

**THE INVESTIGATION OF ADVANCED
THERMOPLASTIC COMPOSITE MATERIALS IN
AEROSPACE APPLICATIONS**

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May 2023

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ABSTRACT

THE INVESTIGATION OF ADVANCED THERMOPLASTIC COMPOSITE MATERIALS IN AEROSPACE APPLICATIONS

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The development of load-carrier reinforced composites is crucial in terms of a wide range of applications, such as aerospace, automotive, sports industry and so on. When these fields are taken into consideration, reducing the excessive weight of structural materials without any sacrifice in the performance is required. Thus, using reinforcement materials (e.g. carbon fibers) for polymeric matrices in composites is the most convenient way to follow. In this study, carbon fiber (CF) was used as a reinforcement material for thermoplastic based composites. Since bare CFs are too fragile to process they must be coated / sized such that the brittleness of CFs can be avoided during industrial applications. Therefore, sizing of carbon fibers is crucial for guiding them into service by protecting the CF's surface. Yet, the traditional sizing agent (i.e. epoxy) is not suitable for handling continuous CF reinforced thermoplastic composites (CFRTPs) with high processing temperatures above 300 °C. In this study a novel sizing agent was developed for this purpose. The effects of this sizing on the CFs' physicochemical as well as surface properties were investigated. As a result, the impact on fiber-matrix interphase behavior can be analyzed. Moreover, the main problem for thermoplastic based composites which is the delamination between the reinforced fiber and thermoplastic matrix can be solved throughout the development of novel coating material so that inert carbon fibers can be made compatible with the matrix. In this thesis, the activation of carbon fiber's surface, then providing a functional sizing agent and method in order to expel the present voids because of incompatibility between CF and thermoplastic matrix (i.e. Polyetherether ketone)

were carried out by enhancing the adhesion. Hence, the wettability of CF by polyetherether ketone (PEEK) matrix was enhanced by altering the surface free energy of CF resulting in optimized adhesion. Thus, the delamination problem in thermoplastic based composites was solved throughout the sizing of CFs.

The first part of this work consists of the elimination of current epoxy coating on the aerospace grade commercial carbon fibers. Then, the application of surface activation method was performed by acidic modification to make CFs ready for sizing process. The formation of functional groups (-COOH, -OH) on CF's surface was achieved after degrading of present epoxy coating throughout CFs. As a result, the developed sizing agents could be binded easily onto CF's activated surface through the hydrogen bonding.

In the second part, four different polymeric sizing agents were prepared by taking the chemical compatibility with the matrix into consideration. The sizing process was performed via dip-coating method for the surface-activated CFs. The chemical and physical analyses for neat and treated CFs were carried out via microscopic and spectroscopic techniques. As a result of sizing process, the enhanced compatibility between the matrix and reinforcement material was proved by the Contact Angle Analysis and surface free energy calculations according to Young's equation.

Keywords: Adhesion, carbon fibers, composites, delamination, polyetherether ketone (PEEK), thermoplastics

ÖZET

HAVACILIK UYGULAMALARINDA İLERİ TERMOPLASTİK KOMPOZİT MALZEMELERİN GELİŞTİRİLMESİ

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Yük taşıyıcı takviyeli kompozitlerin geliştirilmesi, havacılık, otomotiv, spor endüstrisi gibi geniş bir uygulama yelpazesi açısından önem arz etmektedir. Bu alanlar dikkate alındığında, performanstan ödün vermeden yapısal malzemelerin aşırı ağırlığının azaltılması gerekmektedir. Bu nedenle, kompozitlerde polimerik matrisler için takviye malzemelerinin (örn. karbon fiberler) kullanılması izlenecek en uygun yoldur. Bu çalışmada, termoplastik esaslı kompozitler için takviye malzemesi olarak karbon fiber (CF) kullanılmıştır. Çıplak CF'ler işlenemeyecek kadar kırılgan olduklarından, endüstriyel uygulamalar sırasında CF'lerin kırılganlığından kaçınılabilecek şekilde kaplanmaları / boyutlandırılmaları gerekir. Bu nedenle, karbon fiberlerin uygun metot ve malzemelerle kaplanmaları, CF'nin yüzeyini koruyarak hizmete girmelerini sağlamak için çok önemlidir. Bununla birlikte, geleneksel haşıl maddesi (yani epoksi), 300 °C'nin üzerindeki yüksek işleme sıcaklıklarına sahip sürekli CF takviyeli termoplastik kompozitlerin (CFRTP'ler) işlenmesi için uygun değildir. Bu çalışmada, bu amaç için yeni bir haşıl maddesi geliştirilmiştir. Bu kaplamanın CF'lerin fizikokimyasal yanı sıra yüzey özellikleri üzerindeki etkileri araştırılmıştır. Sonuç olarak, fiber-matriks interfaz davranışı üzerindeki etki incelenebilmektedir. Ayrıca, termoplastik esaslı kompozitler için temel problem olan takviyeli elyaf ve termoplastik matris arasındaki delaminasyon, yeni kaplama malzemesinin geliştirilmesiyle çözülebilir, böylece reaktif olmayan karbon elyaflar matris ile uyumlu hale getirilebilir. Bu tezde, karbon fiber yüzeyinin aktivasyonu, ardından fonksiyonel bir haşıllama ajanı

ve CF ile termoplastik matriks (Polietereter keton) arasındaki uyumsuzluktan kaynaklanan mevcut boşlukları azaltmak için adezyonu arttıracak bir yöntem geliştirilmiştir. Bu nedenle, polietereter keton (PEEK) matrisi ile CF'nin ıslanabilirliği; CF'nin yüzey serbest enerjisi değiştirilerek, optimize edilmiş adezyon ile arttırılmıştır. Böylece, termoplastik esaslı kompozitlerdeki delaminasyon problemi, CF'lerin kaplanması yöntemiyle çözülmüştür.

Bu çalışmanın ilk bölümünde, havacılık sınıfı ticari karbon fiberler üzerinde mevcut epoksi kaplamanın kaldırılması, ardından CF'lerin haşıl işlemine hazır hale getirilmesi için yüzey aktivasyon yönteminin uygulanması yer almaktadır. CF'leri çevreleyen mevcut epoksi kaplamanın bozunmasının ardından, CF'nin asidik modifikasyon ile yüzeyinde başarılı bir şekilde fonksiyonel kimyasal gruplar (COOH, OH) oluşturulmuştur. Sonuç olarak, geliştirilen haşıllama malzemeleri hidrojen bağı yoluyla CF'nin aktifleştirilmiş yüzeyine kolayca bağlanabilmektedir.

İkinci bölümde, matris ile kimyasal uyumluluğu dikkate alınarak dört farklı polimerik haşıl malzemesi hazırlanmıştır. Kaplama yöntemine karar verildikten sonra yüzeyi aktive edilen CF'ler için daldırma yöntemiyle kaplama işlemi yapılmıştır. Saf ve işlenmiş CF'ler için kimyasal ve fiziksel analizler, mikroskopik ve spektroskopik tekniklerle gerçekleştirilmiştir. Kaplama işlemi sonucunda, Temas Açısı Analizi ve Young denklemine göre yüzey serbest enerji hesaplamaları ile matris ve takviye malzemesi arasındaki artan uyumluluk kanıtlanmıştır.

Anahtar kelimeler: Adezyon, karbon fiberler, kompozitler, delaminasyon, polietereter keton (PEEK), termoplastik

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To My Daughter

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CHAPTER 1

Introduction

1.1. General Understanding of Polymer Composites

A composite material is defined as a material made up of two or more constituent mediums with apparently different physical or chemical properties, thus when they are combined a new material is produced with characteristics different from the individual components [1]. In structural and load bearing applications composites mostly consist of a reinforcement phase (i.e. fibers) and a bulk phase (i.e. matrix) surrounding the reinforcing material [2]. The load is mainly transferred through the fibers (e.g. Kevlar, polyethylene, glass fiber or carbon fiber) in composites. The polymer matrix serves to firmly bind the fibers together and uniformly transfer the load on them. On the other hand, the fibers in composites serve as the main load-carrier component because of their higher mechanical strength and modulus.

The matrix can be polymer, carbon, ceramic or metal [3–7]. The main reason for using reinforced polymer composites in a wide range of industrial applications (e.g. aerospace, automotive, construction) is that polymer composites offer impressive mechanical strength in addition to their lightweight. For instance, it was revealed by Victrex that manufacturing of bracket by using polymer composite (i.e. polyetherether ketone based matrix) provided 70% weight saving compared to the bracket made up of stainless steel [8]. The high mechanical strength to weight ratio of fiber reinforced polymer-matrix composite has made it an attractive material in

terms of energy and cost-saving compared to the conventional load-bearing materials like steel. Moreover, polymer matrix composites are advantageous due to their high stiffness, good corrosion resistance and long life time. Unlike ceramic-matrix and metal-matrix composites, polymer-matrix composites are distinctly easier to fabricate as they have relatively low processing temperature. Therefore, the development of load carrier reinforced composite material is in-demand for class B structural parts of aircrafts such as spars and ribs in wings. The use of CFRTTP composite in primary structural parts of aircrafts leads to less fuel consumption compared to using metals and their alloys. Furthermore, thermoplastic composites have significant advantages in terms of their reshaping and remolding properties so that energy and cost can be saved on the production line compared to processing of thermoset based composites [9–11].

The main research fields in the production of new generation and high-technology structural parts in aircrafts are based on the development of advanced materials and new methods to meet the expectations for high performance, light weight and subsequently less fuel consumption. To clarify, the reduction in the weight of each individual aircraft only by one pound results in totally 11.000 gallons of fuel saving per year in American Airlines that operates a fleet of around 600 planes [12]. It is noted that the usage rate of advanced composites in entire aeronautical applications in the United States is about 50% [13]. The weight reduction for aircrafts with the help of fiber reinforced polymer composites in place of their metal counterparts is crucial as it is related with several factors including number of assembled elements, fuel efficiency, speed, and increased flight range. Therefore, fiber reinforced composites have been used extensively in aeronautics since 1950s as alternative to

metals and alloys due to their enhanced physical and chemical properties in addition to the affordable manufacturing processes [14].

The chemical structure of the matrix determines the resistance of the polymeric composites to processes that includes chemical attacks, impact damage, water absorption, and high temperature creep. On the other hand, fibers are embedded in the matrix in order to strengthen the matrix and consequently final composite overall. The fiber reinforced composite materials are usually stronger than steel while they weigh much less. This advantage leads the fiber reinforced composites to be widely used in aerospace industry as the fuel efficiency is a crucial parameter. Thus, the air pollution can be minimized by this way. In addition, fiber reinforced polymer composites present other significant benefits in aerospace industry in terms of reduced scrap formation, design flexibility, improved corrosion and fracture resistance. Yet, there are some drawbacks of polymer matrix composites need to be considered such as swelling owing to the moisture absorption and debonding at the interface of fiber and matrix due to the chemical mismatch [15]. In this thesis, the applicable solution to debonding problem in carbon fiber reinforced thermoplastic (CFRTP) composites is proposed by the enhancement of optimized adhesion between fiber and matrix. As a result, the performance of polymer composite was upgraded in terms of physical and chemical properties.

The polymer composites in aerospace applications are classified into two groups according to their matrix type; thermoset and thermoplastic matrices as they provide high mechanical strength [2,7,16]. In the following section these two polymer matrix composites are explained.

There are continuing studies on the development of coating materials for enhanced

CFs in the context of reinforced composites. However, in the current know-how, proposing a way to improve the CF's physicochemical properties individually (i.e. thermal endurance, mechanical strength, chemical resistance etc.) is lacking. Various studies based on the interfacial behavior in composites, especially considering thermoset-matrix based composites exist [17–26]. However, there is a need for addressing the sizing material for CFs to enhance physical, chemical, and mechanical properties. In addition, literature is insufficient in terms of integration of the achieved improvement in the physicochemical properties into CF reinforced thermoplastic composite materials. In this sense, there is a lack of literature for using TP as matrix since many studies are based on thermoset based matrix materials, such as epoxy resin [17–23,25,26].

The main research fields in the production of new generation and high-technology structural parts in aircrafts are based on the development of advanced materials and the new methods to meet the expectations for high performance/light weight ratio. In this regard, due to their enhanced physical and chemical properties in addition to the affordable manufacturing processes fiber reinforced composites have been using extensively in aeronautics since 1950s as alternative to metals and alloys [14]. Composite materials which are currently being used in aerospace applications are mainly based on thermosets, particularly epoxy resins in pre-impregnated composites. Despite their mechanical strength, high levels of dimensional stability and the cost-effective manufacturing thermoset composites have considerable drawbacks. They cannot be recycled, remolded or reshaped, and they are difficult to the surface finish. On the other hand, instead of using thermoset based composite matrices proceeding with thermoplastics is more advantageous since fiber

reinforced thermoplastic composites provide high-impact resistance, remolding/reshaping capabilities, chemical resistance and long lifetime. Moreover, extensive research was carried out for the investigation of the interface because debonding phenomenon between inert CF and TP matrix is the crucial problem for polymer matrix composites. That is why a significant amount of study has been devoted to solve this problem by improvement in fiber-matrix interphase to preserve the mechanical strength of composite. However, the problems arising with TP composites are the difficulty in control of fatigue propagation because of the delamination phenomenon. Hence, in our study we focus on the molecular interactions between fiber and matrix to solve the delamination problem.

Polyether ether ketone has been considered as a promising TP polymer matrix to use in advanced engineering composite materials because of its excellent thermal stability in addition to its high resistance to chemical corrosion which leads to a long life time [27]. PEEK exhibits exceptional tensile properties. According to ISO 527 test method, PEEK has 98 MPa tensile strength at yield and 4.0 GPa tensile modulus at 23 °C. The polymer exhibits excellent creep resistance. Maksimov *et al.* points out that at a stress level of 30 MPa the total strain transcends the instantaneous elastic strain only by a factor of 1.15 after 14-month tests [28]. The polymer has high surface resistivity and volume resistivity. It can maintain good insulating properties in a broad temperature range during environmental changes. PEEK has notable thermal resistance as its continuous use temperature is up to 260 °C. Furthermore, crystallinity imparts excellent resistance to wide range of liquids. Besides, PEEK has low friction and good dimensional stability that makes it so advantageous in terms of aerospace applications [9,29,30].

Carbon fibers as reinforcement material have been used in a wide range of applications such as aerospace, automotive, sports industries and *etc.* due to their lightweight, mechanical strength and low expansion coefficient [31]. Yet, because of the inert nature of PEEK polymer chains and low surface energy of CFs adhesion between the matrix and reinforcement material is poor and this weakens the mechanical performance of thermoplastic composites under loading, leading to debonding and pullout [9,32]. The mechanical strength of the CF reinforced PEEK composite is mainly based on the nature of interfacial interaction between CF (reinforcing phase) and PEEK (matrix). Current commercial TP composites suffer from weak interfacial interaction which causes debonding between fiber and matrix due to the poor wetting of inert fibers. Therefore, surface activation of CF via chemical tailoring is needed in order to achieve the optimized adhesion between CF and PEEK leading to less void content and consequently enhanced mechanical strength for CFRPs.

In the literature, continuing studies on the development of coating materials for enhancing the interface between CFs and polymer matrices such as polyimide (PI), PEEK, etc. exist in the context of reinforced composites. There are various types of methods including ozone, plasma, and liquid-phase oxidation which have been applied to increase the interfacial strength in CF reinforced PEEK composites [33–35]. Yet, these methods cause cavities on CF's surface that result in the loss of the fiber's mechanical strength [36]. Thus, better surface functionalization can be achieved by sizing, in which CFs are coated with specific sizing agents [37]. In this concept, metal-organic frameworks (MOFs), grafting by PEEK-NH₂ and decoration of CF surfaces with PEI nanoparticles, carbon nanotube (CNT) or

graphene oxide (GO) are proposed sizing applications to obtain increased interlaminar shear strength (ILSS) in CFRTPs [10,11,38–40]. However, there are considerable disadvantages of the current sizing methods. For instance, MOFs suffer from the drawback of poor stability as degradation of organic linkers may lead to losing their activities [41]. On the other hand, PEEK-NH₂ grafting is performed with a surfactant that leads to a nano-structure formation on CF's surface that causes a crucial problem during consolidation to obtain CFRTP composites [42,43]. Furthermore, application of nanoparticles as part of the sizing formulation results in agglomeration due to their high surface area and reactivity meanwhile inhomogeneous distribution along CF's surface might disrupt the mechanical strength of CFRTP [44]. In addition, the current know-how does not include a way to improve physicochemical properties (i.e. thermal endurance, mechanical strength, chemical resistance etc.) of CF reinforced PEEK composites since a variety of interfacial studies are based on thermoset oriented composites [17–26] instead of TP. However, the present epoxy coating around CFs is not convenient to be used in high-temperature TP matrices including PEEK because of poor adhesion and low thermal stabilities [45]. Therefore, there is a need for addressing novel sizing materials for CFs which is reinforced in high-temperature PEEK matrix. In this study, it was shown that synthesis of hydroxylated PEEK (HPEEK) as a sizing agent is advantageous because its chemical and physical compatibility is quite high with the PEEK matrix. Thus, the improved surface roughness and SFE of functionalized CF led to a significant enhancement in adhesion between CF and matrix. Hence, the effect of this improvement in interfacial binding on the

mechanical properties of consolidated CFRTP composites was revealed in this work.

In this thesis, we aimed to enhance the mechanical properties of PEEK composite materials against harsh conditions through the functionalization processes in our interphase studies. In this regard, activation of carbon fiber's surface through acidic modifications and developing a functional and cost-effective sizing agent for CF were carried out to obtain better binding of sizing polymer to the matrix. Advanced mechanical, physical and chemical properties are the ultimate goals for aeronautical applications throughout the improvement of adhesion between reinforcement phase and TP matrix. Hence, we investigated new types of blend polymers by adjusting the concentration ratios to improve the wettability of CF embedded in thermoplastic matrix. Herein, we proposed the enhancement of interfacial interactions in CFRTP through the construction of H-bonding between PEEK and sizing material surrounding reinforced CF.

