ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL

ENHANCEMENT OF INTERFACIAL PROPERTIES FOR HIGH PERFORMANCE POLYETHYLENE FIBERS PRODUCED VIA GEL SPINNING

M.Sc. THESIS

Oğuz Kağan ÜNLÜ

Department of Polymer Science and Technology

Polymer Science and Technology Programme

JUNE 2023

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ISTANBUL TEKNİK ÜNİVERSİTESİ ★ LİSANSÜSTÜ EĞİTİM ENSTİTÜSÜ

JEL ÇEKME YÖNTEMİ İLE ÜRETİLEN YÜKSEK PERFORMANSLI POLİETİLEN LİFLERİN ARAYÜZ ÖZELLİKLERİNİN GELİŞTİRİLMESİ

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HAZİRAN 2023

Oğuz Kağan ÜNLÜ, a M.Sc. student of ITU Graduate School student ID 515211011, successfully defended the thesis/dissertation entitled "ENHANCEMENT OF INTERFACIAL PROPERTIES FOR HIGH PERFORMANCE POLYETHYLENE FIBERS PRODUCED VIA GEL SPINNING", which he prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

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To my family,

FOREWORD

First of all, I would like to thank my thesis advisor, Assoc. Prof. Dr. Ali KILIÇ, who I am honored to work with, for his guidance, endless support and shared valuable knowledge with me during my study. I am grateful to Aybeniz SEYHAN and TEMAG Lab team for their support and helps specially during my studies.

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June 2023

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ABBREVIATIONS

ASTM : American Society for Testing and Materials
ATR : Attenuated Total Reflection
DGEBA : Bisphenol A Diglycidyl Ether
DR : Drawing Ratio
DSC : Differential Scanning Calorimeter
FTIR : Fourier-Transform Infrared
GA : Gluteraldehyde
HDPE : High-Density Polyethylene
HPPE : High-Performance Polyethylene
IFSS : Interfacial Shear Strength
IPDA : Isophorone Diamine
IUPAC : International Union for Pure and Applied Chemistry
kV : One Thousand Volts
L/D : Length / Diameter
LDPE : Low Density Polyethylene
LLDPE : Linear Low-Density Polyethylene
LOY : Low Oriented Yarns
MWCNTs : Multi-Walled Carbon Nanotubes
PAN : Polyacrylonitrile
PE : Polyethylene
PEW-g-MAH: Polyethylene Wax Grafted Maleic Anhydride
PDA : Poly Dopamine
PPy : Polypyrrole
RED : Relative Energy Difference
rGO : Reduced Graphene Oxide
SEM : Scanning Electron Microscope
TA : Tannic Acid
UHMWPE : Ultra High Molecular Weight Polyethylene
UV : Ultraviolet
XPS : X-Ray Photoelectron Spectroscopy

SYMBOLS

^{o}C	**:** Celcius
%	**:** Percentage
δ_p	**:** Permanent dipole-permanent dipole forces
δ_h	**:** Hydrogen bonding forces
δ_d	**:** Dispersion forces
R_a	**:** Distance between two point in hansen space
R_o	**:** Interaction radius of polymers
µ	**:** Micrometer

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ENHANCEMENT OF INTERFACIAL PROPERTIES FOR HIGH PERFORMANCE POLYETHYLENE FIBER PRODUCED VIA GEL SPINNING

SUMMARY

Fibers are materials with high length/diameter ratios, having adjustable fineness, mechanical properties. High performance fibers exhibit excellent mechanical properties such as high modulus, high strength, high abrasion resistance, thermal resistance, low density. One of the methods used to produce high performance fibers is gel spinning, in which the chains are partially entangled in liquid-gel form and connection with each other , rather than solution or melt unlike other methods (dry spinning, wet spinning, melt spinning). In this thesis, ultra high molecular weight polyethylene (UHMWPE) was dissolved in paraffin oil and high performance UHMWPE fibers were obtained by gel spinning method. The gel obtained by dissolving UHMWPE in paraffin oil is formed into filaments by passing through the spinnerettes after extrusion, then passes through the quenching and extraction bath, drying and winding in the final stage. High tensile strength, low specific density, great impact resistance, and exceptional chemical resistance are just a few of the excellent qualities of ultra-high molecular weight polyethylene (UHMWPE) fiber. It is frequently utilized in fishing, aircraft, biomedicine, and ballistic, among other things. UHMWPE fiber has a very high degree of crystallinity (>99%) and macromolecular orientation (>95%), which leads to a high modulus and tenacity of UHMWPE fiber. Gel spinning is a difficult and advanced engineering process. UHMWPE concentration is one of the parameters that determine fiber strength which was kept as 8% wt in this study. For this research, n-hexane was used in the extraction bath to remove paraffin oil from spun UHMWPE fibers. Following the solvent extraction procedure, the fibers undergoing hot drawing with different drawn ratios. The differential scanning calorimeter is used to analyze the thermal and crystallization properties of the fibers in their drawn, undrawn, and gel-state forms. Two newly peaks are observed when DR reached to 40. These peaks shows orthorombic-hexagonal transition. An orthorhombic structure represents a prism-like crystal structure with three unequal edges and internal angles, whereas a hexagonal structure resembles a hexagon with six equal edges. The tensile test was used to reveal the effect of drawn ratios on performance and it was revealed that with the increase in drawn ratio, the mechanical strength would increase by a maximum of 322.71%. Simultaneously, this thesis also focuses on investigating the enhancement of interface properties in UHMWPE fiber/epoxy composites.There are numerous surface treatment methods used to improve the coaction between fibers and composite materials, chemical etching and corona discharge are two commonly used methods to enhance the fiber- epoxy interaction. In this thesis study, the optimum corona discharge result was revealed by experiments performed at different voltage and time parameters. Then, the obtained results from corona discharge method were compared with the results obtained when the surface was modified via chemical etching, and it was seen that hydroxyl and carboxyl groups were formed on the surface more effectively in the chemical etching method. Glutaraldehyde, which is used as a

cross-linking agent in chemical etching method, can form bonds with OH functional groups due to its chemical structure. Thus, the hydroxyl groups formed on the UHMWPE fibers become able to cross-link with the hydroxyl groups in the epoxy. Tests have shown an increase in both mechanical performance and adhesion properties.

