

4.3 Compression Test

According to compressive test results, the most strength mixture has been H3. In this mixture 6 mm surface treated glass fibers have been used. The highest compressive strength of 12 mm glass fibered mixture has been again Run 11 with 25.21 MPa. Increasing fiber/cement ratio has been decreased the compressive strength. The same behavior has been observed in flexural tests. There has been occurred an exception about this situation in Run12. In comparison of Run 12 and Run 14, they have got the same w/c and p/c ratios. The only difference has been that Run 12 has got higher fiber

content than Run 14. In spite of the fact that, Run 12 has got higher compressive strength. The reason of this exception might be that high water content of run 12 can cause more homogenously distribution of fibers. Therefore, Run 12 has got higher compressive strength than Run 14 although, Run 12 has got higher fiber ratio. In compression tests, the results of hybrid specimens have been quite high in comparison of the other specimens but the conditions have not been equal with flexural results. It is possible to say that glass fibers have been more effective to improve compressive strength than hybrid fibers. The results of compression tests and summary of regression analysis of compression test results are given in Table 4.4 and in Table 4.5. Compression stress-deflection curves of specimens, which have 0.54 w/c, 0.64 w/c and 0.74 w/c ratios, are given in Figures (4.11-4.14). The contour and surface graphs of compression tests are given in Figures (4.15-4.20).

Run	w/c	p/c	f/c	Compressive
number		(%)	(%)	Strength
				(MPa)
Run2	0.47	15	1.5	20.23
Run5	0.54	10	2.1	18.64
Run 11	0.54	10	0.9	25.21
Run 10	0.54	20	2.1	16.50
Run 15	0.54	20	0.9	19.04
Run 8	0.64	6.6	1.5	22.25
Run 1	0.64	15	1.5	22.78
Run 16	0.64	15	1.5	22.41
Run 17	0.64	15	1.5	22.99
Run 18	0.64	15	1.5	22.96
Run 9	0.64	15	0.5	21.94
Run 13	0.64	15	2.5	17.98
Run 6	0.64	23.4	1.5	15.22
Run 4	0.74	10	0.9	17.73
Run 12	0.74	10	2.1	23.87
Run 14	0.74	20	0.9	18.30
Run 3	0.74	20	2.1	14.84
Run 7	0.81	15	1.5	17.74
H1	0.64	15	2	21.79
H2	0.64	15	2	21.39
H3	0.64	15	2	26.90
H4	0.64	15	2	22.81

 Table 4.4: Results of compression tests.

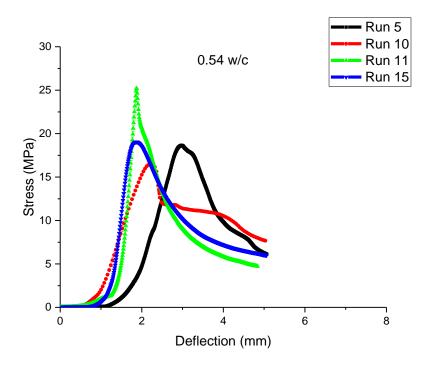


Figure 4.11: Compressive stress-deflection curve of 0.54 w/c ratio specimens.

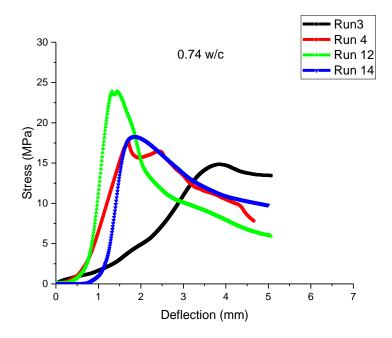


Figure 4.12: Compressive stress-deflection curve of 0.74 w/c ratio specimens.

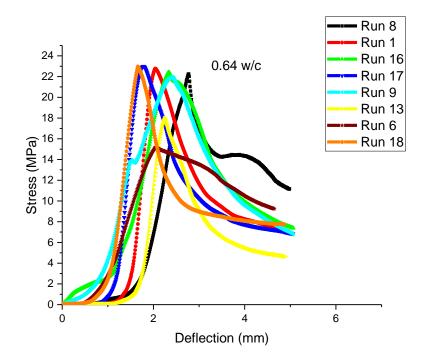


Figure 4.13: Compressive stress-deflection curve of 0.64 w/c ratio specimens.