1.1.1. Thermoset Based Polymer Composites

The wide range of polymer composites used in aeronautical applications consists of the thermoset matrix such as epoxy resin, polyesters, and phenolics because of their ease of handling during production and accumulated know how about operating methods [46]. Thermosets are made up of cross-linked polymer chains held together by strong covalent bonds. Cross-linked polymeric chains constitute the network structure of thermoset, which cannot be broken on heating. Moreover, thermoset polymers remain hard when they are heated [47]. Therefore, this type of polymer matrix is not suitable for remolding or reshaping. This leads to the

inefficiency in terms of cost and energy as the process cannot be reversed if any problem occurs during manufacturing.

1.1.2. Thermoplastic Based Polymer Composites

Although thermoset-matrix based polymer composites have a wide range of usage, thermoplastic-matrix based polymer composites are gaining more and more attention nowadays owing to their significant advantages. For instance, thermoplastic-matrix based composites have no curing process, also unlike thermoset-matrix based composites they exhibit flexibility in remolding and reshaping that results in lower cost of production. Furthermore, reinforced thermoplastic (TP) composite has high-temperature resistance, excellent mechanical strength, and low moisture content [13,48].

The new era in aerospace industry begins with the use of advanced engineering thermoplastics such as polyetherether ketone (PEEK), polyether imide (PEI), polyphenylene sulfide (PPS) for high-temperature applications. Unlike the network structure of thermoset, thermoplastic polymer has tangled chains, that is there is no cross-links between polymer chains. On the other hand, the weak forces of attraction between chains enables remolding and reshaping of thermoplastics. Also, they soften when heat is applied, i.e. thermosoftening, and remain hard when they are cooled. They can be exposed to heating / cooling cycles several times without any change in their chemical and mechanical properties [49]. Furthermore, thermoplastic materials as a part of circular economy play an important role in sustainability and protection of environment through recycling processes [50]. Besides many advantages of using reinforced thermoplastic composites in aerospace applications there is a crucial problem needs to be overcome that is

debonding phenomenon occurring due to poor adhesion between reinforcing phase and thermoplastic matrix [51]. In this thesis, aforementioned phenomenon is examined and an applicable solution to this debonding problem is proposed.

1.1.3. Characteristics and Lineup Production of Carbon Fiber

Carbon fibers are structurally made of carbon atoms in a form of long and fine threads having diameter in the range of micrometer. The carbon atoms are bonded with each other in such a way that the crystal planes are arranged to be parallel throughout the axis of fibers. This parallel conformation of crystal planes makes CF substantially stronger than other fibers [52–56]. CF is indicated as *high-modulus CF* for high-temperature usage while *high-strength CF* for low-temperature treatments [52,57,58]. The superior mechanical properties of CF in both tension and compression mode made it pioneer reinforcement material in polymer composites rather than other synthetic fibers. Furthermore, the lightweight and corrosion-resistant characteristics of CF as a result of its high strength to weight ratio makes CF unique for structural applications. These distinctive properties are governed by the origin of CF from which it is derived. The essential performance of the polymer composite is based on high amount of carbon content lengthening chain to make high molecular weight (M_w) and high degree of oriented crystal plains along fiber axis.

In lineup production, CF is predominantly derived from polyacrylonitrile (PAN) precursor. The efficiency of carbon yields as well as its combination of compressive and tensile strength make PAN favorable precursor.

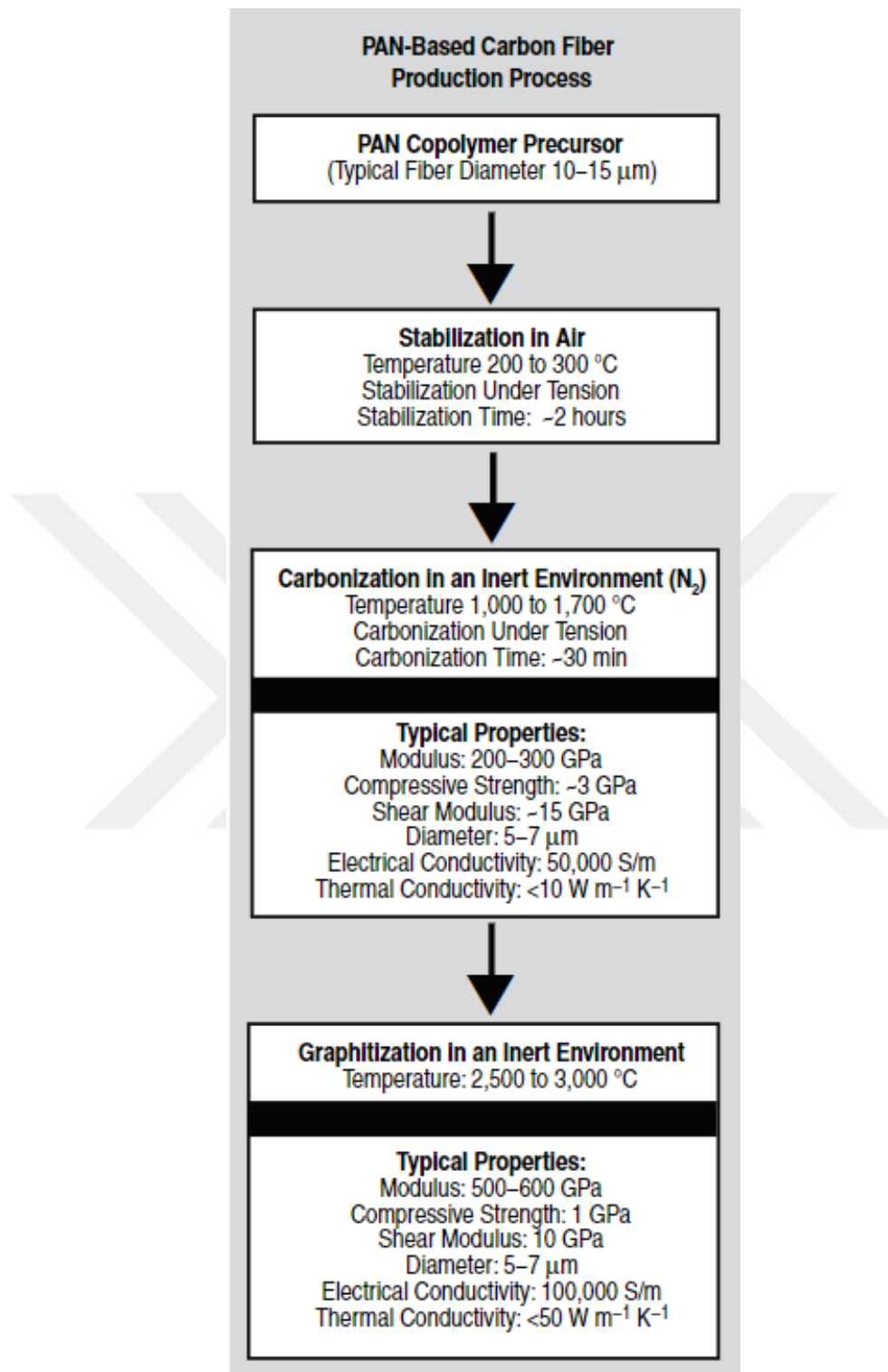


Figure 1. A PAN-based carbon-fiber processing flow chart. Reprinted with permission from ref [59]. Copyright 2005 Springer.

Derivation of carbon fibers from PAN involves polymerization step for PAN, electrospinning of fibers, thermal adjustment and stabilization, carbonization, then graphitization. Instead of homopolymer the copolymer of PAN is used during CF production because the alignment of molecular chains is hindered while spinning due to the highly polar nitrile groups of PAN homopolymer. The comonomers involve acrylic acid, methacrylate, and methacrylic acid in a rate between 2 to 15 percent. The utilization of comonomers disrupts the nitrile-nitrile interaction in some measure that leads to the better chain alignment. Typical carbon yield from PAN precursor is noted as 50-60 % [59].

The use of carbon fiber in aerospace industry has become dominant due to its high strength (3-7 GPa) and high modulus (200-500 GPa) in addition to low density (1.75-2.00 g/cm³) allowing for improved mechanical properties of carbon fiber reinforced polymer composites [59]. The aim of producing CFRTCP composite materials is based on the necessity of lightweight load-bearing material with enhanced mechanical, physical, and chemical properties which its individual components are not able to provide. Besides, the optimization of performance during service life is the main consideration for using structural polymer composites. The advanced properties of CFRTCPs are mainly governed by their microstructure in addition to the interaction between fiber and matrix along interphase region [60]. Since polymers have prominent benefits such as high degree productivity, energy efficiency, and ease of processing they provide low cost of production, which is highly important parameter for aerospace applications.

The primary objective of recent studies in the field of polymer composites is based on the investigation of physicochemical interaction between polymer matrix and

CF at their interfacial region. This kind of interaction is obtained either through van der Waals force or hydrogen bonding in between reinforcing phase and matrix [52,61,62]. If the surface free energy (SFE) of CF surpasses the SFE of TP matrix the binding efficiency between them can be enhanced by optimized adhesion. Therefore, in this thesis it is aimed to improve CF's wettability by PEEK matrix through sizing treatment so that void content in CFRTP composite can be diminished. As application of sizing alters the physical and chemical properties of CF's surface the compatibility, hence binding strength between CF and PEEK are enhanced. As a result, the main encountered problem in CFRTP composites, which is so-called debonding issue, is overcome by achieved improvement in SFE and wettability property of CF in PEEK matrix.

1.1.4. Physical and Chemical Properties of Polyetherether ketone

In this study, polyetheretherketone (PEEK) was used in the preparation of sizing agents to implement into CF reinforced PEEK composites. Polyetheretherketone is known as a high-performance, advanced engineering thermoplastic polymer. It is distinguished by a distinctive combination of properties. These properties range from excellent mechanical strength and chemical resistance to high temperature performance.

1.1.4.1. Chemical Structure of PEEK

Polyetheretherketone is a member of polyketone family and it is a semicrystalline thermoplastic polymer. Since its structure brings in superior chemical, physical, and

mechanical properties PEEK is the widely preferred polymer matrix in CFRTs for aeronautical applications. The linear and branched characteristics of PEEK's polymer chains allow thermosoftening while heating [63]. As a result, in carbon fiber reinforced PEEK composites remolding and reprocessing of the polymer become possible during manufacturing of structural parts.

Polyetherether ketone is obtained by step-growth polymerization through the dialkylation process of bisphenolate salts. The synthesis route involves either 1,4-bis(4-fluorobenzoyl) benzene or 4,4-difluorobenzophenone in the presence of alkali carbonates. After removal of both polymerization solvent and alkali metal fluoride, the polymer is isolated [64].

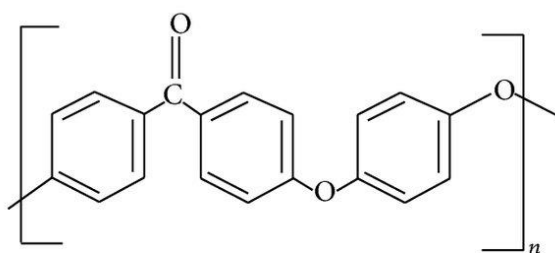


Figure 2. Chemical structure of polyetherether ketone.

The polymer exhibits one of the highest transition temperatures due to its stiff aromatic backbone. Thus, it can retain at elevated temperatures as high as 240 °C [65].

1.1.4.2. Key Properties of PEEK

Polyetherether ketone is a fully recyclable engineering plastic which makes it cost-effective. Also, it exhibits excellent long-term chemical resistance that substantially increases its service life. The polymer provides excellent thermal resistance that

facilitates its usage for high-temperature applications. Its continuous use temperature is noted up to 260 °C. PEEK has significantly high melting temperature (T_m), i.e. 341 °C, while its glass transition temperature (T_g) is 143 °C [66–72]. The aromatic rings in backbone of PEEK hinder the segmental motion of polymer chains. As a result, the polymer exhibits high T_m and high T_g .

The need for manufacturing of lightweight and mechanically strong structural materials with high chemical and thermal resistance points out use of CF reinforced PEEK composites in aerospace applications.

The high-temperature flexural modulus of PEEK can further be advanced by CF reinforcement. The reinforcement also improves fatigue and creep resistance. The PEEK composite can withstand high loadings for long functioning periods at elevated temperatures without any permanent deformation [73,74].

Carbon fiber reinforced PEEK composite has superior tensile properties. Its tensile strength is noted as 200 MPa even at 299 °C [75].

Polyetherether ketone shows high volume resistivity and the polymer preserves its surface properties in changing environmental conditions.

The polymer has excellent thermal properties that are attributed to the stability provided by the aromatic backbone consisting of the bulk of monomer units. The thermal decomposition of PEEK is a two-step process in which the first peak of degradation is observed at around 555 °C that is much higher than for majority of polymers [76]. The centred decomposition peak appears at 585 °C due to the random chain scission of ketone and ether bonds [77,78]. Then, the second decomposition stage begins above 600 °C that is referred to cracking and

dehydrogenation of crosslinked residue remained from the first step of decomposition resulting in a thermally stable carbonous char [76].

The crystalline structure of PEEK results in great chemical resistance. On the other hand, this chemical inertness of PEEK makes it insoluble in all common organic solvents. It does not undergo hydrolysis so that it can be used for a long time under steam or high-pressure water without any significant property degradation [79]. Because of exceptional chemical and thermal resistance, low friction, good dimensional stability, and also long life properties of PEEK and its composites provide a wide range of utilization area in aerospace industry for carbon fiber reinforced PEEK composites. Yet, the chemical inertness of CF and PEEK remains being a problem that needs to be solved. Therefore, in our study we focus on this debonding phenomenon in order to enhance the adhesion between CF and PEEK. Hence, we impart activation and functional surface coating for CF in order to increase the compatibility between reinforcing material and PEEK matrix.

1.1.4.3. Limitation of PEEK

Polyetherether ketone is considerably expensive for large-scale applications. Moreover, it has high processing temperature that makes it difficult to process in the laboratory. Thus, injection molding is used to process PEEK in industry. Moreover, the polymeric chains in PEEK are so packed that makes diffusion of solvents into the structure difficult. Hence, chemical resistance causes insolubility of PEEK in all common solvents [80–82]. Besides, a wide range of research results show that it can be attacked by sodium and halogens [83–87].

1.1.5. Physical and Chemical Properties of Polyether imide

Polyether imide (PEI) was used during sizing process in this study. PEI as a sizing material has good chemical compatibility with PEEK that is, they can bind each other through covalent interactions. Hence, it decreases the void percent between PEEK matrix and coated CF through enhanced adhesion. PEI is featured as high-performance engineering polymer due to its outstanding mechanical, and thermal properties. The incorporation of ether and imide groups is the characteristic of PEI that is attributed to high-temperature performance and good melt processing.

1.1.5.1. Chemical Structure of PEI

Polyether imide is an amorphous engineering thermoplastic whose thermal, mechanical, and electrical properties are outstanding. PEI is produced through the polycondensation reaction between bisphenol-A dianhydride (i.e. tetracarboxylic dianhydride) and diamine [88].

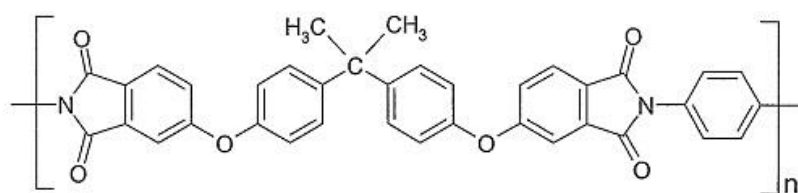


Figure 3. Chemical structure of polyether imide.

The ether linkages present in backbone of PEI imparts melt processing property. The imide ring in the chemical structure of PEI offers good mechanical properties

and thermal resistance. As thermal behavior of PEI represents polyimides it is feasible to use in high-temperature applications [89].

1.1.5.2. Key Properties of PEI

Polyether imide is characterized by its inherited flame retardancy without any reinforcement material. The polymer has relatively high T_g (215 °C) and T_m (340-360 °C) in addition to long-term service temperature (160-180 °C) as a result of its high softening point (220 °C) [90,91].

Polyether imide provides distinctive mechanical properties and high modulus for producing mechanically strong structural parts in aerospace applications. Its flexural modulus is 3.5 GPa with tensile strength at break 115 MPa [92]. The polymer has high Young's modulus (~3 GPa) and very good maintainance of mechanical feature at high temperatures [93,94]. PEI also exhibits good hydrolytic stability. Furthermore, it displays high rigidity and exceptional dimensional strength in addition to good electrical properties and chemical resistance [92].

1.1.5.3. Limitation of PEI

Polyether imide has high cost for excessively demanding applications. Processing of the polymer is not easy because hot mold is needed during injection molding that adds extra step to the manufacturing procedure of PEI. Also, it is prone to stress cracking as a result of chemical attacks by aromatic compounds, acetates, halogenated polar solvents, especially by chlorinated solvents [95]. Despite of the outstanding dimensional stability of PEI at elevated temperatures under load it has very high processing temperature (365-375°C) that makes treatment of PEI difficult [92].

1.2. Sizing of Carbon Fibers

As the bare carbon fibers are brittle they need to be protected while handling. Hence, a thin and homogeneous coating, i.e. sizing, is applied to the fiber's surface so that fiber filaments can be handled easily during compounding with matrix in composite processing. The sizing is a kind of bond between matrix and fiber that holds them together. On the other hand, sizing plays a crucial role to determine the surface properties of fiber and consequently the physicochemical properties of final composite after reinforcement. For instance, chemical and water resistance, oxidative and thermal stability depend on the sizing formulation. Moreover, degree of adhesion between matrix and reinforced fiber determines the properties of composite interphase and subsequently mechanical strength of the resultant composite material. Without any sizing on CF's surface there is no interaction between inert CF and PEEK that weaken the mechanical properties of final composite due to poor adhesion between reinforcement material and thermoplastic matrix.

In this study, the design and development of a polymeric sizing material which is compatible with the surface of the CF for the purpose of avoiding any separation between fiber and coating material was focused on. To do so, surface chemistry, roughness and crystallinity were studied. Furthermore, effects of the coating on CF's thermal and mechanical properties were analyzed. Afterwards, the interfacial locking of the CF with the matrix in thermoplastic composites (PEEK/CF, HPEEK/CF, PEI/CF) is main subject within the frame of this thesis.