JEL ÇEKME YÖNTEMİ İLE ÜRETİLEN YÜKSEK PERFORMANSLI POLİETİLEN LİFLERİN ARAYÜZ ÖZELLİKLERİNİN GELİŞTİRİLMESİ

ÖZET

Polietilen, düşük maliyeti, yüksek kimyasal direnci, iyi elektrik yalıtım özellikleri, kolay işlenebilirliği ve düşük sıcaklıklarda bile güçlü ve esnek olması gibi özellikleri nedeniyle birçok alanda yaygın olarak kullanılan uzun zincirli alifatik bir hidrokarbondur. Termoplastik polimer piramidine göre, polimerler moleküler ağırlığı arttıkça daha iyi performans sergilerler, buna karşılık işlem seçiminde sınırlayıcı ve belirleyici faktör moleküler ağırlıktır. Yüksek moleküler ağırlığa sahip polietilen lifler, yüksek kopma dayanımı ve young modülüne sahip olacak şekilde işlenebilir. UHMWPE'den üretilen yüksek performanslı polietilen lifler, savunma sanayi, denizcilik, otomotiv, tıp gibi birçok alanda tercih edilmekte ve geleceğin endüstri sahnesinde ihtiyaç duyulmaktadır. Yüksek performanslı polietilen lifler, ham madde UHMWPE'nin (1-6x10^6 g/mol) parafin yağı gibi uygun bir çözücüde ısı altında homojen dağılımı sonrasında, jel çekme yöntemi kullanılarak üretilmektedir . Jel çekme yöntemi, yaş çekme yöntemi ile karıştırılmamalıdır. Jel çekme yönteminde düze paketi koagülasyon veya ekstraksiyon banyosunun içinde değildir. Banyolar ve düze paketi arasında 1-25 mm hava boşluğu bulunmaktadır. Düzeden çıkan polietilen jel önce soğutma banyosu ve daha sonra ektraksiyon banyosundan geçirilir, ardından kurutulup makaraya sarılır. UHMWPE çözelti oranı ve çekme hız/oranı, lif mukavemetini artırmak için bu süreçte en önemli işlem parametrelerindendir. Bu çalışmada, ağırlıkça %8 konsantrasyonda UHMWPE jel lifler, belirli katkılarla süspanse edilerek jel çekme yöntemiyle üretilmiştir. Jel çekme için, önceki çalışmalardan farklı olarak, 1.75 mm çapında monofilament düze ile zıt yönlü çift vidalı ekstruder kullanılmıştır. Çift vida ekstrüzyon hızı, polietilen moleküllerine uygulanan kesme kuvveti üzerinde önemli bir etkiye sahiptir ve çözünme sürecini etkiler. Çift vida hızı çok düşük olduğunda, polietilen moleküllerine uygulanan kesme kuvveti yetersiz kalır ve bu da parafin yağ çözücüsünde yetersiz karışma ve çözünmeyle sonuçlanır. Eğer vida hızı yüksek olursa tam olarak jelleşme gerçekleşemez. UHMWPE'nin çözücüsü olarak parafin yağı seçilirken, parafin yağının liflerden ekstrakte edilmesi için n-hekzan kullanılmıştır. Ekstraksiyon sıvısı olarak kullanılan n-hekzanın sıcaklığı ekstraksiyon süresini etkileyen parametlerden biridir. Bu çalışmada oda koşulları seçilmiştir. Çözücü çıkarımını takiben, lifler farklı oranlarda sıcak çekime tabi tutulmuştur. Bu yöntem, yeni oluşan zincir yapısını stabilize etmeye, öncü grupların kristallenmesini artırmaya, ekstrüde edilen polimer zincirinin geri katlanmasını önlemeye ve lifin termal bozunmasını en aza indirmeye yardımcı olur. Diferansiyel taramalı kalorimetre (DSC) yardımıyla, ekstrakte edilmiş sıcak çekim uygulanmış, sıcak çekim uygulanmamış ve jel halindeki liflerin termal özellikleri incelenmiştir. DSC verileri, jel halindeki liflerden (ekstrakte edilmemiş), ekstrakte edilmiş fakat sıcak çekime tabi tutulmamış liflerden ve ekstrakte edilmiş sıcak çekime tabi tutulmuş liflerden elde edilmiştir. Jel halindeki liflerde büyük miktarda parafin yağı bulunmakta ve parafin yağı kristalleşmediği için jel lifin erime