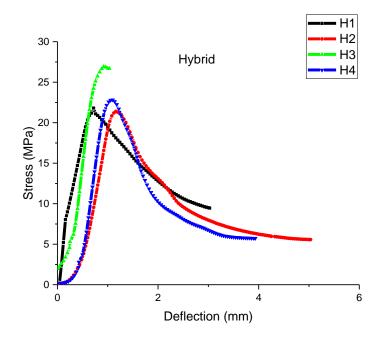


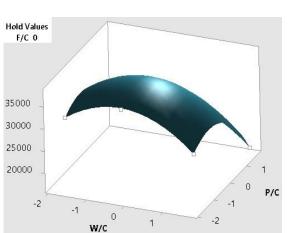
Figure 4.14: Compressive stress-deflection curve of hybrid fibered specimens

S	R-sq	R-sq			
	•	(adjusted)			
2490.85	86.46%	74.27%			
Coded Coefficien	nts				
Term	Coefficie	Se Coef.	T-Value	P-Value	VIF
	nt				
Constant	36524	1016	35.95	0.000	1.00
W/C (X ₁)	-1048	674	-1.55	0.151	1.00
$P/C(X_2)$	-3350	674	-4.97	0.001	1.00
$F/C(X_3)$	-1535	674	-2.28	0.046	1.02
$W/C*W/C(X_1^2)$	-2074	656	-3.16	0.010	1.02
)					
$P/C*P/C (X_2^2)$	-2234	656	-3.41	0.007	1.02
$F/C*F/C$ (X_3^2)	-1540	656	-2.35	0.041	1.00
W/C*P/C	-30	881	-0.03	0.974	1.00
W/C*F/C	2358	881	2.68	0.023	1.00
P/C*F/C	-1114	881	-1.27	0.234	1.00

Table 4.5: Summary of regression analysis of compression test results

$$y = 36524 - 1048X_1 - 3350X_2 - 1535X_3 - 2074X_1^2 - 2234X_2^2 - 1540X_3^2 - 30X_1X_2 + 2358X_1X_3 - 1114X_2X_3$$
(4.3)

The general equation, which has been obtained by regression analysis for compressive strength, has been given in Equation 4.3. It has been seen that p values of w/c, w/c*p/c, w/c*f/c, and p/c*f/c are higher than 0.05 and they have been insensitive. Therefore, the Equation 4.4 must be used.



 $y = 36524 - 3350X_2 - 1535X_3 - 2074X_1^2$ (4.4) - 2234X_2^2 - 1540X_3^2 + 2358X_1X_3

Figure 4.15:Surface graph of compression test where f/c is zero.

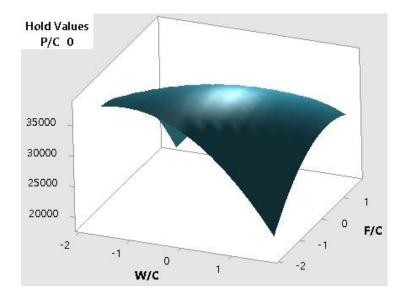


Figure 4.16:Surface graph of compression test where p/c is zero.

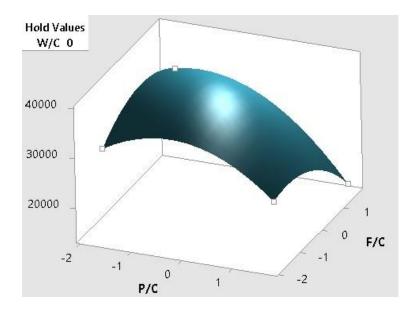
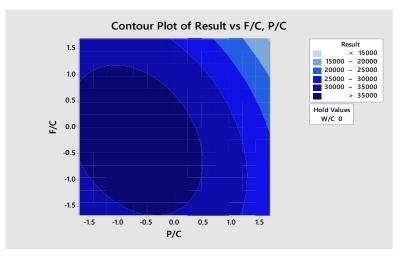
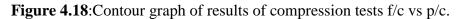


Figure 4.17:Surface graph of compression test where w/c is zero.

In the surface graphs of compression tests, the coded values of w/c, p/c and f/c ratios are given in Table 3.12. The results of tests are represented with load (N). The contour graphs of compression tests are given in Figures (4.18-4.20).





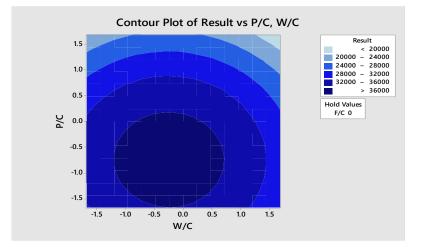


Figure 4.19:Contour graph of results of compression tests p/c vs w/c.