There are four main sizing methods for carbon fiber: Wet/chemical method (acidic treatment), dry/gaseous method (plasma treatment), multi scale method (nanoparticle coating), multi functional method (MWNT coating) [24]. Functionality of CF is ensured by generating functional groups, i.e. NH, NH₂, OH, COOH on fiber's surface. In current composite applications carbon nanotubes are coated on CF to make the surface of fiber functional in compatible matrices, i.e. epoxy resin, thermoset, and polyamide [17,21,26]. For promoted interfacial adhesion NH and NH₂ is compatible with polyamide, polyester, polyurethane matrix polymers whereas OH and COOH is compatible with thermoplastic, thermoset, vinyl ester matrix polymers [24]. In our study, carboxyl (COOH) and hydroxyl (OH) functional groups were generated on CF's surface in order to strongly bind the sizing agent onto activated CF's surface through hydrogen bonding (H-bonding).

Sizing plays a pivotal role in fiber-matrix interphase in order to determine the performance of CF reinforced thermoplastic composite [96–99]. The key parameter to improve the interfacial interactions in CF RTP is the compatibility of the fiber's sizing and resin matrix. Therefore, optimized adhesion between reinforcing phase and matrix leads to enhanced mechanical properties for the obtained composite by eliminating debonding between CF and PEEK. In this study, the noteworthy impact of sizing formulation on physical, chemical and mechanical properties of carbon fiber reinforced thermoplastic composite was presented. Hence, it was shown that modifying the surface chemistry of fiber throughout sizing process was improved wettability of carbon fiber by PEEK matrix. The better adhesion between sized CF

and PEEK led to the significant increase in tensile strength and toughness of the final composite laminate.

The main advantages of sizing to composites are fatigue performance, tensile strength, chemical and heat resistance. In sizing formulation, the type of fiber and resin, final composite applications are essential. To illustrate, the requirements for thermoplastic matrix differ from thermoset matrix or processing of carbon fiber is not same with glass fiber. This thesis focuses on the interfacial interactions between CF and thermoplastic PEEK matrix since low-weight CFRTs provide high strength in addition to less scrap formation during compounding.

In this study, a compatible sizing agent for CF reinforced PEEK composite was developed. Then, wettability and surface free energy relation and its impact on mechanical properties of composite was investigated. Morphology, surface chemistry, tensile and fatigue performance of treated/untreated CF and final composite were analyzed via various spectroscopic and microscopic techniques. Sizing was carried out by using dip coating technique as it can be seen in Figure 4. Then, the sized samples were cured.

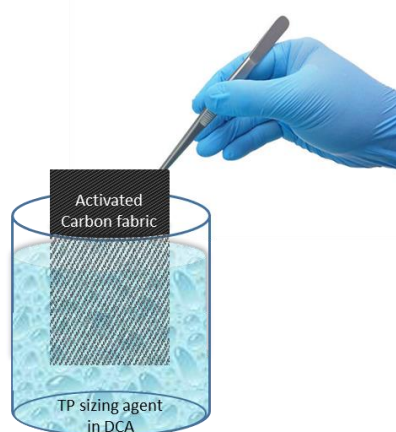


Figure 4. The depiction of sizing process for activated CF.

CHAPTER 2

Sizing with Surfactant in Chloroform Medium

2.1. Objective of the Study

The development of load-carrier reinforced composites is crucial for a wide range of applications, such as aerospace, automotive, sports industry and so on. Reducing the excessive weight of structural materials without any sacrifice in the performance is crucial for these applications. Thus, using reinforcement materials (e.g. carbon fibers, glass fibers) for polymeric matrices in composites is the most convenient way to follow. In this study, carbon fiber (CF) was used as a reinforcement material for thermoplastic based composites. Bare CFs are too fragile to process so they must be coated / sized such that the brittleness of CFs can be avoided at the final product. The traditional sizing agent (i.e. epoxy) is not suitable for handling continuous CF reinforced thermoplastic composites (CFRTPs) with high processing temperatures above 300 °C. In this study, a novel sizing agent in chloroform medium was developed for this purpose by using emulsion / solvent evaporation technique. The effects of this sizing on the CFs' physicochemical as well as surface properties were investigated. In addition, the impact on fiber-matrix interphase behavior is also analyzed.

The inferior adhesion between a reinforcement material and a matrix is one of the most important obstacles to overcome in the thermoplastic (TP) composite materials as it causes significant delamination problems. To this end, this study aims to overcome the poor wettability between reinforcing phases of carbon fiber (CF) and TP polyetherether ketone (PEEK) matrix; by enhancing the interfacial interactions through the functionalization of CF's inert surface. Herein, activated CF's surface was tailored by applying polymeric coating/sizing agents that have different chemical structures. Thus, wettability results were obtained for CFs per each sizing agent. The sizing agents were designed to maximize the similarity between the surface chemical structure of CF and the matrix itself. This way, we optimized the adhesion between the CF surface and the PEEK. Therefore, we overcame the current debonding problem caused by poor adhesion through interfacial interaction improvements. These improvements are achieved by forming hydrogen bonds (H-bonds) between modified CF and PEEK. We also investigated the attained physicochemical and mechanical characterizations of our final composite for aerospace applications.

2.2. Experimental

In this work, polyether imide (PEI) and its solution blend with polyetherether ketone (PEEK) were chosen as alternative sizing agents for CF reinforced polyetherether ketone (CF/PEEK) composites. The aim for using this type of composite is that CFRTPs have significant potential to be applied in aerospace industry instead of metals and thermoset composites as it is a highlighted need to reach high performance / weight ratios in aircrafts. The elimination of present

coatings in commercial CFs via de-sizing methods (e.g. thermal, chemical) is needed as epoxy is not compatible with the thermoplastic matrix and therefore, causes delamination in CFRTs. The thermal de-sizing method was used in contrast to chemical etching since the CF surface has to be prevented from any possible damage physically and chemically.

2.2.1. Materials and Methods

Materials

Granular PEI with 3 mm nominal granule size and powder PEEK with mean particle size of 80 microns were obtained from Sigma Aldrich. The carbon fibers 12K, T700 from Toray Industries, Japan, were used as received. As a sizing medium chloroform was used to dissolve sizing agents. Furthermore, sodium dodecyl sulfate (SDS) and Triton X-100 were used as ionic and nonionic surfactants, respectively in order to achieve the binding of the sizing material onto the CF surface through hydrophilic interactions.

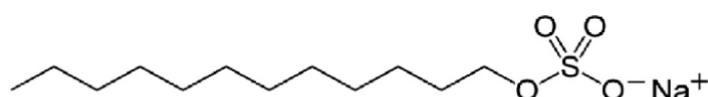


Figure 5. Chemical structure of SDS ionic surfactant.

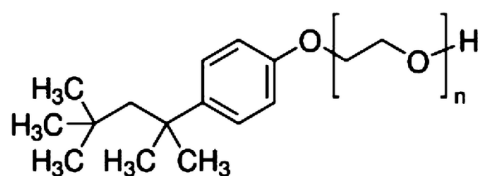


Figure 6. Chemical structure of Triton X-100 nonionic surfactant.

Preparation of Sizing Agents

Regarding the solvent-based sizing agent, two batches were prepared by using PEI only and the solution blend of PEI & PEEK.

1st batch: 0.5 wt% of granular PEI was homogenously dissolved in chloroform. It was observed that dissolving of PEI was a problem to be handled (i.e. Toluene, isopropanol, dimethyl sulfoxide, ethanol were studied, but they were not useful for dissolution of the main sizing agent). Thus, halogenated polar solvents, particularly chlorinated ones, were found successful to dissolve PEI. Later, 10 wt% SDS and Triton X-100 stock solutions were used as surfactant in the concentration of 0.5 wt%. In emulsion / solvent evaporation method, the optimum concentration for using a surfactant for the preparation of an aqueous dispersion of a thermoplastic (TP) sizing agent for CF is between 0.3 wt% and 1 wt% [45]. Hence, 0.5 wt% of SDS and Triton X-100 were prepared separately from the related stock solutions by using the formula; $M_1V_1 = M_2V_2$ where the notation “1” refers to the situation before the dilution and “2” refers to the situation after the dilution, while “M” indicates the molarity and “V” indicates the volume. The addition of the surfactant was carried out drop by drop during the mechanical stirring of the PEI solution. Later on, the stirring of the final solution continued for 12 h in order to obtain the first sizing agent homogenously.

2nd batch: 0.25 wt% of powder PEEK and 0.25 wt% of granular PEI were blended by solution mixing in chloroform. Later, 0.5 wt% SDS and Triton X-100 surfactants were added into the solution in separate beakers. Finally, a surfactant-stabilized emulsion was obtained as second sizing agent after 12 h mechanical stirring was applied.

Sizing Treatment of Carbon Fiber

Various sizing techniques, such as *electrodeposition*, *spray coating* or *bath coating* exist [20–22,24,100]. In this study, *dip coating* method was utilized for sizing treatment of the CF bundle. However, before the sizing process heat treatment was applied to remove epoxy on CF. At this stage, the degradation temperature of CF was determined through Thermal Gravimetric Analysis (TGA) in order to avoid causing any harm to CF itself. Therefore, the application of heating up to 450 °C for the thermal de-sizing of any current coating (e.g. epoxide) was considered safe in terms of chemical and physical unity of the CF. Consequently, CF bundles were de-sized in a radiant oven at 400 °C for 10 min and as a result grain CFs were obtained. Later, the sizing treatment was carried out through *dip coating* for both 1st and 2nd batches by using ionic and nonionic surfactants, separately. After coating, CF surface dried at room temperature meanwhile the remaining chloroform in the sizing agent evaporated off. Afterwards, rigid sized CF bundles were obtained.

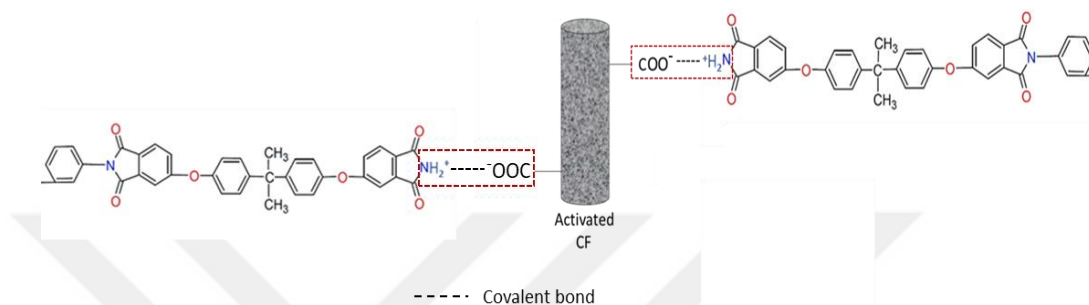
2.3. Media and Sizing Agents

In this part, chloroform was used as sizing medium while PEI and its solution blend with PEEK were used as sizing agents.

2.4. Results and Discussion

As the chemical compatibility of polyetherimide (PEI) and polyetheretherketone leads to strong adhesiveness we use imide linkages in order to avoid any cleavage problem that may occur between fiber and matrix. Moreover, there will be a

covalent bond occurring between Carbon (C) and Nitrogen (N) during the sizing of CF with PEI that provides the desired attachment of sizing polymer onto the fiber's surface. The obtained C-N bond is strongly polarized towards Nitrogen as the electronegativities of N and C are 3.04 and 2.55, respectively [101].



Scheme 1. Depiction of covalent bonding formed between the activated surface of CF and PEI based sizing agent.

The characterization part consists of the investigation of the changes in morphology, viscoelastic, chemical and physical properties of CFs and the alteration in the surface free energy of CFs so that the wettability by the matrix could be analyzed after the functionalization and modification throughout the sizing process.

2.4.1. Thermal de-sizing

First of all, a thermal de-sizing process was carried out to epoxy-coated Toray T700 CFs at 400 °C for 10 min. As a result, the sizing process onto bare CF bundles was utilized. Afterwards, epoxy-coated CFs were compared with CF samples after the de-sizing process in order to analyze that whether any change has occurred in the chemistry of CF bundles due to the coating. Thus, elemental and morphological

analyses were carried for epoxy-coated and plain CFs by Energy Dispersive X-Ray (EDX) and Scanning Electron Microscope (SEM), respectively.

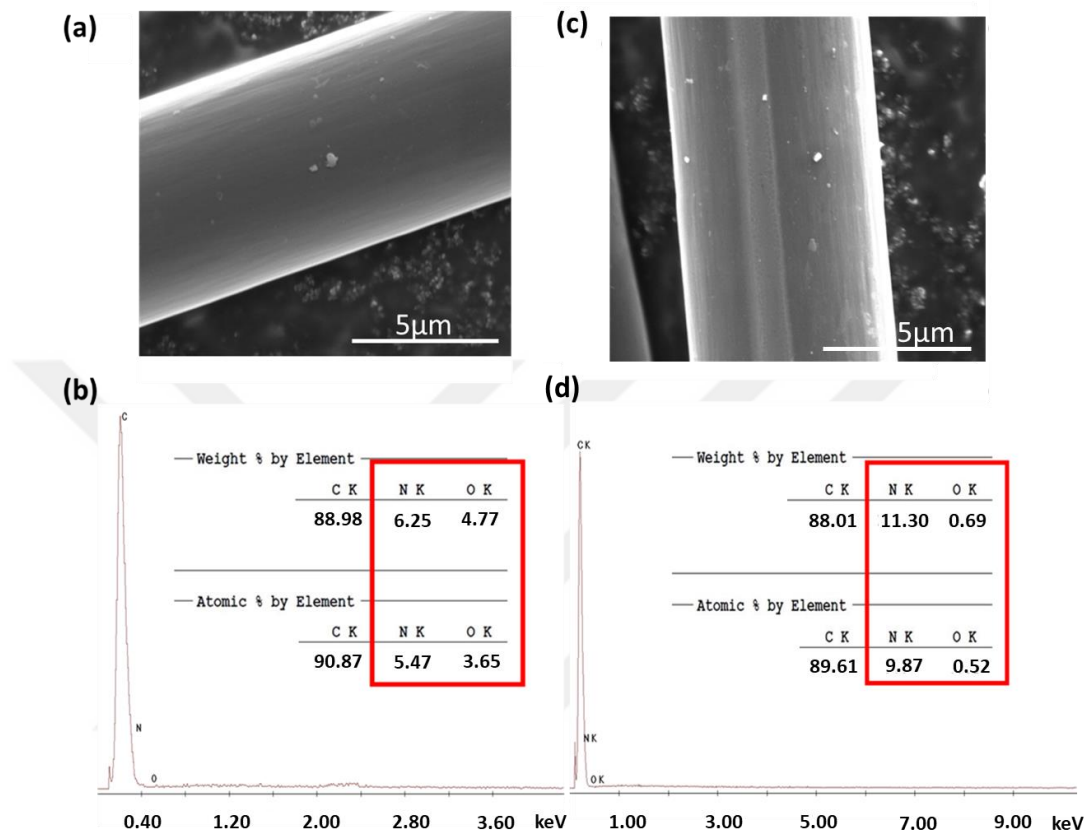


Figure 7. Morphology and elemental analysis of untreated CF (a, b) and de-sized CF (c, d) via SEM and EDX, respectively.

It is observed that the oxygen content on the CF surface is decreasing because of the removal of epoxide. As a result, it was proved that the present epoxide coating in T700 CF was eliminated through thermal de-sizing that was aimed for. Also, morphology images indicate that surface roughness of CF increased after thermal de-sizing was performed. It leads to the better interfacial interaction between reinforcement material and matrix in composite [24,102,103].

On the other hand, when thermal decomposition of the epoxy on untreated CF carried out, the bare surface of the fiber becomes more attractive for the air composing elements under ambient condition except oxygen. EDX results indicate that the oxygen binding affinity decreased while nitrogen affinity increased during the thermal de-sizing due to the interaction between the accumulated charges on carbon fibers and nonbonded nitrogen whose electron affinity is -0.72 eV. Another explanation might be there is no stable N^- exists, thus it easily binds onto the CFs consisting of free surface charges. Hence, the PEI based sizing agent could bind more effectively to the CF surface through the nitrogen side groups. Also, any possible oxidation can prevent the CF surface from the strong binding of the sizing agent.

2.4.2.Sizing of Bare CFs

Firstly, the emulsions of PEI and PEI-PEEK blend were prepared in chloroform sizing medium, separately. The sizing agents were obtained by using emulsion / solvent evaporation method [45]. This technique was used to prepare a stable aqueous dispersion of sizing polymer. The dispersion of sizing polymer at 0.5 wt% in a 0.5 wt% surfactant solution was prepared for both PEI only and PEI-PEEK blend as it was explained in detail in experimental section. Then, de-sized CF samples were dipped into the sizing emulsions for 2 hours. Finally, the coated CF samples were cured and chloroform was removed.

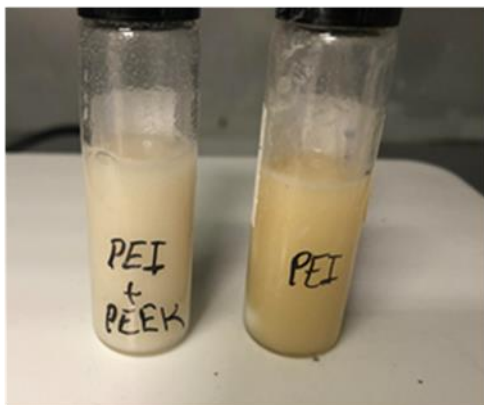


Figure 8. Emulsion of polymer sizing agents.

Secondly, chemical and morphological analyses of CF surfaces were performed in order to show the presence of coating after sizing of plain CF. During sizing process without using the surfactant, a compatible sizing could not be achieved. Therefore, surfactant was used in order to achieve the desired interaction by preventing any possible phase separation between inert CF surface and polar sizing agent.