tepe noktası, çekilmiş ve çekilmemiş liflere göre daha küçüktür. Parafin yağın ekstrakte olmasıyla birlikte polimer zincirleri daha düzenli yapıya geçme eğilimi göstermişlerdir. Çekilmiş liflerden elde edilen DSC verilerinde 2 adet omuz piki görülmektedir. Bunlar ortorombik hekzagonal geçişleri göstermektedir. Ortorombik hekzagonal geçiş, sıcaklık, basınç ve diğer dış etkenler sonucunda atomların pozisyonundaki değişikliklerden kaynaklanır ve malzeme yeni bir kristal yapıya sahip olur. Çekme oranlarının performans üzerindeki etkisi çekme testleriyle araştırılmıştır. Çekme oranı arttıkça, kalınlık en az 40 mikrona kadar düşürülmüş ve çekme dayanımı maksimum 322,71% oranında artmıştır. Sıcak çekim uygulamasında liflerde kısmi degredasyon ve erime bölgeleri gözlenmiştir. Sıcak çekim süresince, rezistans yüzeyinin liflere temas etmesiyle oluştuğu düşünülmektedir ve taramalı elektron mikroskop ile bu düşünce desteklenmektedir. Üretilen liflerin SEM görüntülerinde mikrofibril yapı elde edildiği görülmüştür. Liflerin yanı sıra son zamanlarda UHMWPE liflerden üretilen kompozit yapılar gelişme göstermektedir. Bir çok alanda kullanılan bu kompozitler yüksek mekanik dayanımı ve hafifliği, kimyasal direnci açısından avantajlıdır. Üretilen liflerle hafif ve dayanımı yüksek kompozit uygulamaları çalışılmıştır. Bu tezde, lifler ile epoksi reçine arasındaki etkileşimi artırmak için yaygın olarak kullanılan asit ile yüzey aşındırma ve corona deşarj yöntemleri incelenmiştir. Corona deşarj işlemi yüksek gerilimli iletken varlığında hava gibi akışkan bir gazın iyonlaşmasıyla meydana gelen bir deşarj işlemidir. Corona deşarj işlemi, plastik malzemelerin boya tutma özelliklerini iyileştirmek, medikal alanda kullanılan implantların yüzey uyumluluğunu artırmak, elektronik malzemelerin yapışma özelliğini geliştirmek gibi bir çok endüstriyel alanda kullanılmaktadır. Corona deşarj işlemi sırasında farklı voltajlarda, farklı sürelerde corona deşarja maruz bırakılan liflerin FTIR sonuçları incelenmiş ve arasından en iyi parametrenin 12 kV 10 dakika olduğu gözlenmiştir. Çalışmada uygulanan aşındırıcı karışım nitrik asit, sülfürik asit ve su karışımından oluşmuştur. Tez sonuçlarına göre, asit aşındırma işlemi ve corona deşarj yöntemi, UHMWPE lif/epoksi kompozitlerinin arayüz özelliklerini geliştirmede etkili olduğu bulunmuştur. FTIR sonuçlarına göre özellikle asit aşındırma işlemi, lif yüzeyinde fonksiyonel grupların oluşmasında başarılı olmuştur. Bu yüzden kompozit üretiminde asit aşındırma yöntemi seçilmiştir. Oluşan fonksiyonel gruplar lif ile epoksi reçine arasındaki yapışmayı ve etkileşimi artırmıştır. Asit aşındırmadan kaynaklanan pürüzlü yüzey, lifin yüzey alanını ve yüzey enerjisini arttırmaktadır. Bu, lif ile epoksi reçine matrisi arasında daha iyi ıslanma ve yapışma sağlamaktadır. Daha sonra epoksi ile kimyasal çapraz bağlamak için UHMWPE lif üzerine gluteraldehit graftlanmıştır. Epoksi reçinede epoksi olarak Bisphenol A diglycidyl ether (DGEBA), kürleştirici ajan olarak amin bazlı Isophorone diamine (IPDA) kullanılmıştır. Amin üzerinden ilerleyen çapraz bağlanmada epoksi reçine üzerinde hidroksil grupları boşta kalmaktadır. Gluteraldehit (GA) güçlü bir antibakteriyel etkiye sahip bir aldehit türevidir. GA, polimer zincirleri arasında kimyasal bağlar oluşturarak, kompozitlerin mekanik dayanımını arttırma etkisi göstermektedir. Liflerin yüzeyine graftlanan gluteraldehit ile iki yüzey arasında asetal köprüleri oluşmaktadır. Bunu doğrulamak için gluteraldehit graftlanmış UHMWPE lifin FTIR sonuçları incelenmiştir. C-O bağlarının oluşumu çapraz bağlanmayı kanıtlar niteliktedir. 0.3 gr UHMWPE lif belirli ölçülerdeki kalıba yatırılmış ve epoksi döküm işlemi yapılmıştır. 36 saat boyunca oda sıcaklığında ve vakum altında kürleşen epoksi, çekim testine tabi tutulmuştur. Epoksinin, işlem yapılmamış UHMWPE lifin ve yüzeyi tedavi edilmiş gluteraldehit aşılanmış lifin çekim testine göre ara yüzey uyumlaştırmasının başarılı olduğu görülmüştür. Boş epoksi numunesine göre 99.35% bir artış gözlenmiştir. Çapraz bağlanma, lifler ile epoksi matris arasındaki yük

transferini ve ara yüzey yapışmasını geliştirerek kompozitin mekanik dayanımını ve termal stabilitesini arttırmaktadır. Üretilen kompozitlerin SEM görüntülerinde, yüzeyi tedavi edilmemiş liflerin matris ile yaptığı ara yüzeyde herhangi bir teması yokken, tedavi uygulanmış liflerin kilitlenme yaptığı görülmüştür. Bu sonuç ara yüzey kesme kuvvetinin arttığına işaret etmektedir.

1. INTRODUCTION

1.1 Purpose of Thesis

The first purpose of this thesis is to produce high strength and lightweight UHMWPE fibers. The gel spinning method is first examined in order to understand its principles and applications. These systems utilize polymers with high molecular weight, and they rely on the use of solvents to enhance chain mobility during processing. The solvents used for polyethylene include aromatic hydrocarbons such as decalin, xylene, and toluene. It is important to note that these solvents can be hazardous if they come into contact with the skin, are inhaled, or ingested. For that reason paraffin oil was selected. Gel spinning parameters such as concentration effect, solvent effect, temperature were investigated comprehensively.

Another purpose of this thesis was to enhance the interfacial properties between UHMWPE fibers and commercial epoxy resin. For the composite applications generally silicone adhesives are applied on the interface. In this thesis, two approaches were utilized which are acid treatment and corona discharge. After the treatments, gluteraldehyde grafting method was investigated. Novel agents were proposed during the studies.

1.2 Literature Review

Polymer is a Greek word reproduced from the words poly meaning many and mer meaning repeating unit. After the first synthetic polymer was developed by Leo Hendrik Baekeland in 1907, the International Union for Pure and Applied Chemistry (IUPAC) accepted this year as the beginning of the plastic age [1]. A polymer consists of repeating parts and these parts are linked by covalent bonds. In order for monomers to form polymers, the polymerization reaction must take place and, monomers assemble a chain structure by bonding during the reaction.The physical properties of polymers are mostly determined by their molecular weight therefore, the change in molecular size causes a significant change in the physical property of the polymer;

such that according to this molecular weight, many variational properties can be derived.

A polymer chain can be made up in a variety of architectures and forms. These chain types are called linear chain, branched chain, random chain, radial chain and cross-linked chain. The linear chain structure is the simplest type, the chain consists of a continuous and long array of atoms. Side reactions are prevented by polymerization of bifunctional monomers in the presence of stereospecific catalysts. An example of this is high-density polyethylene (HDPE). It is formed using Ziegler-Natta catalysts. In the branched chain structure, long or short side chains are connected to the main chain, forming a branched structure. A variety of architectures can be acquired according to the shape of the branching. Another structure, the random chain structure, creates the identical repeat unit with many different lengths of chains coming together. In the lack of stereospecific catalysts, high pressure in the range of 1000 to 3000 atm and high temperature in the range of 100 °C to 200 °C and are required for the formation of the random chain structure [1]. Low density polyethylene (LDPE) has such a structure and obtained by forming a random chain structure of long chains formed by hydrogen transfer reactions and short chains formed by backbiting reactions. In the last type of cross-linked chain structure, the cross-links in the chain are linked by covalent forces. The chain structure is classified as low density and high density based on the crosslink density on average per volume. Polymers can be classified regarding to cost and performance as engineering and standart plastics. Figure 1.1 shows, thermoplastic polymer pyramid in terms of cost and performance [2].