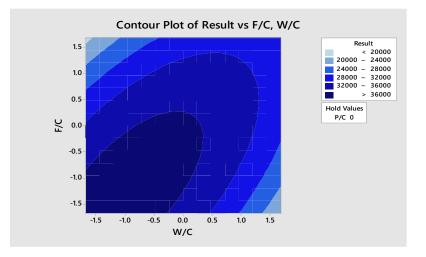


Figure 4.20:Contour graph of results of compression tests f/c vs w/c.

4.4 Weight Loss of Specimens

Mortar specimens lose their weight after their production because of evaporation of the water inside of the specimens. Cement particles are hydrated by water and provides mechanical properties. Therefore, water is very important for concrete and mortar specimens to obtain good mechanical properties. However, excess water evaporates in time. Depending on water evaporation, porosity increases in specimens and this decreases mechanical properties. If the water-cement ratio is high, the porosity will be also high in time. That is why water balance is very important for mortars and concretes. Weights of specimens after moulding, after water cure and after 60 days are given in Table 4.6.

Run	First weight	After water	After 60 days	Weight
number	(g)	cure (g)	(g)	Loss
Run 1	440.3	446.1	413.86	7.22%
Run 2	367.8	372.0	352.83	5.15%
Run 3	432.73	443.0	397.9	10.18%
Run 4	-	463.16	419.03	9.52%
Run 5	-	377.0	351.66	6.72%
Run 6	-	433.96	395.0	8.97%
Run 7	-	448.3	394.0	12.11%
Run 8	-	479.8	445.25	7.20%
Run 9	456.3	463.86	430.73	7.14%
Run 10	347.6	360.73	335.0	7.13%
Run 11	429.46	436.63	411.86	5.67%
Run 12	448.4	460.36	415.26	9.79%
Run 13	385.03	392.33	361.23	7.92%
Run 14	439.33	450.66	397.33	11.83%
Run 15	414.46	421.46	391.19	7.18%
Run 16	451.66	460.93	423.0	8.22%
Run 17	444.0	456.33	420.0	7.96%
Run 18	448.0	458.6	422.1	7.95%
H1	426.96	437.7	400.66	8.46%
H2	418.66	429.06	390.0	9.10%
H3	453.8	462.16	423.46	8.37%
H4	423.36	434.23	394.66	9.11%

Table 4.6: Weights of specimens after moulding, after water cure and after 60 days.

5. CONCLUSIONS AND RECOMMENDATIONS

- First, it is seen that there has been a critical value of polymeric modifiers used in mortars. In comparison of Run 11 and Run 15, it is clear to understand that increasing polymer content from 10% to 20%, has been decreased both of flexural and compressive strength of mortars. This situation has also been observed at other mixtures.
- Second, it is understood that increasing fiber content has decreased both of flexural and compressive strength. The best results have been obtained with 0.9% fiber content in single 12 mm glass fibered specimens. It is possible to achieve higher fiber contents due to following different mixing process or using better production methods.
- It has been observed that, mechanical properties of mortars have been more sensitive to increasing polymer content rather than increasing fiber content.
- There is an exception that increasing fiber-cement ratio has not decreased the compressive strength in Run 12. Comparing Run 12 and Run 14, Run 14 has got quite high water-cement value (0.74). High content of water in Run 14 may cause more homogenously distribution of fibers and it may increase the workability. This situation gives information about if these experiments will be repeated with higher technical production methods to achieve good workability even at low w/c ratios, higher mechanical test results may be obtained.
- Although H3 group of specimens have got high w/c value (0.64) and 15% polymer content, the highest mechanical results have been achieved in this mixture in which, 6 mm surface treated fibers have been used. These fibers may increase the properties of mortars because the treated surface of fibers have better interactions with matrix materials. Therefore, there is higher binding effect between fiber surface and matrix materials.
- Finally, the flexural results of hybrid fibered specimens have been quite high. These results show that hybrid fibers can be good choice to increase flexural

strength. But the same positive effect can not be observed for compression test results.

- It is important that high flexural test results of hybrid fibered specimens have been achieved with 2% f/c where balling effect of single fibers has decreased the strength of specimens. It is seen that combination of different fibers and different length of fibers synergym has been observed and hence the flexural strength has been increased.
- According to these results, combinations of different fibers have good potential to achieve higher mechanical properties. More hybrid fibered, polymer modified mortar specimens should be produced and their contribution on properties should be further investigated.