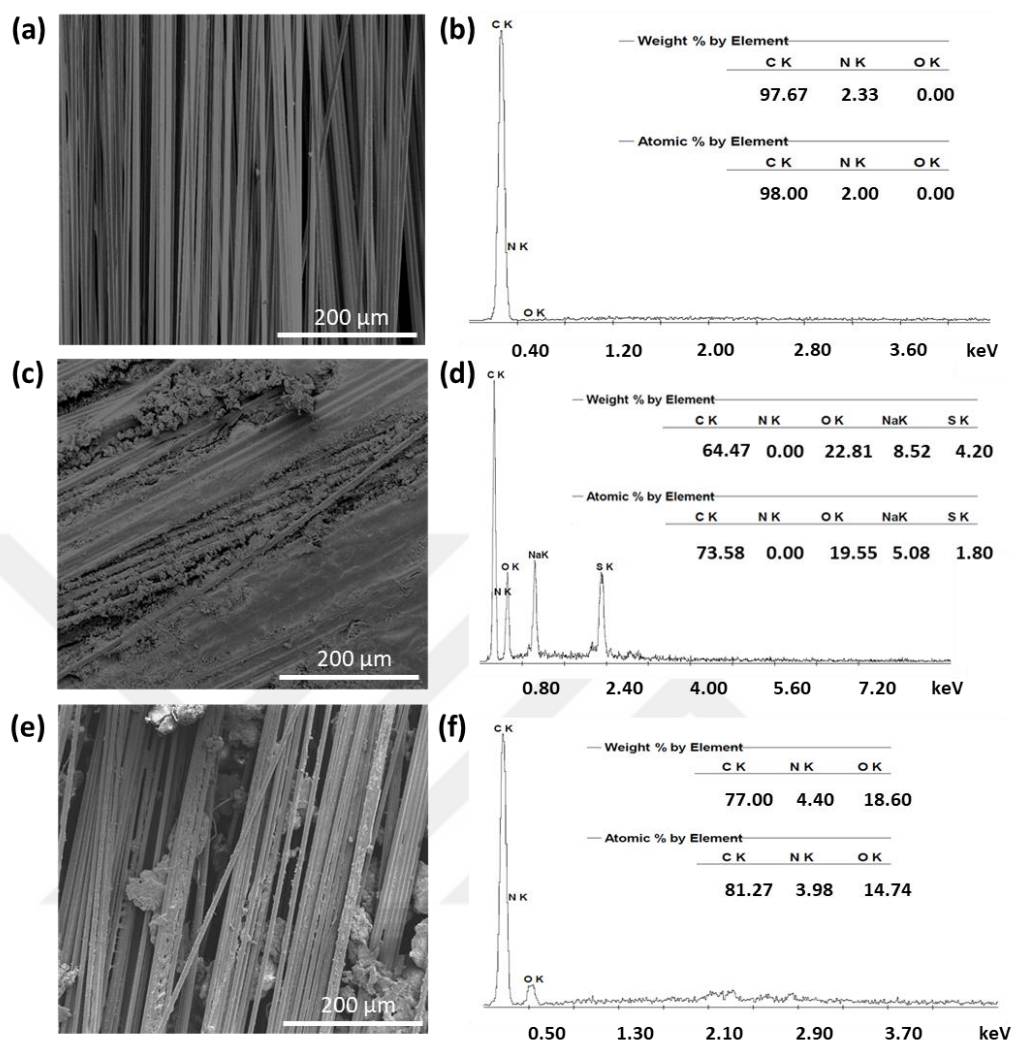


Figure 9. Morphology and elemental analysis of plain CF (a, b); PEI sized CF (c, d); PEI-PEEK blend for sizing of CF (e, f) via SEM and EDX, respectively.

The SEM morphology images show that there are regional agglomerations caused by the particles in sizing emulsion. Furthermore, the atomic percent by elements indicates that the O/C ratio increases when the sizing was applied onto CFs whereas the smallest value belongs to the thermally de-sized plain CF.

In addition, surface topography of untreated and modified CFs was analyzed via an Atomic Force Microscope (AFM).

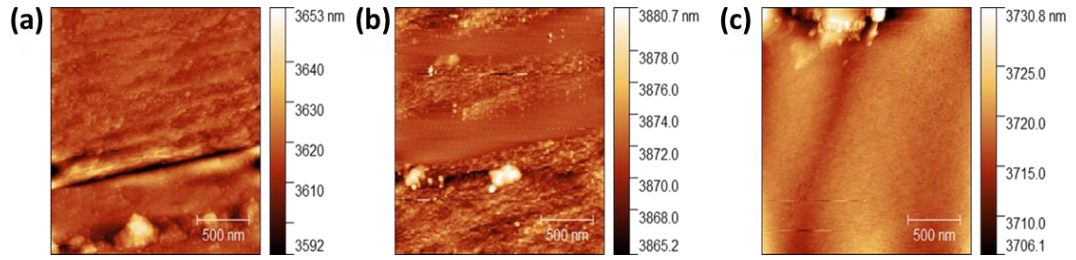


Figure 10. AFM height profile of plain CF (a), PEI sized CF (b), and PEI-PEEK blend for sizing of CF (c).

The average surface roughness R_a was determined for each sample. The R_a value is 3.70 ± 2.59 nm for plain CF; 1.01 ± 0.65 nm for PEI sized CF; and 1.71 ± 1.14 nm for PEI-PEEK sized CF. Hence, coating of thermally de-sized CFs by emulsion of a polymeric sizing agent and surfactant makes the CF surface slippery by decreasing the average surface roughness. Moreover, the static electrification of CF is another parameter needs to be considered here. Unlike chopped fibers the charge accumulation occurs on continuous CFs while handling, especially during the process of friction and rubbing [104]. Hence, the weaved fabric form made up of single fibers is preferred during manufacturing.

Since the sizing surrounding the fiber sample prohibits the static electrification of CF, the R_a value for the sized CFs is found to be smaller in comparison to plain CF. Thus, the result facilitates the binding of the sizing agent throughout the CF surface. However, morphology and topography images show that emulsification caused agglomeration. Moreover, using surfactant led to nano-structure formation in fiber-matrix system that is not desired for the mechanical properties of final composite.

The adhesion capacity of CF with PEEK matrix was investigated via Contact Angle Analysis. Then, the surface free energy of CF was examined before and after sizing by using Young's equation.

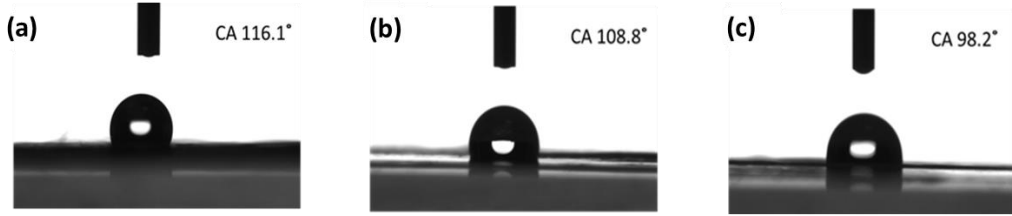


Figure 11. Contact Angle results for plain CF (a) and sized CF with PEI (b), PEI-PEEK blend (c).

According to Young's equation [105];

$$\gamma_{sl} = \gamma_s - \gamma_l \cos \theta \quad (\text{Eq. 1})$$

$$\gamma_{sl} = \gamma_s + \gamma_l - 2(\gamma_s \gamma_l)^{1/2} \quad (\text{Eq. 2})$$

where γ_s indicates surface free energy (SFE) of solid, γ_l is surface tension of liquid (72.8 mJ/m² for water), γ_{sl} is interfacial free energy between solid and liquid, and θ represents solid/liquid contact angle.

Consequently, the compatibility between treated CF and PEEK matrix was achieved when the surface free energies of sized CFs are compared with SFE of PEEK, i.e. $\gamma_{\text{PEEK}} = 40.1 \text{ mJ/m}^2$ [106]. In this study it was showed that sizing of CF by PEI and PEI-PEEK solution blend polymeric sizing agents substantially increased the CF's surface free energy from 5.43 mJ/m² to 8.36 mJ/m² for PEI and 13.38 mJ/m² for PEI-PEEK solution blend. The Contact Angle measurements indicate that when the plain CF is sized, the hydrophilicity of the CF's surface enhances. Hence, the wettability of the CF surface by PEEK has been improved.

Yet, the complete wettability could not be achieved as SFE of carbon fiber is still smaller than SFE of PEEK matrix.

2.5. Conclusion

In this study, design and development of polymeric sizing materials which are compatible with the surface of CF, and thus do not lead to any separation between fiber and coating material, were focused on. The compatibility of the reinforcement material and matrix was achieved through the sizing of carbon fibers via blending of PEEK and PEI. Hence, nitrogen bridges through the fiber surface facilitate the interfacial locking of CF with the thermoplastic matrix. However, complete wettability between CF and PEEK could not be succeeded due to present agglomerations caused by emulsion of sizing polymer and nano-structures formed by surfactants in chloroform/water system before addition of CFs to coat them.

Obviously, the presented results are open to further improvements with respect to industrial applications. The next step would be the spooling of the modified CF bobbins in such a way that the fiber bundles can be twined in unidirectional (UD) form which in turn could be used in the manufacturing of CFRTPs.

CHAPTER 3

Sizing with Engineering TP Polymers and Solution Blend in Dichloroacetic Acid Medium

This work is partially described in the following publication [107];

“Effects of Thermoplastic Coating on Interfacial Interactions in Advanced Engineering Composites for Aerospace Applications”

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3.1. Experimental

3.1.1. Materials and Methods

Materials

Aerospace grade and high-strength polyacrylonitrile (PAN) based carbon fabric made up of 7-micron carbon fibers which are weaved in unidirectional (UD) form

were obtained from the Hexcel Corporation, USA. Powder polyetherether ketone (PEEK) with mean particle size 80 μm and granular polyether imide (PEI) with nominal granule size 3 mm were supplied by Sigma-Aldrich. APTIV PEEK films were obtained from Victrex. Sodium borohydride (NaBH_4), dichloroacetic acid (DCA), 2,2-dimethyl-1,3-dioxane-4,6-dione (Meldrum's acid), nitric acid (HNO_3 , 65%), dimethyl sulfoxide (99%), absolute ethanol (99.9%), and all the other chemicals and reagents were of analytical grade and received from Sigma-Aldrich, unless otherwise stated. Ultra-pure deionized water ($R \geq 18 \text{ M}\Omega \text{ cm}^{-1}$) from Milli-Q plus water purification system (Millipore, Bedford, MA, USA) was used throughout the study.

In addition, it was observed that using carbon fibers as roving is not convenient due to their tendency to accumulate excessive electrostatic charge on them. Thus, the homogenous sizing process was restricted and characterization of the CFs through Atomic Force Microscopy (AFM) in tapping mode was negatively affected because the gathering electrostatic charges results in distortion of the images as it can be seen in previous chapter. Moreover, during the sizing process the bundles were separated and entangled with each other which makes the processing of CFs very difficult. As a result, we started to use CFs in the form of fabrics which are made up of weaved bundles of carbon fibers in unidirectional (UD) form. The main issue to take into consideration with the carbon fabric is that their lifetime and protection of fabric from the environmental hazards, hence it must be kept in dark and cool storage. Otherwise, the fabric itself disentangles within a period.

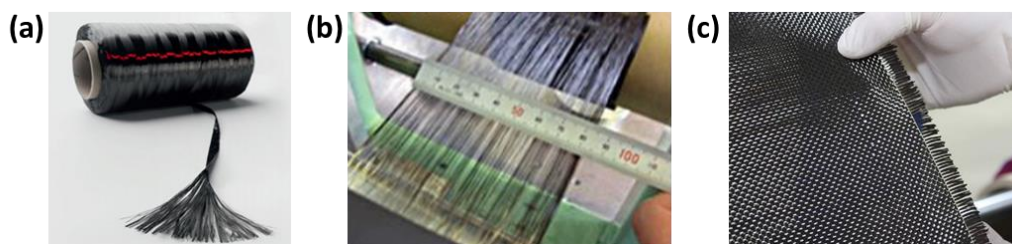


Figure 12. (a) 12K CF original tow (5 mm), (b) 12K CF spread tow (80 mm), (c) carbon fabric.

In this study, carbon fabrics were activated by acidic treatment, then sized. Thus, forming H-bond between treated CF's surface and sizing agent eliminates phase separation, i.e. sizing agent can strongly bind to CF through the functional groups after acidic treatment beforehand.

Instrumentation

In the characterization of CFs, chemical fingerprints of the samples were determined via Raman spectroscopy using a confocal Raman microscope (WITec Alpha 300R). Raman spectra were acquired from 800 to 2200 cm^{-1} at an excitation wavelength of 532 nm. Chemical and elemental analyses were carried out using X-ray Photoelectron Spectroscopy (XPS) (Thermo Fisher Scientific Inc., USA). Measurements were conducted with a step size of 0.1 eV, a spot size of $\sim 400 \mu\text{m}$, and a pass energy of 30 eV. X-ray diffraction (XRD) patterns were recorded to obtain the crystallinity degree of samples using an X-ray diffractometer (X'pert pro MPD, PANalytical). The copper (Cu) K_{α} irradiation source, i.e. 40 kV, 45 mA, $\lambda = 1.5418 \text{ \AA}$, was used in XRD measurements. The morphology analysis was determined using a high voltage environmental SEM (Quanta 200 FEG) with a spot size of 3.0 and 5 kV voltage. Moreover, topography analysis was performed through 3D laser scanning using a Keyence VKX 100 Microscope. FTIR spectra were

obtained to analyze chemical bonds in the material using a Bruker Alpha-II Platinum ATR FT-IR spectrometer. The spectral range for FTIR was determined between 4000-400 cm^{-1} with a wavenumber resolution of 2 cm^{-1} while the number of acquisition scans for both background and sample was fixed at 64. CA measuring in sessile drop mode was performed to analyze the wettability of CFs using a Dataphysics OCA 20 with distilled water in a dosing volume of 1.5 μL and a dosing rate 0.5 $\mu\text{L/s}$. A furnace (Thermolyne, 48000) was used for thermal de-sizing of CFs. An Instron mechanical tester with a 100 kN load cell was used for tensile tests applied to composites consisting of neat and sized CFs under ambient conditions.

3.1.2. De-sizing of Epoxy Coating on CFs

The neat carbon fiber was obtained through thermal de-sizing of the epoxy-coated CFs in the furnace at 400°C for 10 min. Subsequently, the resultant fabric was rinsed with acetone to get rid of the surface contamination due to degradation of epoxy coating. Since acidic treatment may change physical and chemical properties of the fibers surface, a thermal de-sizing method was preferred [108].

3.1.3. Surface Activation of CF

In this work, neat polyacrylonitrile (PAN)-based carbon fibers were chemically modified with nitric acid in order to improve the interaction between carbon fiber surface and thermoplastic-based polymer sizing material. It is crucial to design and introduce the suitable surface functional groups on carbon fiber for different sizing agents that are compatible with the matrix. In previous part of the study explained in second chapter, it was observed that using cationic surfactant (i.e. sodium dodecyl sulfate, SDS) hindered the effective coating around the carbon fibers (CFs)

as it led to the formation of agglomerate on the fiber's surface in addition to the interference of Na^+ ion in the system. As a result, a non-ionic surfactant, i.e. Triton X-100, was used in order to obtain binding of the sizing agent onto CFs through hydrophilic interactions. Yet, this surfactant caused nanostructure formation of the polyetherimide (PEI) and polyetherether ketone (PEEK) in chloroform/water system before addition of CFs to coat them. Therefore, SDS and Triton X-100 were eliminated to obtain an effective binding through the hydrophilic interaction, thus they were replaced with nitric acid (HNO_3) in order to activate the CFs via the formation active chemical groups such as $-\text{O}-\text{C}-$, $-\text{C}=\text{O}$, $-\text{O}-\text{C}=\text{O}$ on the surface of the carbon fiber. Consequently, the activation of CF's surface chemically leads to the increase in the total surface energy and polarity that facilitates the enhancement of the wettability of the CFs with the thermoplastic matrix. It is not preferred to use sulfuric acid (H_2SO_4) in order to activate the CF's surface as the aliphatic amine and alkane functional groups of the carbon fiber reinforced polymer (CFRP) could be activated by sulfuric acid including chain scission reactions that cause interfacial descension between the carbon fiber and resin [109].

Surface activation of CF was separately studied using two different acids: HNO_3 and Meldrum's acid. Afterwards, the activated CF products were compared in terms of surface polarity of CFs and their physicochemical properties to choose the optimum activation method.

In the first case, the CFs were activated by dipping them in HNO_3 at 90°C for 1.5 h. Then, the modified CFs (HNO_3 -act-CF) were washed with water and oven-dried at 80°C for 3 h.

Alternatively, high yield of carboxyl functionalization is achievable if second surface activation of CF is performed using Meldrum's acid solution [110]. Hence, Meldrum's acid solution was prepared by dissolving 1.5 g Meldrum's acid in 100 mL ethanol under stirring at 30 °C. Then, CFs were dipped into the obtained acid solution for 2 h. The functionalized CFs (Meldrum-act-CF) were oven-dried after washing with water for 10 times to remove any excess acid on CF.

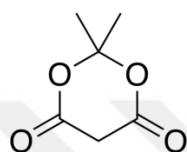


Figure 13. Chemical structure of Meldrum's acid.

Meldrum's acid is deprotonated acid with pK_a 4.83-4.93 in H_2O [111]. The reason why Meldrum's acid was functional in this process lies within its resonance structure that stabilizes this acid. Additionally, it is indicated by Ehlert *et al.* that Meldrum's acid reactions are known to have significantly high yield, i.e. over 80% [110]. As a result, high density and complete coverage of functional groups is expected. The high reaction yield, non-oxidative nature, and ability to generate the versatile carboxylic acid group make this functionalization treatment ideal for carbon fibers [112,113].

3.2. Media and Sizing Agents

Solution processing is a widely used technique for the preparation of polymer nanocomposites to achieve good dispersion. However, it has been rarely applied to PEEK or HPEEK since PEEK is well known for its chemical resistance and is only soluble in limited kinds of solvents at elevated temperatures [114]. Recently, the

phase behavior of PEEK in dichloroacetic acid (DCA) solvent was studied and it was found that PEEK can remain dissolved in DCA even at room temperature for a long period of time at low concentrations [115]. This provides a route for preparing good-quality PEEK blended composites via a solution approach. In this phase of our study, we used a solution processing to prepare our sizing agents by using DCA as a sizing medium. PEI, PEEK, HPEEK and PEI-PEEK solution blend were prepared as sizing agents in DCA medium. Unlike emulsions in chloroform medium, clear sizing solutions were obtained in DCA so that agglomeration problem could be solved by obtaining homogenous coating.

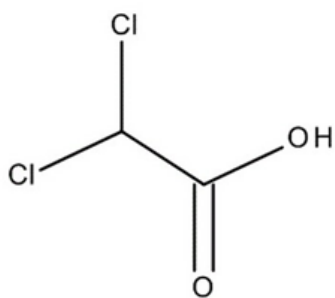


Figure 14. Chemical structure of dichloroacetic acid, DCA.