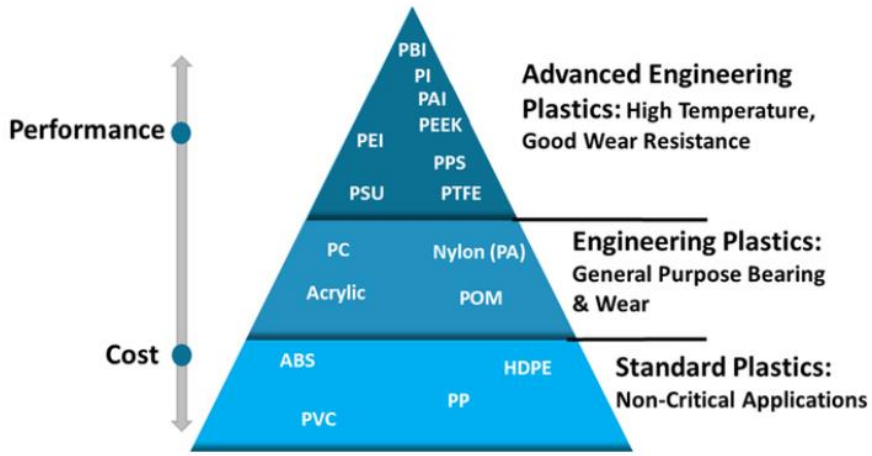

Figure 1.1 : Thermoplastic polymer pyramid in terms of cost and performance [2].

1.2.1 Polyethylene

Polyethylene is a long chain aliphatic hydrocarbon and is widely used in many fields due to its excellent chemical resistance, low cost, great electrical insulation properties, easy processing, and strenght and flexiblity even at low temperatures.

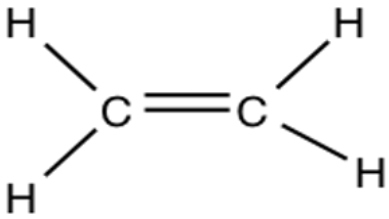

Figure 1.2 : Chemical structure of ethylene [2].

However, low tensile strength, high gas permeability, low softening temperature are the limitations of PE. Its presence in textile industries is unquestionably significant in filament yarn spinning. PE may be utilized as both a reinforcement and a matrix, which is important for composite applications ranging from medical applicaitons to automotive and protection applications such as anti-ballistic personal protective armor. Polyethylene was produced by Fawcett in 1933 from ethylene [2]**.** Figure 1.2 and 1.3 shows the chemical structure of ethylene monomer and polyethylene. After 20 years of being produced by high pressure processes after its discovery, it was produced at lower temperature and pressure with the development of the Ziegler Natta method. Commonly used market-oriented polyethylene types synthesized with various chain structures and molecular weights are low-density polyethylene (LDPE), linear low-density polyethylene (LLDPE), high-density polyethylene (HDPE), ultra-high molecular weight polyethylene (UHMWPE). Polyethylenes obtained by high-pressure processes are considered low-density polyethylene (LDPE), polyethylenes obtained by Zigler Natta method are considered high-density polyethylene (HDPE). Ultra-high molecular weight polyethylene (UHMWPE), on the other hand, offers unique physical and mechanical properties with its impact and abrasion resistance, chemical inertness.

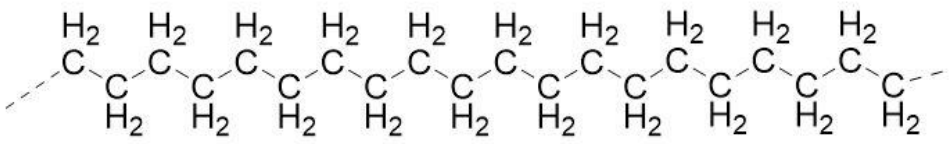

Figure 1.3 : Chemical structure of polyethylene [2].

UHMWPE is synthesized in 3 steps; It is first synthesized from ethylene gas in the presence of a Ziegler-Natta catalyst. It is then recovered as an implant and finally machined. Every change that occurs during these processes affects the polymer.It has three unique phases, about 10% monoclinic crystalline, 30% amorphous phase, and 60% orthorhombic crystalline. When its thermal properties are examined according to its structure, its glass transition temperature is around -160°C and melting is observed in small crystal regions at temperatures between 105-115 ºC. As seen from the DSC analysis, UHMWPE shows the highest point of melting temperature at 137°C [3] **.** Its mechanical properties are directly dependent on its average molecular weight. It exhibits high wear resistance, fatigue resistance, impact resistance and a low friction coefficient is low. Polyethylene has a simple chain structure that enables the formation of various crystal forms, making it suitable for a wide range of applications. The flexible polyethylene chains with a planar zig-zag configuration readily undergo crystallization. [4].

1.2.2 Fibrous material

In general fibers are defined as one dimensional material characterized by flexibility, fineness and high length/thickness ratio, [5]**.** They are formed by the combination of atoms into molecules, they can be organic or inorganic. Fibers are classified in two main categories as man-made fibers and natural fibers (Figure 1.4). Cotton, linen, wool, coir, abaca can be given as examples of natural fibers, regenerated fibers viscose, lyocell, modal, synthetic fibers, polyamide, polyester, polyolefines can be given as examples of man-made fibers. Natural fibers are classified in 3 main categories as animal- based, plant-based and mineral-based. Mineral-based fibers are fibers obtained from inorganic materials found in nature, such as rock, slag. Animal fibers are protein-based natural fibers such as silk, wool and hair. Vegetable fibers are based on cellulosic, fibers such as linen, jute, cotton can be given as examples of this category. Synthetic fibers, on the other hand, are formed by a process called polymerization, many various synthetic fibers can be obtained according to the way of polymerization. The spinneret and spinning conditions used while obtaining synthetic fibers determine the characteristic properties of the fibers. Additional materials such as mattifiers, antistatic agents, antioxidants and pigments are added during the spinning process to add extra properties to fiber. High-strength fibers used in the field of engineering are examined under the class of high-performance fibers [5].