REFERENCES

- [1] Zhang, H. (2010). Building Materials in Civil Engineering, Science Press, Beijing.
- [2] Gonçalves, M., C., and Margarido, F. (2013). Materials for Construction and Civil Engineering-Science, Processing and Design, Springer,
- [3] Veiga M., R. (2001). Performance of wall coatings: Contribution to the study of their cracking resistance, *PhD Thesis*, Porto University, Faculty of Engineering, Porto.
- [4] Veiga M., R. (2004). Wall coatings: functions and requirements, LNEC/ FUNDEC Course on Wall coatings pathology, Lisbon.
- [5] Veiga M., R. (1996). Specialization course on wall coatings, National Laboratory of Civil Engineering, Lisbon.
- [6] Paulo, R. (2006). Characterization of traditional mortars, MSc Thesis, Aveiro University, Aveiro.
- [7] Duarte, C. (2001). Technical dictionary. European Mortar Industry Organization, Brussel.
- [8] JC/T480-92, (2002). State Bureau of Quality and Technical Supervision. National Standards, P.R.C.
- [9] Kajiwara, K. (2009). Synthetic textile fibers: structure, characteristics and identification, *Identification of Textile Fibers*. Otsuma Women's University, Japan.
- [10] Houck, M., M. (2009). Identification of Textile Fibers, Woodhead Publishing, Cambridge.
- [11] Chawla, K., K. (1998). Fibrous materials, New Mexico Insitute of Mining and Technology, Cambridge University Press, Cambridge.
- [12] Hornbostel, C. (1991). Construction Materials: Types, Uses and Applications, A Wiley-Interscience Publication.
- [13] Chawla, K., K. (2012). Composite Materials: Science and Engineering, Springer-Verlag, New York.

- [14] Hazimmah, D.S., Mohd, S and Cheng, H.T. (2011). Engineering properties of epoxy polymer cement concrete reinforced with glass fiber, *Journal of Engineering and Applied Sciences*, 6, 191-199.
- [15] Cherif, C. (2016). Textile Materials for Lightweight Constructions, pp. 14, Springer-Verlag, Berlin.
- [16] Li C, Victor. (2002). Large Volume, High-Performance Applications of Fibers in Civil Engineering, *Journal of Applied Polymer Science*, 83, 660-686.
- [17] Ohama, Y. (1995). Handbook of Polymer Modified Concrete and Mortars, Noyes Publications, USA.
- [18] Cresson, L. (1923). British Patent, No: 191,474 dated 12.1.1923.
- [19] Lefebure, V. (1924). British Patent, No:217, 279 dated 5.6.1924)
- [20] Cooke, G. B. (1941). U.S. Patent No: 2,227,533 dated Jan. 7.1.1941
- [21] Jaenicke, J., Knoop, H., Miedel, H., and Schweitzer, O. (1943). U.S. Patent No:2, 311, 233 dated 16.2.1943.
- [22] Dow Chemical Co., Midland, Michigan (1959). "Dow Latex 560 for Portland Cement Compositions"
- [23] Rohm & Haas Co., Philadelphia (1964). "Rhoplex MC-4530, Cement Mortar Modifier"
- [24] Dikeou, J. T., Cowan, W. C., DePuy, G. W., Smoak, W. G., Wallace, G. B., Steinberg, M., Kukacka, L. E., Auskem, A., Colombo, P., Hendrie, J. M., and Manowitz, B. (1971). Concrete-Polymer Materials (Third Topical Report), REC-ERC-71-6 and BNL 50275 (T-602), Bureau of Reclamation, Denver, and Brookhaven National Laboratory, New York.
- [25] Donnelly, J. H. (1965). U.S. Patent, No: 3,198,758 dated 3.8.1965.
- [26] **Duff, R. A.** (1973). U.S. Patent, No: 3,753,849 dated 21.8.1973.
- [27] Szukiewicz, W. (1959). U.S. Patent, No: 2,902,388 dated 1.9.1959.
- [28] Wagner, H. B. (1960). Methylcellulose in water-retentive hydraulic cements, Industrial and Engineering Chemistry, 52, 233-234.
- [29] Shibazaki, T. (1964). Properties of Masonry Cement Modified with Water-Soluble Polymers, *Semento-Gijutsu-Nempo*, 17, 194-199.
- [30] Riley, V. R., and Razl, I. (1974). Polymer additives for cement composites a review, *Composites*, 5, 27-33.