3.2.1. Synthesis of the Hydroxylated PEEK (HPEEK)

HPEEK was synthesized and then characterized via spectroscopic techniques by analyzing chemical bonds to prove that whether we obtained HPEEK as a product. Later, the final product was used as a sizing agent for CF. As a brief synthesis procedure of HPEEK, in the first stage PEEK powder was vacuum dried at 120 °C for 4 h. Dried PEEK powder (6 g) was added gradually into the stirred solution of NaBH₄ (1.8 g) in 150 mL DMSO. The suspension was stirred at 120 °C for 20 h. After cooling to room temperature, the reaction mixture was filtered and the

creamish solid was washed with ethanol, HCl, and deionized water, respectively. The product was finally oven-dried at 80 °C to give 5.8 g HPEEK as cream-colored powder.

3.2.2. Sizing Treatment onto the Activated CFs

Regarding the solvent-based sizing agent, four different sizing agents were prepared by separately dissolving of PEI, PEEK, hydroxylated PEEK (HPEEK) and the solution blend of PEI- PEEK in DCA solvent. Herein, each polymer at 2 wt% in DCA was stirred at 185°C until the polymer was fully dissolved. The last sizing agent (PEI-PEEK solution blend) was also prepared by dissolving of 1 wt% of each polymer in DCA solvent at 185 °C. Then, the activated CFs were homogenously coated with the sizing polymers using a dip-coating method for 2 h at room temperature (RT). In this method, a substrate material (i.e. CF) is submerged in the solution of coating material (i.e. sizing polymers in DCA) to generate a thin and uniform layer of the sizing onto the flat substrate [116]. The coated CFs were cured in a vacuum oven at 60 °C.

3.3. Results and Discussion

3.3.1. Effects of Thermal De-sizing

The thermoset based composites have been heavily studied so far in a wide range of industrial applications [17,18,21,22,25,26]. Therefore, present aerospace-grade commercial CFs are mainly epoxy coated in order to make the reinforcement material compatible with the thermoset matrix in addition to making the processing of fibers easy by preventing them from any physical damages due to the brittle

context of the material. However, in order to produce cost effective structural parts for aircrafts the thermoplastic based composites have been studied in our work due to their significant advantages in terms of reshaping and remolding. Hence, the process for the manufacturing of composite materials can be reversible which leads to saving time and energy by minimizing the scrap formation. Since in this work we need to make the CFs coherent with our thermoplastic matrix, i.e. PEEK, so first of all, the current epoxy coating on the CFs should be removed. Herein, thermal de-sizing was used at a pre-determined degradation temperature to decompose the epoxy coating on the CFs without any physical and or chemical damage of CF itself. The neat CFs were obtained after heating at 400 °C for 10 min. Figure 17 compares the Raman spectra of the CFs before and after the thermal de-sizing process to remove the epoxy coating. Since the amount of epoxy surrounding CFs is so small ($\sim 0.3\%$), no significant alteration was observed in Raman spectrum of the neat CF, rather than the change in the intensity of the finger-print signals of CF. Herein, the increase in the intensity of characteristic signals of C-C in the frequency region of 1300-1600 cm^{-1} indicates that the current epoxy coated was eliminated while the CF preserved its integrity after thermal de-sizing process [117].

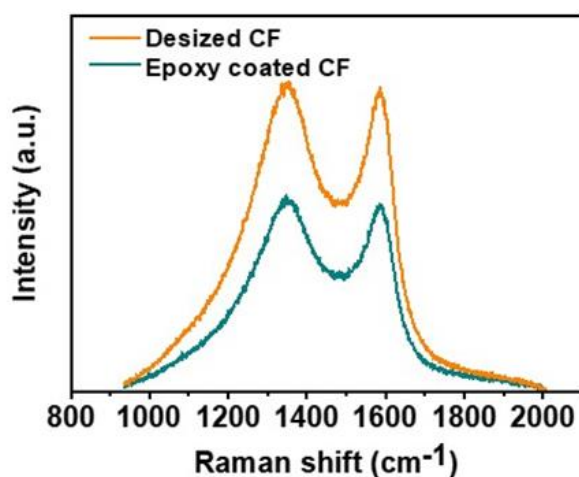


Figure 15. Raman spectra of epoxy-coated CFs before and after the thermal desizing process.

3.3.2. Surface activation of CFs

The inert surface of neat CF was activated through the acid treatment in order to prevent the phase separation occurring between sizing agent and CF's surface. This acidic modification forms the functional groups on CF's surface such as carboxyl and hydroxyl groups. By this way, the CF's surface will not be inert anymore so that the sizing material could be attached easily and surround the fibers effectively through the H-bonding. For this, the neat CFs were separately treated by HNO_3 and Meldrum's acid solution and the resultant activated CFs were characterized by Raman, XPS, ESEM, 3D laser scanning microscope and contact angel analysis techniques.

Figure 18 exhibits the Raman spectra of the neat and activated CFs. Therein, in Raman spectrum the shoulder between $3000\text{--}3500\text{ cm}^{-1}$ is assigned to the bond stretching vibration of O-H [118], confirming that CF was successfully

functionalized via acidic modification. However, the hydroxyl signal of the Meldrum-act-CFs was more intense than HNO₃-act-CFs.

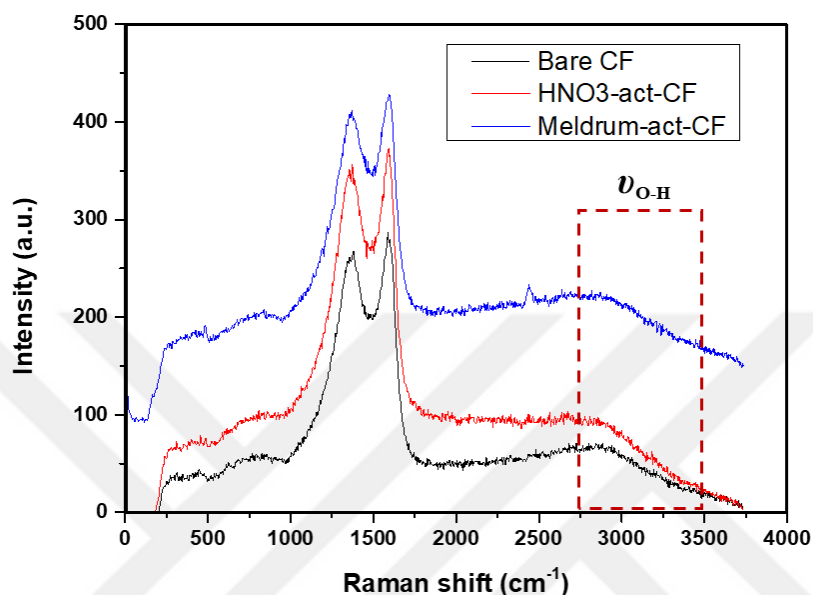


Figure 16. Raman spectra of neat and activated CFs by HNO₃ and Meldrum's acid.

The changes in the chemical composition of the CFs caused by the acid treatment and the bonding involved were studied in detail via XPS. Figure 19 a-d illustrates the high resolution XPS surveys together with the C1s and O1s spectra of neat CFs, HNO₃-act-CFs and Meldrum-act-CFs. From the XPS survey spectra of the neat and activated CF samples (Figure 19a), the obtained atomic percentages showed that the oxygen content was increased after the acid treatment of the CF, where the O/C was found to be 0.25 for neat CFs, 0.25 for HNO₃-act-CFs, and 0.27 for Meldrum-act-CFs. Furthermore, the XPS C1s and O1s spectra of the CF samples (Figure 19 b-d) showed a significant increase in the oxygen content of Meldrum-act-CFs as it is observed by the high intense C-OH and COOH peaks (Figure 19d). Therefore, surface modification of the CFs through the Meldrum's acid was more effective

than HNO₃ and led to the formation of more surface hydroxyl and carboxyl functional groups. The C1s spectrum of Meldrum-act-CFs (Figure 19d) was fitted into six peaks assigned to C-C (284.65 eV), C-O (286.26 eV), C=O (287.39 eV), O-C=O (289.02 eV) bonds and π - π^* (291.14 eV), respectively. The O1s core level peak of this sample (Figure 19d) was resolved into two component centered at 532.50 and 533.50 eV corresponding to the C=O/COOH and C-OH bonds, respectively.



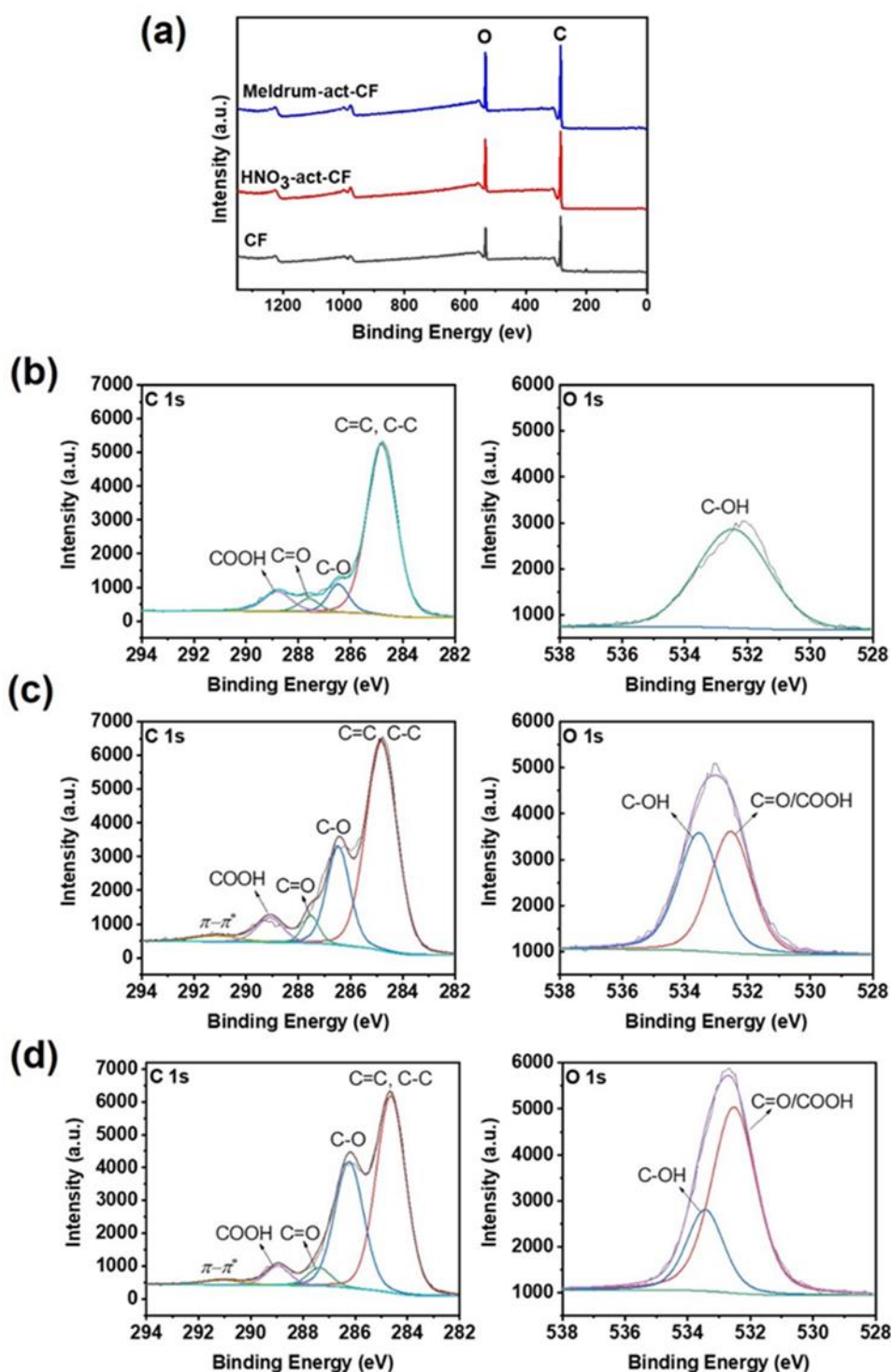


Figure 17. (a) XPS survey of neat and activated CF samples, XPS spectra of C 1s and O 1s regions for (b) neat CFs, (c) activated CFs by HNO₃, and (d) activated CFs by Meldrum's acid.

The surface morphology and topology of the neat and activated CF samples were investigated using ESEM and 3D laser scanning microscope, respectively. Figures 20 a-j show the top-view and angular SEM images of the neat and activated CF samples along with their surface topography images. As it was observed, the neat CF's surface seems smooth whereas the acid activation caused abrasion on the fiber's surface. Consequently, SEM images show the increment in surface roughness throughout the application of HNO_3 and Meldrum's acid to neat CFs. In order to determine the surface roughness parameters (R_z , R_a , and R_q), 3D topography images were obtained via Keyence VKX 100 Microscope where R_z indicates the average of 5 highest peaks and 5 deepest valleys, R_a is the arithmetic average roughness value, and R_q represents the root mean square roughness [119]. Herein, the surface roughness values of the samples calculated by the laser scanning microscope (Table 1) revealed that the HNO_3 activation has led to the etching of CF surface as the surface roughness value increased noticeably from $1.60\text{ }\mu\text{m}$ for neat CF to $2.10\text{ }\mu\text{m}$ for HNO_3 -act-CF.

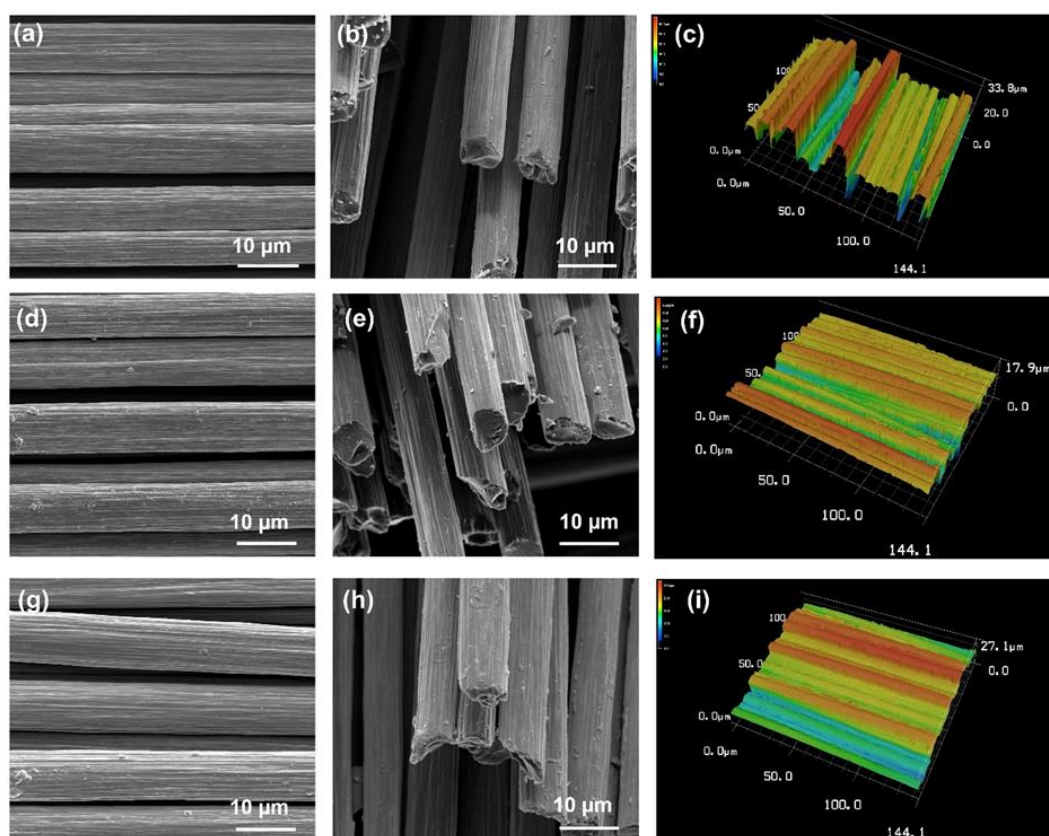


Figure 18. Top-view and angular morphology images of neat CF (a, b, c), activated CF by HNO_3 (d, e, f), activated CF by Meldrum's acid (g, h, i) captured by ESEM and 3D laser scanning microscope, respectively.

Table 1. The calculated surface roughness values for the neat and activated CFs via Keyence VKX 100 Microscope.

Sample Name	Rz (μm)	Ra (μm)	Rq (μm)
Neat CF	1.60	0.22	0.27
Activated CF by HNO_3	2.10	0.28	0.34
Activated CF by Meldrum's acid	1.54	0.22	0.28

The CFs wettability properties before and after the surface activation were investigated by the contact angle analysis (Figure 21) and the results showed that the Meldrum's acid activation of the CFs facilitates the wettability and enhanced the polarity of the inert surface of neat CF. Therefore, based on all the above results, the surface activation of CF by Meldrum's acid was chosen as the optimum activation method.

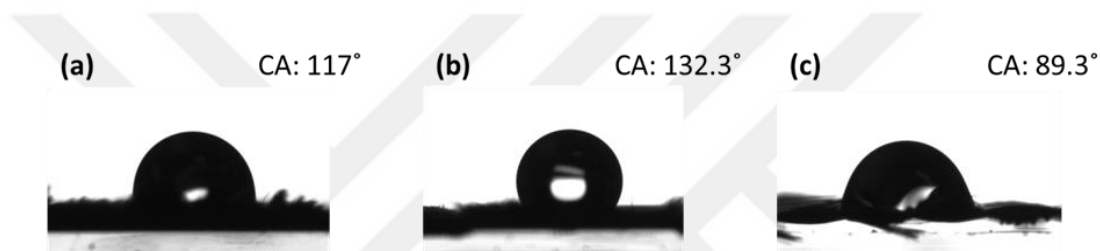
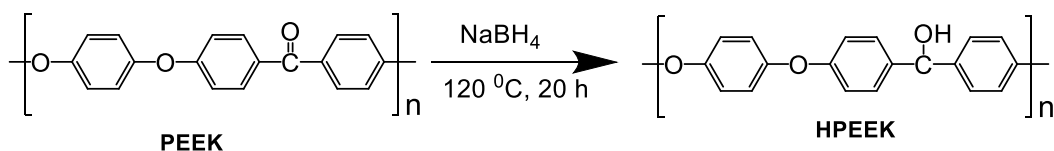


Figure 19. Contact angle analysis of (a) neat CF, (b) activated CF by HNO_3 , and (c) activated CF by Meldrum's acid.