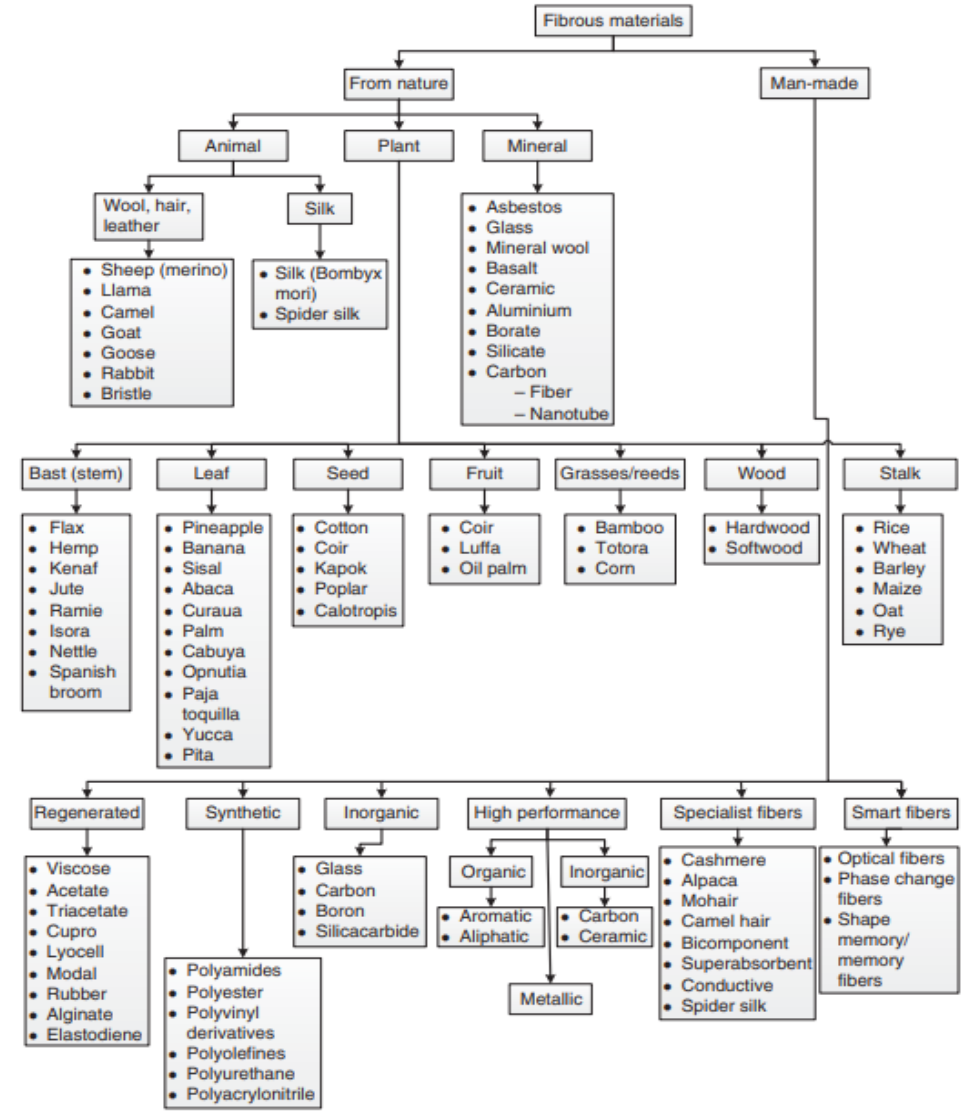

Figure 1.4 : Classification of fibrous materials [6].

1.2.3 High performance fiber

High performance fibers have unique mechanical properties such as high strength, high modulus, low density, high abrasion resistance and thermal resistance. High mechanical strength to weight ratio, and are used in where high performance is required in industrial areas [7]**.** Nylon, polyester, acetate, and other fibers with exceptional technical capabilities were developed throughout the half of the 20th century and and they replaced cotton and rayon as a common reinforcement material in automotive tires. Examples of these are industrial components such as load tendons, ropes, sports equipment, ballistic applications, fiber optics, electronic packaging [8]**.** High performance fibers are classified under four main headings; aromatic fibers, polyolefin fibers, carbon fibers and ingorganic fibers given in Table 1.1. Carbon fiber

is composed of carbon atoms aligned in a crystal-like structure. It has high strength-to-weight ratio, excellent stiffness, and resistance to temperature and corrosion. Carbon fiber composites are widely used in aerospace, automotive, and sporting. Fiberglass is made from fine fibers of glass reinforced with polymer resins. It offers excellent tensile strength, electrical insulation properties, and resistance to heat and chemicals. Fiberglass is commonly used in construction, electrical insulation, automotive components, and marine applications. Kevlar that developed by DuPont is most common fibers of the aramid class, there are hydrogen bonds between the fiber chains, thereby improving its tensile strength. It is also poly (p-phenylene terephthalamide) based [7]. Poly-phenyleneisophthalamide is basis for Nomex® and it was also developed by DuPont. Nomex® differs from Kevlar® in that is meta-aramid while Kevlar ® para-aramid. The change in the structure of the two creates a diversity in their physical properties. For example, in Nomex® fibers, the phenylene ring and the amide group are in an irregular chain structure, so the tensile modulus is lower. On the other hand, Kevlar is very rigid due to the phenylene rings and amide [7].

Table 1.1 : Classification of high performance fibers [5].

Aromatic Fibers	Polyolefin Fibers	Carbon Fibers	Inorganic Fibers
Aromatic Heterocyclic Polymers	UHMWPE	Polyacrylonitrile carbon fiber	Basalt fibers
Aromatic Polyesters		Pitch-based carbon fiber	Boron fibers
Aramids			Carbide fiber
Aromatic Polyimides			

Polyolefin is a polymer consisting of long chains and containing minimum 85% by weight of alkenes. High-performance polyethylene (HPPE) or ultra-high molecular weight polyethylene (UHMWPE) have a excellent mechanical properties such that high modulus and good strength due to it made of polyethlene but HPPE and UHMWPE differs from polyethylene in that they are longer chain and have excellent orientation [9]**.** This difference shown in Figure 1.5.