- [31] Wagner, H. B. (1965). Polymer-modified hydraulic cements *Industrial and* Engineering Chemistry, Product Research and Development, 4, 191-196.
- [32] Ohama, Y. (1973). Study on Properties and Mix Proportioning of Polymer-Modified Mortars for Buildings, Report of the Building Research Institute, No.65.
- [33] Wagner, H. B., and Grenley, D. G. (1978). Interface effects in polymer modified hydraulic cements, *Journal of Applied Polymer Science*, 22, 821-822.
- [34] Kolthoff, M., and Stenger, V.A. (1932). The adsorption of cations from ammoniacal solution by silica gel, *Journal of Physical Chemistry*, 36, 2113-2126.
- [35] Zimbelmann, R., (1985). A contribution to the problem of cement-aggregate bond, *Cement and Concrete Research*, 15, 801-808.
- [36] Monteiro, P. J. M., Maso, J. C., and Ollivier, J. P., (1985). Microstructure of the steel-cement paste interface in the presence of chloride, *Cement* and Concrete Research, 15, 953-958.
- [37] Su, Z., Bijen, J. M. J. M., and Larbi, J. A. (1991). Influence of polymer modification on the hydration of portland cement, *Cement and Concrete Research*, 21, 242-250.
- [38] Su, Z., Larbi, J. A., and Bijen, J. M. J. M. (1991). The interface between polymer-modified cement paste and aggregates, *Cement and Concrete Research*, 21, 983-990.
- [39] Afridi, M. U. K., Ohama, Y., Iqbal, M., and Demura, K. (1990). Morphology of Ca(OH)₂ in polymer-modified mortars and effect of freezing and thawing action on its stability, *Cement and Concrete Composites*, 12, 163-173
- [40] Afridi, M. U. K., Ohama, Y., Iqbal, M. Z., and Demura, K. (1989).
 Behaviour of Ca(OH)₂ in polymer modified mortars. *The International Journal of Cement Composites and Lightweight Concrete*, 11, 235-244.
- [41] Crisp, S., Prosser, H. J., and Wilson, A. D. (1976). An infra-red spectroscopic study of cement formation between metal oxides and aqueous

solutions of poly(acrylic acid), *Journal of Materials Science*, **11**, 36-48.

- [42] Rodger, S. A., Brooks, S. A., Sinclair, W., Groves, G. W., and Double, D. D., (1985). High strength cement pastes, *Journal of Materials Science*, 20, 2853-2860.
- [43] Chandra, S., Bermsson, L., and Fiodin, P., (1981). Behaviour of calcium hydroxide with styrene-methacrylate polymer dispersion, *Cement and Concrete Research*, 11, 125-129.
- [44] Larbi, J. A., and Bijen, J. M. J. M. (1990). Interaction of polymers with portland cement during hydration: A study of the chemistry of the pore solution of polymer-modified cement systems, *Cement and Concrete Research*, 20, 139-147.
- [45] Ohama, Y. (1987). Principle of latex modification and some typical properties of latex-modified mortars and concretes adhesion; binders (materials); bond (paste to aggregate); carbonation; chlorides; curing; diffusion, *ACI Materials Journal*, 84, 511-518.
- [46] Diab, A., M., Elymany, H., E., Ali, H., A. (2014). The participation ratios of cement matrix and latex network in latex cement co-matrix strength, *Alexandria Engineering Journal*, 53, 309-317.
- [47] **Plank, J.** http://www.bauchemie-tum.de/master framework/?p=Late&i=12&m=1&lang=en (17 Nov. 16 17:38)
- [48] Carlos, E., M., G. (2015). Influence of vinyl acetate-versatic vinylester copolymer on the microstructural characteristics of cement pastes, *Materials Research*, 8, 51-56.
- [49] Alvarez, L., F. (2000). Approximation model building for design optimization using the response surface methodology and genetic programming, *M.Sc. Thesis*, Department of Civil and Environmental Engineering, University of Bradford, UK.
- [540 Özçelik, S. (2013). High Sensitivity Analysis Of Inorganic Anions In PVI Coated Capillary By Capillary Electrophoresis With Sample Stacking: Method Optimization Using Chemometric Experimental Design, *M.Sc Thesis*, ITU Chemistry Department, İstanbul.
- [51] Majumdar, A., West, J., M., De Vekey, R. (1985). Acrylic polymer modified GRC, *Composites*, 16, 33-40.

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