3.3.3. Synthesis and Characterization of HPEEK

In this work, HPEEK as one of the sizing agents of CFs was synthesized by partial carbonyl reduction of the PEEK as it is shown in Scheme 1. Then, the product was fully characterized by FT-IR, XPS and XRD techniques.



Scheme 2. Synthesis of HPEEK.

FT-IR was used to study the changes in the chemical structure of the PEEK induced by the functionalization procedure. Figure 22 compares the FT-IR spectra of PEEK and HPEEK. The appearance of the hydroxyl stretching signal around 3400 cm^{-1} and the decrease in the intensity of PEEK carbonyl signal at 1650 cm^{-1} , in the FT-IR spectrum of HPEEK compared to PEEK confirmed the success of carbonyl reduction of PEEK to introduce hydroxyl groups on the PEEK polymer chains.

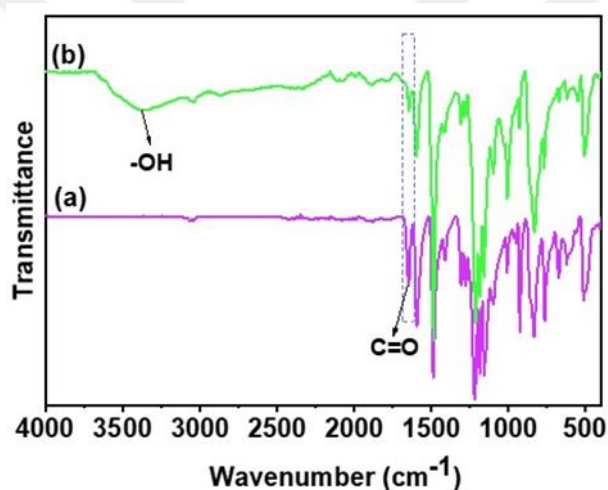


Figure 20. FT-IR spectra of (a) PEEK and (b) HPEEK.

The carbonyl reduction of PEEK to HPEEK was further studied by XPS. Figure 23 compares the high resolution C1s and O1s spectra of PEEK and HPEEK. The C1s XPS spectrum of PEEK (Figure 23a) was deconvoluted into five peaks which are assigned to C=C (284.65 eV), C-C (285.32 eV), C-O (286.24 eV), C=O (287.05 eV) bonds and $\pi-\pi^*$ (291.64 eV). Two distinct peaks at 531.50 and 533.50 eV in the O1s spectrum of PEEK represent the C=O and C-O-C components, respectively (Figure 23b). The C1s and O1s XPS spectra of the HPEEK (Figures 23c and d) showed the same peaks of PEEK along with an additional signal at 532.85 eV in

the O 1s attributed to the hydroxyl groups (-OH). Therein, the appearance of the -OH peak and the decrease in the intensity of C=O peak in the O1s XPS spectrum of HPEEK compared to PEEK clearly confirmed the successful reduction of the carbonyl groups of PEEK [120].

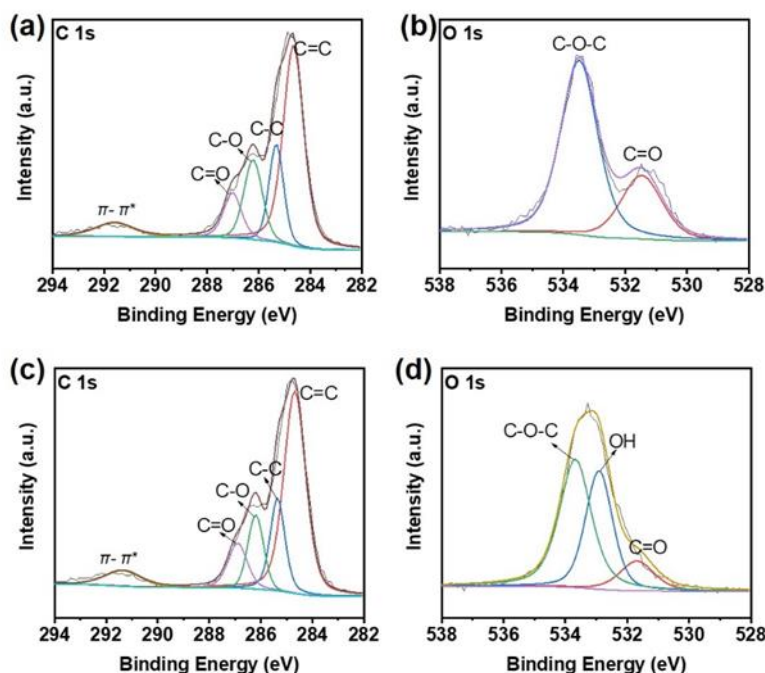


Figure 21. High resolution XPS data of C1s and O1s for (a, b) PEEK and (c, d) HPEEK.

XRD analysis was used to study the changes made on the crystalline structure of PEEK after its carbonyl reduction. The corresponding XRD patterns are shown in Figure 24. The XRD of PEEK exhibited four main peak at 18.8° , 20.7° , 22.8° and 28.9° which can be indexed as the (110), (111), (200) and (211) reflections of the orthorhombic unit cell [121]. The HPEEK showed the similar XRD pattern to that of PEEK, however, the peaks were wider with lower intensity, showing less structural order due to the random distribution of the hydroxyl groups as well as significant reduction in the level of crystallinity of PEEK. Herein, no shift in the

position of the crystalline reflections was observed, which indicates that the hydroxyl groups are not included in the crystal unit cell of the modified PEEK [120].

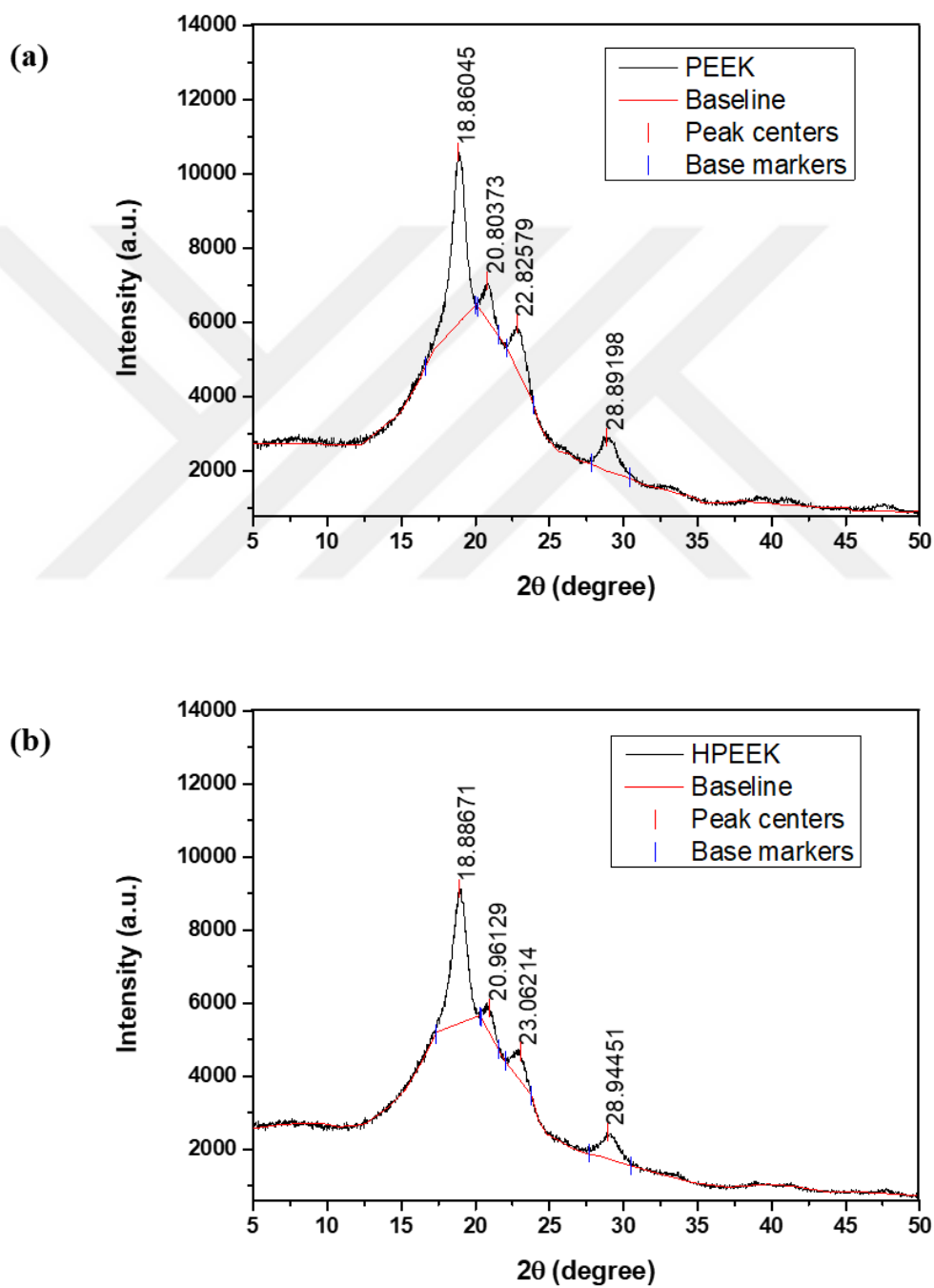


Figure 22. X-ray diffraction patterns of PEEK and HPEEK.

As the study conducted by Tian et al. indicates the crystallinity of PEEK can vary between 0 and 48 % depending on processing conditions [122]. Herein, obtained X-ray diffractograms of PEEK and HPEEK were analyzed and their degree of crystallinity were determined. The crystalline fraction was determined by integrating areas under the crystalline (A_c) and amorphous (A_a) diffraction patterns. The calculation was performed according to the following equation [123];

$$x_c = \frac{A_c}{A_c + A_a} \quad (\text{Eq. 1})$$

The degree of crystallinity for PEEK was obtained as 12 % whereas it was 8 % for HPEEK. This decrease in the crystallinity with an HPEEK sizing agent facilitates the load transfer ability through the reinforcing phase which was supported by mechanical test results presented in Section 3.5.

The nucleation occurs in the formation of a crystal from a solution in which molecules become ordered in a conformation characteristic of a crystalline solid. The high crystallinity % imposes the raise of nucleation occurrence. This nucleation effect on CF weaken the mechanical strength of load carrier reinforcing phase. Hence, it was observed that crystallinity degree of PEEK was decreased after its hydroxylation. As a result, the nucleation effect of CF was also decreased while the load transfer ability of the reinforcement material in TP composite was enhanced. As decrease in crystallinity % of semicrystalline PEEK within composites resulted from the reduced nucleation effect of CF by sizing with HPEEK. Furthermore, the hydrogen bonding between HPEEK and CF in addition to the good compatibility with matrix itself (PEEK) enhanced the interfacial interactions [9].

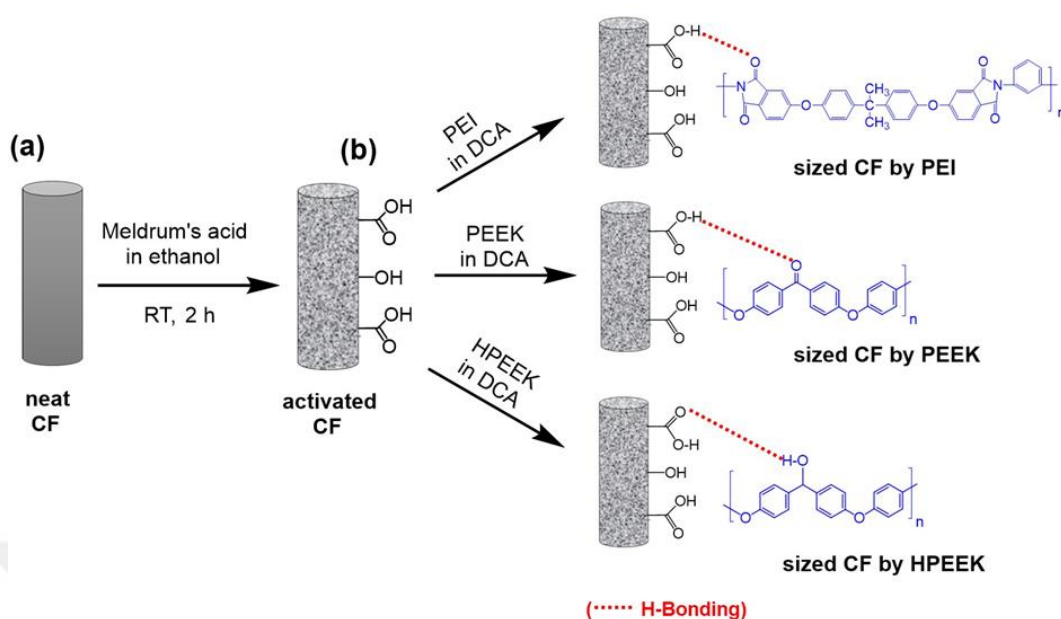
3.3.4. Sizing treatment of the activated CFs

Regarding the solvent-based sizing agent, four different sizing agents were prepared by separately dissolving PEI, PEEK, HPEEK and the solution blend of PEI-PEEK in a DCA solvent. Herein, after many trials to determine the optimized concentration it was observed that each polymer at 2 wt% can completely dissolve in DCA. Subsequently, the solution was stirred at 185 °C until the polymer was fully dissolved. The last sizing agent (PEI-PEEK solution blend) was also prepared by dissolving 1 wt% of each polymer in the DCA solvent at 185 °C. Afterwards, activated CFs were homogenously coated with sizing polymers using a dip coating technique for 2 h at room temperature (RT). In this method, a substrate material (i.e. CF) is submerged in a solution of the coating material (i.e. sizing polymers in DCA) to form a thin and continuous layer of sizing onto the flat substrate [116]. At last, coated CFs were cured in a vacuum oven at 60 °C.



Figure 23. The solvent-based sizing agents prepared by 2wt% polymer dissolved in DCA medium: PEI, PEI-PEEK blend, PEEK, and HPEEK solutions (from left to right).

Since the chemical compatibility is essential to provide enough adhesion between the reinforcement material and the thermoplastic matrix, four different solvent-based sizing agents were first prepared from PEEK, PEI, PEEK-PEI blend and HPEEK in DCA as described before in Section 3.4. The main reason for using PEI, PEEK and their blends as sizing agents is because the chemical compatibility between these polymers and PEEK matrix is excellent due to the similarity in their chemical structures. Furthermore, these high-performance engineering thermoplastic polymers are characterized by a combination of distinctive mechanical, thermal, and chemical properties which make them dominant in aerospace applications. Scheme 2 represents the Meldrum's acid activation of CF and its sizing with the PEI, PEEK, and HPEEK. Figure 25 shows the photographs of the polymer solutions in DCA. The dip coating method was used to homogenously coating of the Meldrum-act-CFs by each of the papered sizing polymers and finally, all the sized CF samples were investigated by ESEM, 3D laser scanning microscope and contact angel analysis methods in order to select the best sizing polymer.



Scheme 3. The representation of (a) surface activation of CF using Meldrum's acid and (b) sizing of Meldrum-act-CF by the studied polymers.

The effect of sizing process on the surface properties of the activated CFs was examined by ESEM and 3D laser scanning microscope. Figures 26 a-l exhibit the top view and angular ESEM images of the sized CFs samples together with their surface topography images. From Figure 26, the surface roughness has been increased after sizing of the activated CFs. The obtained surface roughness values (Table 2) indicate that the most significant effect was observed through the sizing of activated CF by HPEEK. When all three surface roughness parameters (R_z , R_a , R_q) are analyzed for neat and HPEEK-sized CFs, the change is in a range of 0.1 – 0.2 μm . Unlike, when neat CF is compared with other three sized CF samples the alterations in arithmetic average and root square surface roughness are smaller than 0.1 μm .

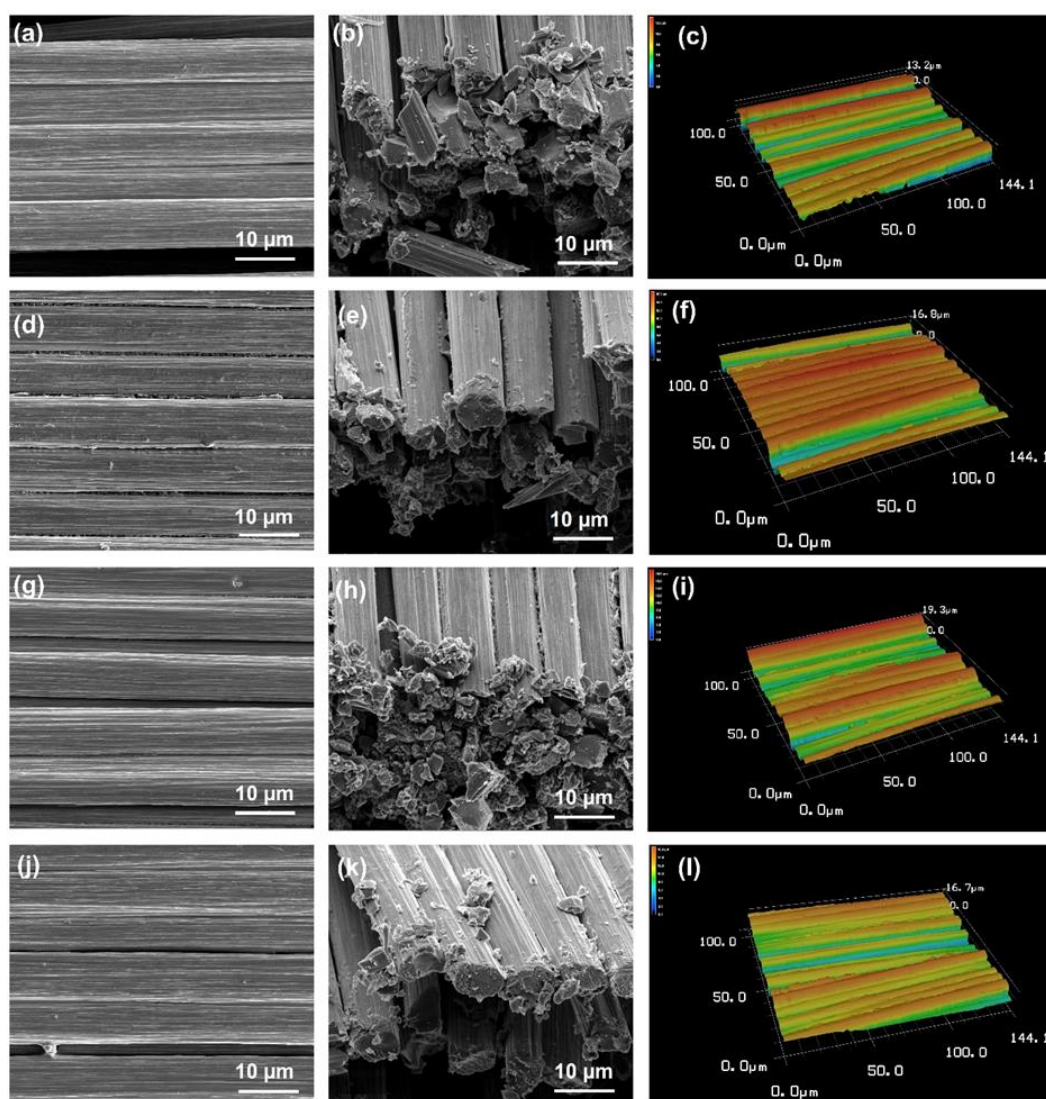


Figure 24. Top-view and angular morphology images of the sized CFs by PEI (a, b, c); PEI-PEEK blend (d, e, f); PEEK (g, h, i); and HPEEK (j, k, l) captured by ESEM and Keyence VKX 100 microscope, respectively.