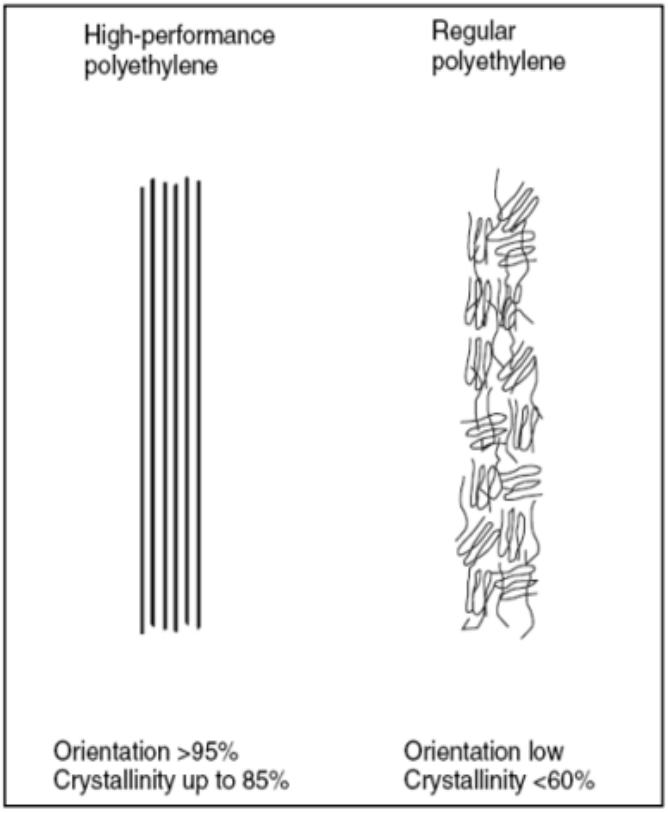

Figure 1.5 : Orientation of HPPE and PE [9].

Among polyolefin fibers, UHMWPE fibers released to the market by DSM High Performance Fibers and by Toyobo/DSM under the name Dyneema® and released to the market by Honeywell under the name Spectra® are frequently used in ballistic protection, ropes and cordage and medical applications [10]**.**

Table 1.2 : Mechanical properties of industrial products produced by DSM [5].

	SK 60	SK 65	SK 75	SK 76
Density (g/cc)	0.97	0.97	0.97	0.97
Tenacity (N/tex)	2.8	3.1	3.5	3.7
Tenacity (g/den)	32	35	40	42
Tensile strength (GPa)	2.7	3.0	3.4	3.6
Specific modulus (N/tex)	91	97	110	120
Specific modulus (g/den)	1025	1100	1250	1250
Modulus (GPa)	89	95	107	116
Elongation (%)	3.5	3.6	3.8	3.8

The composite industry's studies and uses are still limited to ultra high molecular weight polyethylene (UHMWPE) fibers. Mechanical performance of some

performance fiber which produced from DSM and which used in daily life shown in Table 1.2 and 1.3.

Table 1.3 : Mechanical properties of some performance fibers [7].

Fiber	Density g/cm^3	TM GPa	TS GPa	CS GPa
PBO	1.56	280	5.8	0.20
PBT	1.58	325	4.1	0.26-0.41
M5	1.70	330	4.0	1.00
Kevlar 49	1.45	125	3.5	0.35-0.45
Twaron HM	1.45	115	3.2	0.45
P100	2.15	725	2.2	0.48
T 300	1.80	230	3.2	2.70-3.20
Alumina	3.70	350	1.7	6.90
E-glass	2.58	76	3.4	4.20

1.2.3.1 Synthetic fibers spinning methods

In the first step of the synthetic fiber spinning step, the polymer must be converted from a solid state to a liquid state, this step is carried out by methods such as dissolving or melting the polymer. The liquefied polymer is then extruded through a metal nozzle with holes on it and polymer melt or solution drawn from the nozzle into multiple filaments. Single screw and twin screw are two kind of extrusion technique. In single screw extrusion, it creates pressure on the polymer solution or melt and injects the polymer. In twin-screw extrusion, the two screws can rotate together or rotate in the opposite direction, interlock or not, thereby allowing the polymeric materials to mix, coalesce, or react [11]**.** Melt spinning, dry spinning, wet spinning and gel spinning are four main types of synthetic fiber spinning methods [12].

Melt spinning

In the melt spinning method, the polymer is melted at the beginning of the process and then extruded through the spinneret. In the extruder, the polymer is gradually heated several degrees above its melting point. Melting point and flow of melt polymer are effective parameters in this spinning method. The flow behavior of the melt is used to set the pump pressure required to ensure a constant flow of the melt through the spinneret. Simplcitiy of flow is related to viscosity, usually polymers have high molecular weights, but when temperature increase, viscosity decreases, so extrusion

usually takes place at temperatures over the melting point. The basic vertical arrangement of the melt spinning method is given in Figure 1.6. While the polymer coming out of the spinneret is cooled, it is stretched on the one hand, in this way a continuous filament yarn is obtained. During the cooling and drawing processes, it is aimed to align the polymer chains relative to the fiber axis. In this way tensile properties of the filament are upgraded. Spinnerets can have between 500 - 4000 holes and the fiber cross-section and diameter of the filament can be changed according to the cross-sectional shape and hole diameter of the spinnerets [13].

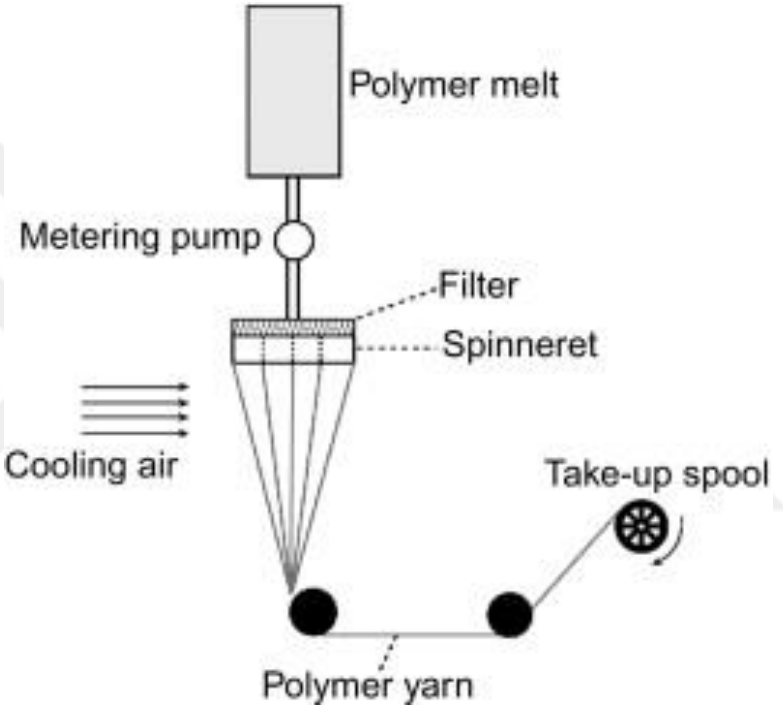

Figure 1.6 : Schematic representation of melt spinning [5].

The properties and construction of the yarn produced are affected by the cooling and drawing phases of the filaments. Depending on the desired properties, different amounts of drawing are applied. At low and medium draw speeds, a second draw step is carried out by heating the filaments to their glass transition temperature. In this way, deformation of the solidified filaments is prevented. The filaments obtained by this method are called fully drawn [13]. The yarns obtained in a different method, where the yarn is first extruded and then hot drawn in a different system, are called low oriented yarns (LOY). The yarns obtained in a different method, where the yarn is first extruded and then hot drawn in a different system, are called low oriented yarns (LOY).

Dry spinning

In the dry spinning method, the polymer is fed in the form of suspension. The process diagram is given in Figure 1.7. In this method, there is no bath as in wet spinning or gel spinning, the polymer is extruded into a heated environment after being dissolved in a volatile solvent. The solvent is evaporated, causing the polymer solution to solidify. In the heated cabinet where the polymer solution is extruded, there is air or an inert gas [11]**.** As the filaments pass through the gas flow area, the solution begins to solidify, polymer concentration rises with the removal of the solvent and continuous filaments are formed.

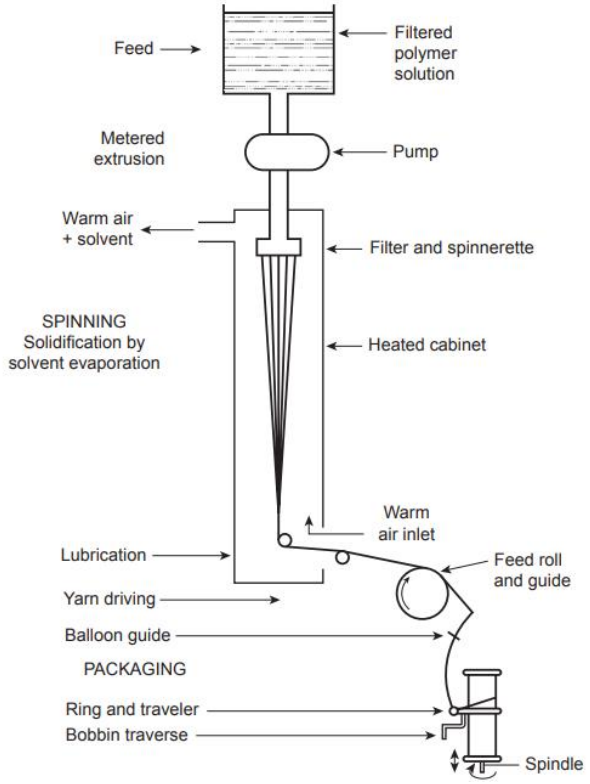

Figure 1.7 : Schematic representation of dry spinning [5].

There is a system used to give twist at the bottom of the cabinet, the filaments coming out of the spinneret are brought together with the twist here to form a continuous filament yarn. In this method, the solvent is recovered in most cases by distillation, gas absorption, condensation methods, thus providing a cost and environmental advantage. Acetate fiber, acrylic fiber, elastane fiber can be obtained by this method.

Wet spinning

In the wet spinning method, the process starts with the dissolution of the polymer in a solvent and this method is suitable for polymers that are not melt spinnable as they

will undergo thermal degradation when melted. The process diagram is given in Figure 1.8. Since the amount of polymer in the solution will affect the viscosity, an appropriate concentration must be selected for the process, and filtering the solution to get rid of contaminants is the first step in the procedure. In this method, the spinneret is immersed in a bath containing a chemical. In this way, the polymer solution solidifies as a result of chemical interaction while leaves the pores of spinneret. As the filaments coming out of the spinneret begin to solidify, they are coiled into the initial godet sets. Then the filaments are conveyed to the second bath in order to align the polymer chains relative to the fiber axis. Then they are dried by passing through the heated drum rolls and they are ready to be wound on the coil.

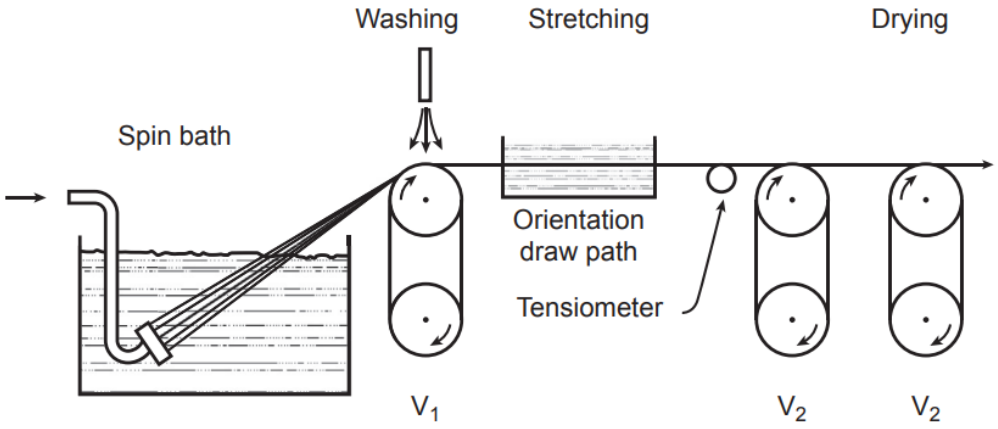

Figure 1.8 : Schematic representation of wet spinning [5].

Polymer concentration, composition and temperature of the polymer and coagulant solution, extrusion rate and residence time in the coagulation bath are parameters controlling the wet spin process. Spinning speed is lower than dry and melt sinning, because the fluid used has a higher viscosity, thus creating tension on the fiber [14]**.** In addition, many different cross-section fibers can be obtained in this method, but due to the bath in the process, it is prone to form circular sections. Fibers such as acrylic, aramid and rayon are spun by this method.

Gel spinning

Very strong fibers with unique properties are created through the process of gel spinning. In the gel spinning method, the solution is in liquid-gel form which is not completely separated, the polymer chains are bound together at various points, thus creating strong interchain forces that improve the tensile strength of the fiber [15]**.** In addition, during extrusion, the shear forces arrange the liquid crystals along the fiber

axis. Figure 1.9 shows, chain orientation in air gap duing gel spinning. The filaments appear with an high degree of orientation in relation to one another, further enhancing strength. Before entering the liquid bath containing chemicals, the fibers exiting the spinneret are exposed to air. Then, the cooling and solidification process continues as it enters the liquid bath. High performance polyethylene and aramid fibers are obtained by gel spinning method. Molecule type, molecular weight, solvent type, solvent concentration, laddering speed, spinning temperature, extraction, strecthing temperature and strecthing magnification are the factors affecting the gel spin process. Although the molecular chain length is influenced by molecular weight, longer chains result in stronger fibers. Because of this, molecular weight significantly affects the fiber strength that may be obtained.