Table 2. The calculated surface roughness values for neat and sized CFs via Keyence VKX 100 Microscope.

Sample Name	Rz (μm)	Ra (μm)	Rq (μm)
Sized CF by PEI	1.35	0.21	0.26
Sized CF by PEI-PEEK blend	1.15	0.15	0.19
Sized CF by PEEK	1.34	0.19	0.24
Sized CF by HPEEK	1.83	0.29	0.34

As 3D laser scanning microscopy results indicate the surface roughness of CFs sized by HPEEK is larger than in comparison to neat CFs (Rz: 1.60 μm , Ra: 0.22 μm , Rq: 0.27 μm , see Table 1). As a result, this increase in the surface roughness led to an optimized interfacial interaction between reinforcing material and matrix. The entanglement molecular weight (M_e) of PEI determined from melt rheology measurements is 3500 while M_e of PEEK is 2100 [124]. Thus, M_e of PEI-PEEK blend would be in between 2100 and 3500.

The obtained above results were correlated with the wettability experiment of the sized CF surface via the contact angle analysis (Figure 27). The surface free energy (γ_s) of all the sized CF samples were also calculated according to Young's equation (Eqs. 2-6) and the obtained values were listed in Table 3.

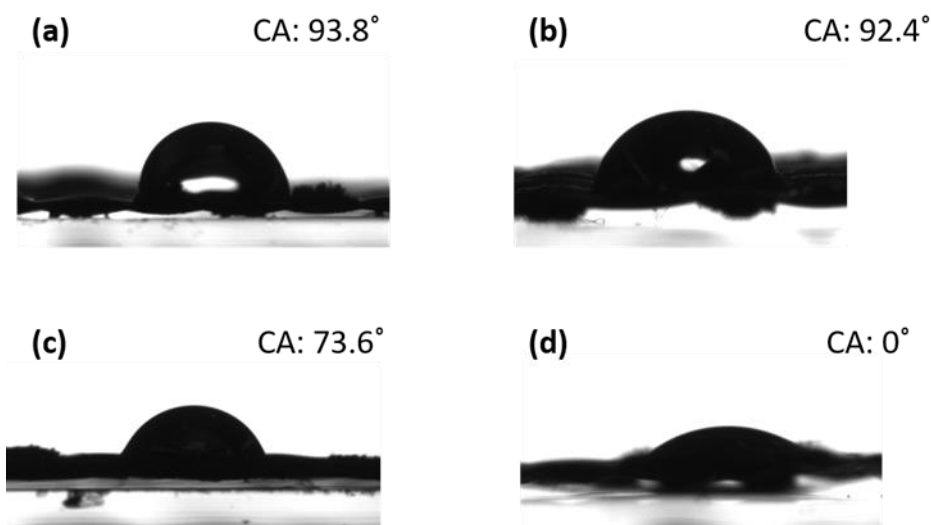


Figure 25. Contact angle analysis of sized CF by different thermoplastic polymers after the surface activation of neat CF by Meldrum's acid: (a) PEI, (b) PEI-PEEK blend, (c) PEEK, and (d) HPEEK.

It was proved that the application of thermoplastic sizing agents increased the surface free energy of CF. Hence surface polarity was enhanced, subsequently adhesion by TP matrix was improved significantly. From Figure 27, the calculated contact angle decreased from 117° for the neat CFs to $\sim 92^\circ$ for the sized CFs by PEI and PEEK-PEI blend as well as 73.6° and 0° for the sized CFs by PEEK and HPEEK, respectively. Herein, the polymeric sizing of the activated CF samples led to the better wettability of the CF by increasing its surface free energy (see Table 3) and among the studied samples, the CF-HPPEK showed the maximum wettability and SFE. Herein, the treatment of the Meldrum's acid-activated CF with HPEEK sizing agent results in the superhydrophilic sample with increased surface polarity. Consequently, the compatibility between treated CF and PEEK matrix was achieved when the surface free energies of sized CFs are compared with SFE of PEEK, i.e. $\gamma_{\text{PEEK}} = 40.1 \text{ mJ/m}^2$ [106]. In our study it was proved that sizing of CF

by HPEEK polymeric sizing agent substantially increased the CF's surface free energy from 5.43 mJ/m² to 72.8 mJ/m². This result leads to the optimized adhesion between fiber and matrix in CFRTP composites that improves the mechanical strength by eliminating delamination problem.

According to Young's equation [105];

$$\gamma_{sl} = \gamma_s - \gamma_l \cos \theta \quad (\text{Eq. 2})$$

$$\gamma_{sl} = \gamma_s + \gamma_l - 2(\gamma_s \gamma_l)^{1/2} \quad (\text{Eq. 3})$$

where γ_s indicates surface free energy (SFE) of solid, γ_l is surface tension of liquid (72.8 mJ/m² for water), γ_{sl} is interfacial free energy between solid and liquid, and θ represents solid/liquid contact angle.

$$\gamma_s - \gamma_l \cos \theta = \gamma_s + \gamma_l - 2(\gamma_s \gamma_l)^{1/2} \quad (\text{Eq. 4})$$

$$2(\gamma_s \gamma_l)^{1/2} = \gamma_l + \gamma_l \cos \theta \quad (\text{Eq. 5})$$

$$\gamma_s = \gamma_l (1 + \cos \theta)^2 / 4 \quad (\text{Eq. 6})$$

Table 3. The results of SFE calculation according to Young's equation.

Sample Name	γ_s (mJ/m ²)
Neat CF	5.43
Sized CF by PEI	15.87
Sized CF by PEI-PEEK blend	16.71
Sized CF by PEEK	29.93
Sized CF by HPEEK	72.8

The application of Meldrum's acid before sizing in order to activate CF's inert surface was already increased surface polarity while the treatment of activated CF with HPEEK sizing agent made hydrophobic CF superhydrophilic. Since the resultant surface free energy of HPEEK-sized CF (72.8 mJ/m^2) is much higher than SFE of PEEK matrix itself (40.1 mJ/m^2) the complete wettability was achieved for CFRTP. As a result of this enhanced adhesion between matrix and reinforcing material, the void content due to the inertness of fiber and matrix in CF reinforced PEEK composite was eliminated.

3.3.5. Consolidation of Reinforcement Material and Matrix

The CF reinforced PEEK composite laminate was obtained by placing 8 plies of activated and then coated carbon fabrics and 9 plies of PEEK films alternately. The dimensions of fabrics and films were 11 cm x 11 cm. The consolidation of reinforcing material and matrix was processed by hydraulic hot press at 395°C under a pressure of 2.5 MPa for 25 min. Subsequently, the consolidated laminate was cooled down to 100°C with 20°C/min temperature ramp by keeping the pressure constant. The volume fraction of CF was 40% in the resultant composite laminate [125,126]. A schematic representation of the entire process for the surface activation and sizing of the CFs as well preparation of their composites with PEEK is shown in Figure 28.

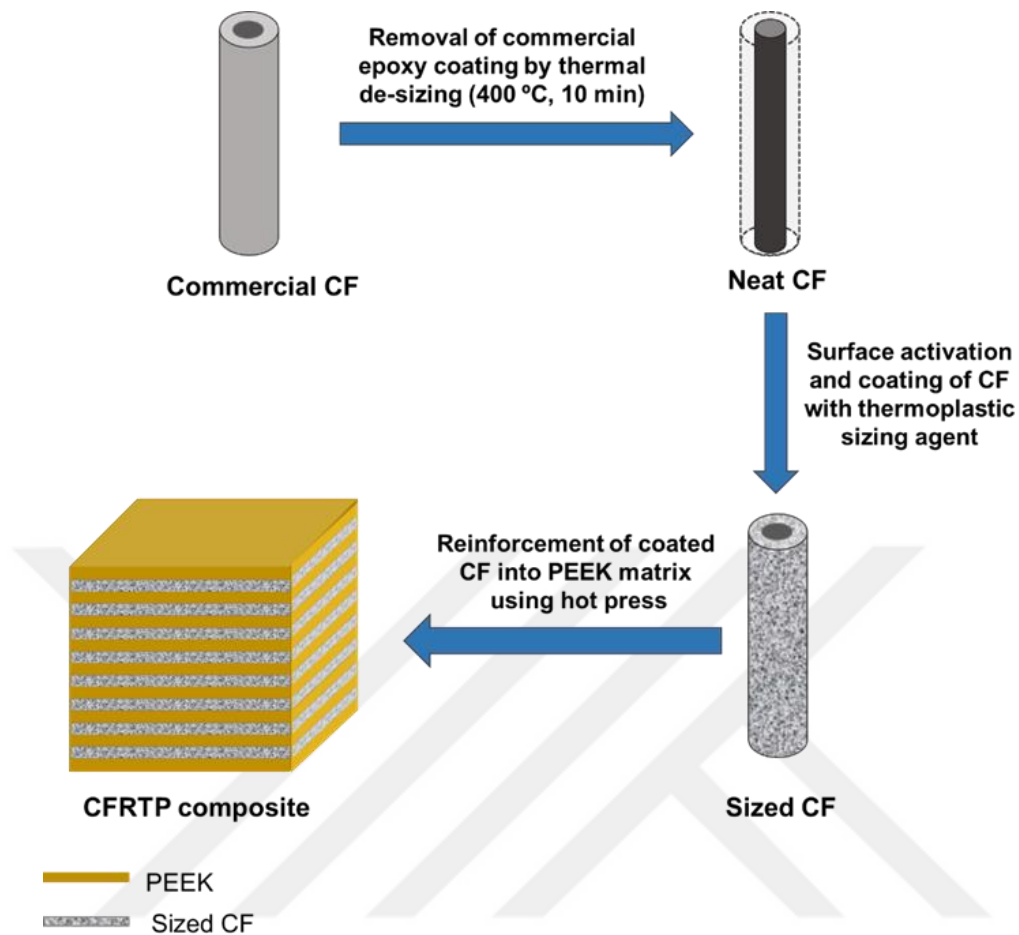


Figure 26. Graphical diagram explaining all treatments applied onto CF to obtain modified CF reinforced PEEK composite.

After composite laminate was processed in Langzauner hot press, the dog-bone shape specimens (in standard of DIN 53504-S3A & ISO 37-3) were obtained via computer numerical control cutting tools.



Figure 27. The hydraulic press used in consolidation of CF and PEEK to obtain reinforced composite laminate (source: DirectIndustry & Langzauner).

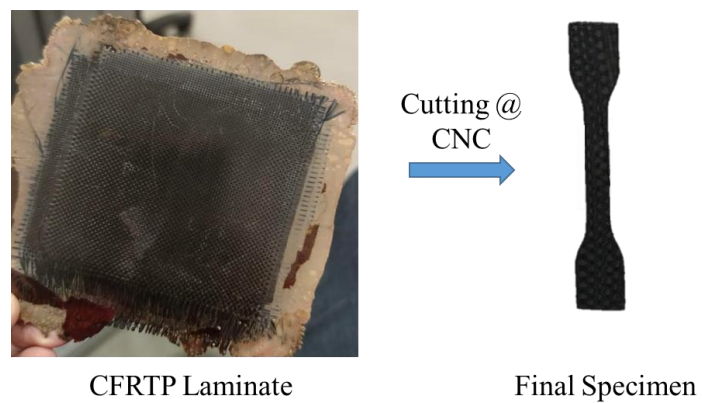


Figure 28. The CF reinforced TP composite laminate and the obtained dog-bone shaped specimen for mechanical tests.

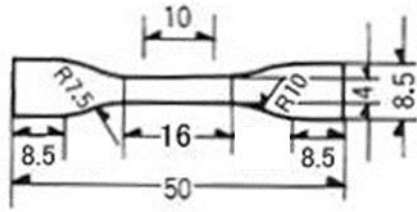


Figure 29. Drawing of the final 50 mm-specimen in DIN 53504-S3A & ISO 37-3 standards.

3.3.6. Mechanical Test Results

Since the outstanding adhesion between PEEK and CF was achieved for sizing with HPEEK the repetitive mechanical tests were applied to the composites made up of neat CFs and HPEEK-sized CFs that are reinforced into PEEK matrix separately. The test samples were prepared by placing 8 plies of neat/treated carbon fabrics and 9 plies of PEEK films alternately with dimension of 11 cm x 11 cm. The obtained laminates were consolidated by hot press at 395 °C and under a pressure of 2500 kN/m² for 25 min. Later, the samples were cooled to 100 °C with a cooling rate of 10 °C/min by keeping the pressure constant. The volume fraction of CF was 40% in resultant composite laminates. Consequently, the dumbbell-shape specimens were obtained from laminates according to the tensile test standards, i.e. ISO 37-3 DIN 53504-S3A. Lastly, tensile tests were applied to two sets of composites by using neat CFs and HPEEK-sized CFs with PEEK matrix.

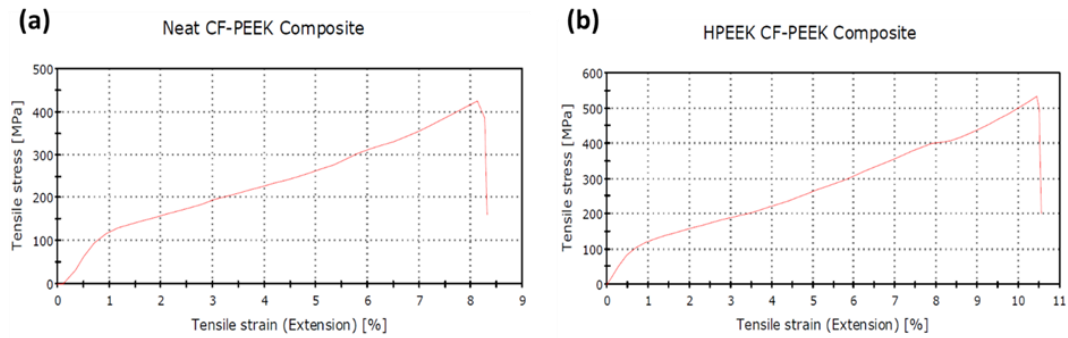


Figure 30. Typical stress-strain curve of composites made up of neat CF (a) and HPEEK-sized CF (b) with PEEK matrix.

Table 4. The calculated Modulus and Tensile stress at Tensile strength for the specimens consisting of neat and treated CFs.

Sample Name	Modulus (E-modulus) [GPa]	Tensile strength [MPa]	Tensile toughness [kJm ⁻³]
Neat CF - PEEK	15 ± 5	473 ± 47	27x10 ³
HPEEK sized CF - PEEK	17 ± 3	508 ± 50	29x10 ³

When the effect of carbon fiber reinforcement was analyzed it was observed that the tensile strength of PEEK was enhanced from 170 MPa to 473 MPa, even more after sizing. It was noted that sizing of CF with HPEEK substantially increased both wettability of the reinforcing material and mechanical strength of the thermoplastic composite with the significant improvement in tensile elongation. The tensile stress at tensile strength and modulus of resultant TP composites were increased at a rate of ~10% by sizing of activated CF with HPEEK. Moreover, tensile toughness for neat CF-PEEK composite was calculated as 27x10³ kJm⁻³ while toughness for

HPEEK sized CF-PEEK composite was obtained as $29 \times 10^3 \text{ kJm}^{-3}$. Thus, sizing of CF with synthesized HPEEK enhanced the mechanical properties of final reinforced TP composite. According to the theoretical model and analysis the greater surface roughness sustains more tensile loads than those with a smooth interface in thermoplastic composites [127]. Here, it was proved that significant increase in surface roughness of CF as a result of sizing with HPEEK led to the outstanding improvement in tensile strength and toughness. Furthermore, the enhanced adhesion between sizing agent and matrix promoted mechanical strength of CF reinforced thermoplastic composite. The obtained ratio in the improvement of mechanical properties of the final TP composite is crucial for aerospace applications.

3.3.6.1. Morphology Analysis after Fracture

The wettability was analyzed for neat-CF based composite and HPEEK-sized-CF composite specimens via ESEM. The effect of coating on interfacial adhesion between fiber and matrix was investigated after tensile tests.

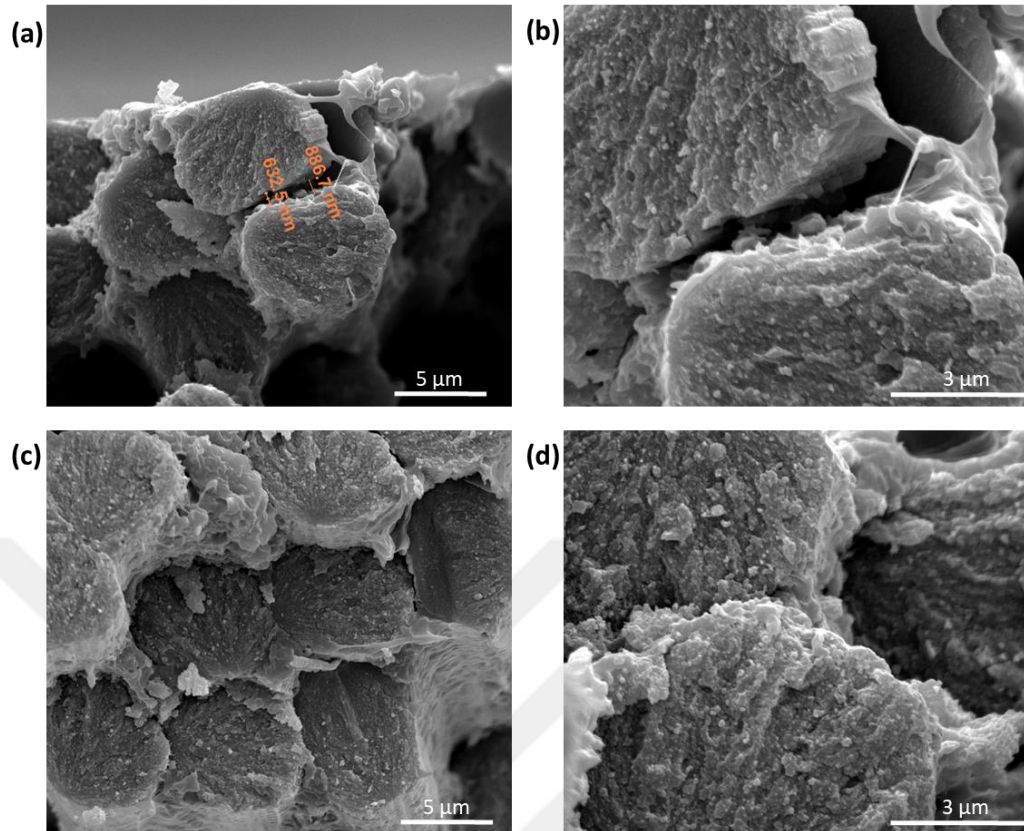


Figure 31. ESEM images of neat-CF based composite (a, b) and HPEEK-sized-CF based composite (c, d) after fracture.

As Figure 33 shows that there are nanometer-scale voids between fiber and matrix in the composite consisting of bare CF. Thus, without coating on CF the void content in final composite is significant than coated one which weakens the mechanical strength of CFRTP (see mechanical test results in previous section). The ESEM results indicate that interfacial adhesion between fiber and matrix is poor for neat CF while HPEEK-sized-CF based composite exhibits optimized adhesion. The HPEEK coating on CF facilitates the binding of CF to the chemically compatible PEEK matrix with the help of H-bonding. Therefore, the mechanical strength of HPEEK-sized-CF based composite substantially greater than the

composite made up of neat CF. As a result, the relation between adhesion and mechanical properties was proved qualitatively and quantitatively.

3.3.7. Thermal Analysis

After obtaining final composites made up of bare CF and HPEEK-sized CF separately, their thermal behaviors were investigated. Moreover, synthesized HPEEK was compared with PEEK in terms of the weight loss (%) corresponding to the degradation temperature via TGA.

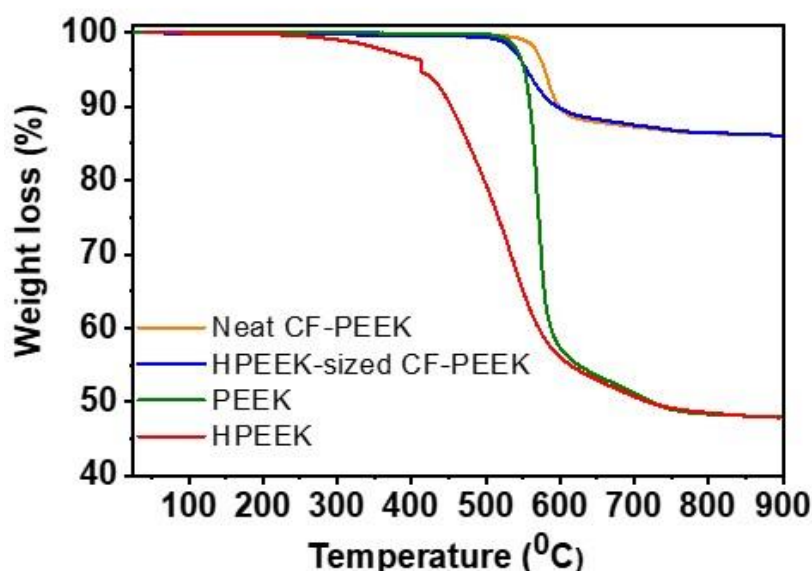


Figure 32. TGA curves of HPEEK, PEEK, and the composites of neat and HPEEK-sized CF.

Thermal stability of the samples was characterized by Thermal Gravimetric Analysis (TGA). The TGA curves were recorded in the temperature range of 25-900 °C with a ramping rate of 10 °C/min under N₂ environment. PEEK exhibits a one-step degradation procedure starting at approximately 510 °C with a total weight loss of 51.96 % from main chain degradation at 900 °C. HPEEK, on the other hand,

showed two degradation stages. Low decomposition stage from 250 °C to 412 °C due to the disappearance of hydroxyl groups (weight loss 3.72 %). The main degradation stage starting at 412 °C (weight loss 48.40 %) is due to the degradation of the main chain of the polymer. The total weight loss of the HPEEK sample at 900 °C is 52.12 %. As TGA curves indicate that when HPEEK and pristine PEEK were heated gradually they exhibit substantially greater total weight loss (~50%) rather than their composite forms (~10%) which were produced by the reinforcement of carbon fibers. Thus, reinforcing enhanced the thermal properties of matrix polymer. Moreover, it was observed that thermal degradation of HPEEK is in the range of PEEK which is a good result in addition to the crucial advantages of HPEEK. As HPEEK has smaller degree of crystallinity than PEEK it exhibits lower activation energy. As a result, HPEEK has less thermal stability than PEEK. Yet, the difference is in the bearable range. Since HPEEK has low degree of crystallinity it reduces nucleation effect that improves the load transfer ability of the reinforcement material. On the other hand, HPEEK-sized-CF made composite exhibits superior adhesion between reinforcing material and matrix phase through H-bonding that results in higher mechanical strength. Therefore, HPEEK is significantly advantageous as a coating material when two composites with and without sized CFs were compared thermally, mechanically, and physico-chemically.

3.4. Conclusion

As a result of this study it was proved that the reinforcement material (i.e. carbon fiber) was made chemically compatible with thermoplastic PEEK matrix by

functionalization and sizing process. Thus, the remarkable increase in the surface free energy of CF after sizing leads to the optimized adhesion between CF and PEEK in CFRTP composite material. It was shown that delamination problem which is due to poor adhesion between inert CF and TP matrix can be overcome by the enhancement of wettability property of CF. As a result of our micro analyses it was observed that altering of CF's surface roughness and chemistry led to the change in polarity. To clarify, the application of HPEEK sizing agent altered surface morphology of CF, subsequently an enormous enhancement in the surface free energy of neat CF from 5.43 mJ/m² to 72.8 mJ/m² was determined. As SFE of neat CF is much smaller than SFE of PEEK (40.1 mJ/m²) without any treatment CF has no wetting feature. Therefore, the poor adhesion between PEEK and neat CF caused debonding that weakens the mechanical strength of CF reinforced PEEK composite. However, in our study commercial nonpolar CF became polar, even superhydrophilic by the application of sizing. To sum up, the significant improvement in interfacial interaction between CF and PEEK matrix was achieved through the increment in the surface free energy of CF. This crucial effect on SFE leads to the strong bonding between CF and PEEK that results in enhanced mechanical strength. For instance, the tensile strength of the corresponding CFRTP improved from 473 MPa to 508 MPa while the tensile toughness rose from 27 x 10³ to 29 x 10³ kJm⁻³. Furthermore, nano-scale voids vanished in relevant CFRTP containing HPEEK sized CFs. In this work, it was shown that delamination problem can be substantially decreased in CFRTP composite materials with the help of induced intermolecular bonding and wettability through surface activation and sizing.

CHAPTER 4

4.1. Summary

The effect of CF's surface properties on interfacial interactions between reinforcement material and thermoplastic matrix was presented in this thesis. It was proved that inert surface of neat CF cannot be wetted by PEEK due to the huge gap between their surface free energies. In this study, the surface free energy of CF was outstandingly increased from 5.43 mJ/m² to 72.8 mJ/m². Hence, the complete wettability of CF by PEEK matrix was achieved throughout surface activation, then sizing processes.

In the first step, the present epoxy coating on commercial CF was eliminated through the thermal de-sizing method because epoxy is not a chemically compatible coating material when CF is reinforced into thermoplastic matrix. Hereby, the neat CFs were obtained to modify according to our purpose.

In the second step, the inert surface of neat CFs were activated by acidic modification in order to avoid any phase separation between CF and sizing agent. Functional chemical groups, i.e. OH, COOH, were generated on CF's surface by using HNO₃ and Meldrum's acid separately. Since Meldrum's acid gave more dominant peaks of functional groups in high resolution C 1s and O 1s XPS spectra compared to HNO₃ the further activation process was completed by Meldrum's acid.

In the third step, four different sizing agents were synthesized through solution blending and hydroxylation. The sizing agents were prepared according to the chemical compatibility to PEEK matrix. Moreover, Dichloroacetic acid was determined as the proper sizing medium as it facilitates the dissolution of sizing agents. The sizing solutions were prepared after adjusting the concentration ratios between sizing medium and the polymer. PEI, PEEK and their solution blend were used as sizing agents as they chemically similar to the TP matrix. Furthermore, HPEEK was synthesized as decrease in crystallinity of semicrystalline PEEK through the hydroxylation within composites results in reduced nucleation effect of CF by sizing with HPEEK. Therefore, HPEEK was an advantageous coating polymer as it improves the load transfer ability of the reinforcement material. Also, H-bonding between HPEEK and CF in addition to the good compatibility with PEEK matrix made HPEEK distinguished among prepared sizing agents.

After sizing process was applied onto activated CFs the consolidation of modified reinforcement material and PEEK matrix was carried out by using automated hydraulic press. As a result, the targeted composite laminate was obtained to analyze in terms of mechanical and thermal properties. After cutting the composite laminate in CNC the standard dog-bone shaped specimens were obtained to use in mechanical tests by Instron. The mechanical test results proved that the composite consisting of HPEEK-sized CFs exhibits greater tensile strength and toughness than the composite consisting of neat CFs. Since the coating material acts as binder between fiber and matrix keeping them together the percent of tensile extension has been increased after sizing. Therefore, the fracture occurred in a longer time for sized-CF-PEEK composite compared to the composite with neat CF.

Thermal analysis showed that the composite consisting of HPEEK-sized-CF exhibits excellent thermal stability even at high temperatures. The thermal degradation for the final composite with sized CFs was noted at around 600 °C that is crucial for aerospace applications.

To sum up, the surface roughness of CF was increased by sizing and consequently surface free energy of neat CF ($\gamma_s = 5.43 \text{ mJ/m}^2$) was outstandingly enhanced leading to the improved mechanical properties without any cutback in thermal resistance of the final reinforced composite. The resultant SFE for HPEEK-sized CF was noted 72.8 mJ/m^2 which is much higher than SFE of PEEK matrix (40.1 mJ/m^2). As a result, the complete wettability was achieved for CFRTP. The effect of optimized adhesion on mechanical properties of carbon fiber reinforced PEEK composite was showed. It was proved that the sizing of carbon fibers led to strong binding between fiber and matrix through H-bonding. Therefore, the sizing agent keeps fiber-matrix system together that latens the fracture of the composite specimen, i.e. tensile toughness of the CFRTP was significantly enhanced by HPEEK sizing agent which also gives the best wettability result.

4.2. Future Perspective

We obtained the aeronautical mechanical standards of structural parts from Turkish Aerospace Industries Inc. (TUSAŞ). These standards must be met by our novel CFRTP composite for safe integration. In addition to the industrial standards, we have selected the currently used epoxy based composites as the reference competitor. Then, the mechanical characteristics of our CFRTP are validated

against both the aeronautical standards and currently adapted epoxy based composites.

Table 5. The mechanical requirements for currently used aircrafts via the mechanical properties of developed CFRTP in our work.

Sample Name	Modulus (E-modulus) [GPa]	Tensile strength [MPa]
Reference Prepreg	7.7	43
HPEEK sized CF - PEEK	17 ± 3	508 ± 50

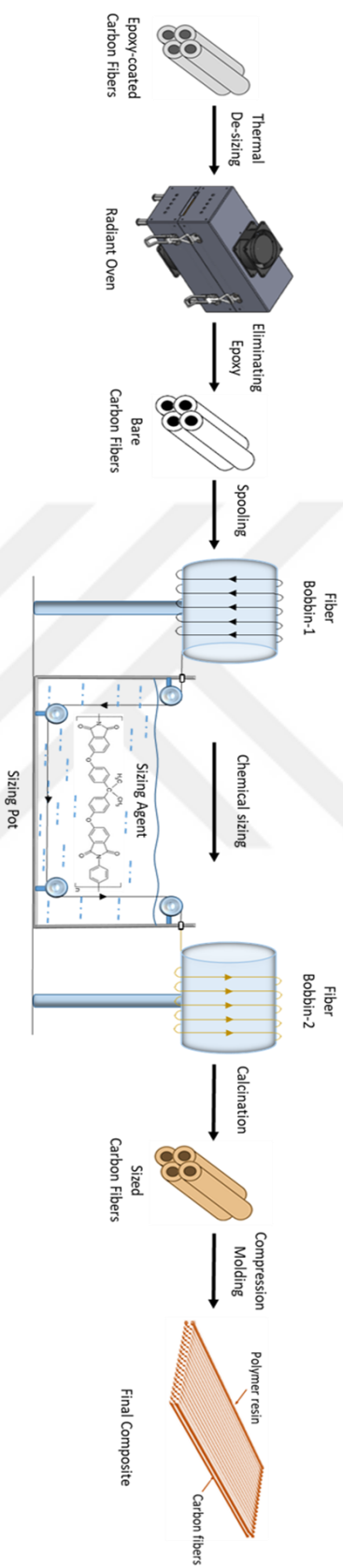
*prepreg: composite made from pre-impregnated fibers and resin.

The success of this project based on fiber-matrix interfacial interactions was proved by the outstanding enhancement in mechanical strength of the final composite. As it was presented in Table 5 the increase in modulus and tensile strength is greater than 100% for the sized CF-PEEK specimen than the epoxy based prepreg. Therefore, sizing is crucial for the fiber reinforced composite materials as current debonding problem in commercial epoxy based equivalents disrupts the mechanical strength of the composite. In this project, debonding between carbon fiber and PEEK matrix was overcome through the chemical compatibility and subsequently by the enhanced surface roughness and adhesion. Furthermore, the potential phase separation was eliminated by the formation of H-bonding between sizing polymer and activated surface of carbon fiber.

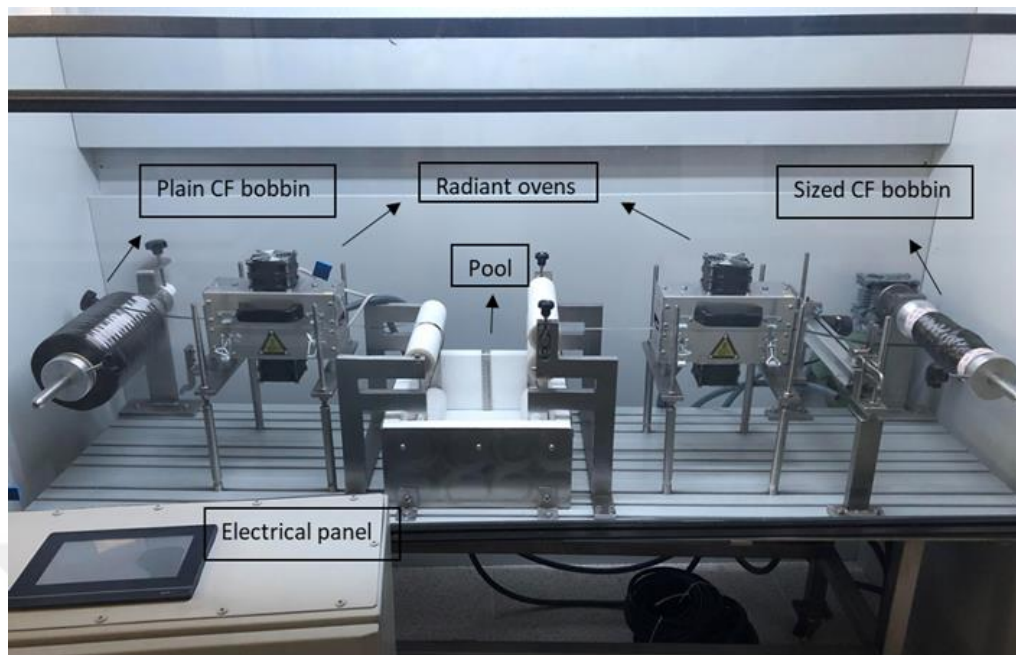
As a result of the enhanced mechanical strength the future study is going to be on processing the geometry of resultant CFRTP laminate. Then, the structural parts of aircrafts are going to be manufactured by using the developed technique. The de-

sizing and sizing processes for carbon fibers will be automatized in one-line manufacturing frame as depicted in following scheme. The spool machine was designed and established for the whole manufacturing processes (see Scheme 4).





Scheme 4. One-line depiction of de-sizing and sizing processes applied to carbon fibers in composites.



Scheme 5. Spool machine to fabricate sized carbon fibers in order to use in prepregs and carbon fabrics.

In this spool machine, the strain of fibers during release and collection can be adjusted via electrical panel. Furthermore, different sizing agents can be studied as the pool for sizing material can be drained away via drain valve under the pool and then refilled with the desired sizing material. The carbon fabrics could be treated and weaved in desired combinations, such as unidirectional, twill or harness satin, after collecting the fibers on a bobbin via this instrument which was designed by our research group. This system overcomes the dependence on foreign suppliers for prepegs. This significantly reduces the cost and time of aircraft structural part manufacturing. As this field has a significant market share nowadays, obtained know-how to build this technology is also value added. Therefore, the results of this project plays a crucial role to integrate the modified carbon fibers into thermoplastic matrix for the ongoing aerospace applications based on reinforced TP composites.

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