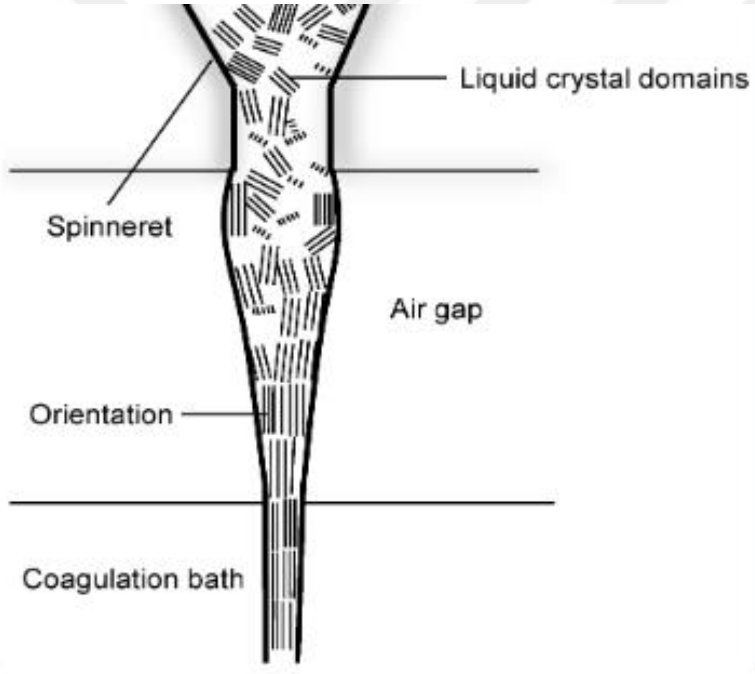

Figure 1.9 : Chain orientation during spinning [16].

Solvent type and solvent concentration are also important parameters. Depending on the solvent type, stability of the fiber influenced by polymer's dissolution rate while the concentration affects the stretching magnification and fiber modulus. Low concentrations provide high fiber modulus and maximum tensile strength [17]. Another parameter, the spinning speed, causes plastic deformation of the fibrils in the fiber when it is too fast, while low spinning speeds negatively affect the fiber extensibility. For this reason, it is very critical to reach the optimum value. Similarly, another parameter that must be kept at an optimum value is the spinning temperature.

A high spinning temperature can cause thermal cracking of the fiber while improving dissolution. On the other hand extraction is significant parameters because by selecting the right extractor, solvent residues can reduce.

The last parameter, stretching, is divided into two, in terms of the effect of stretching temperature and the effect of stretching magnitude. Increasing temperature improves the extensibility of the fiber by increasing the mobility between the molecular chains, this temperature setting is usually kept a small amount below the melting point**.** Growth in orientation slows as stretch amplification increases. At the point where the stretch growth is at its maximum amount, the fiber breaks due to the damage caused by the crystallization. The gel spinning method has been used in the production of ultra-high molecular weight polyethylene (UHMWPE) fiber since the 1980s, schematic diagram is shown in Figure 1.10. Researchers obtained a gel solution of UHMWPE diluted in xylene in a study they conducted in the 1970s [9]**.** According to ASTM definitions, UHMWPE has a molar mass of 3 x 10^6 D, so it cannot be fiberized by conventional methods such as injection molding and melt extrusion**.** Spinning of UHMWPE fiber with gel spinning dates back to 1970s. [8]**.** In elongation flow areas, self-curing of polymer solutions and, how to spin fibers from a concentrated polymer solution was studied in different studies. Based on a study, the spinning process of UHMWPE fiber with gel spinning is given in Figure 1.12 step by step. The process first begins with dissolution.

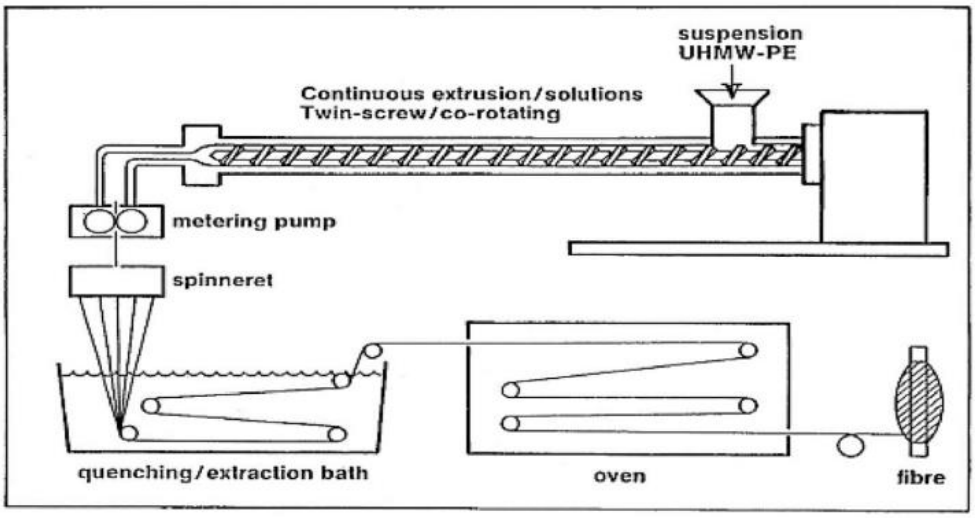

Figure 1.10 : Gel spinning process of UHMWPE fiber [9].

Various solvents such as decalin, dodecane, p-xylene and trichlorobenzene are used to dissolve UHMWPE. In this study, the polymer was dissolved in paraffin oil at 5%wt

concentration at 150°C with gentle stirring for 48 hours. Then the gel at room temperature is fed to the extruder. It is aimed to reduce extrudate distortion by using an extruder with a 6° entry angle and a length of 10 cm. In addition, the fibers were spun at an extrudate speed of around 1m/min in order to avoid too many problems such as melt breakage, elastic turbulence or die swelling. The fibers extracted with n-hexane were drawn at 148°C at 70 draw ratio. As a result of the study, 160 GPa Young's moduli and 4.1 GPa tensile strengths were obtained. Figure 1.11 shows, SEM micrograph of industrial UHMWPE fiber.

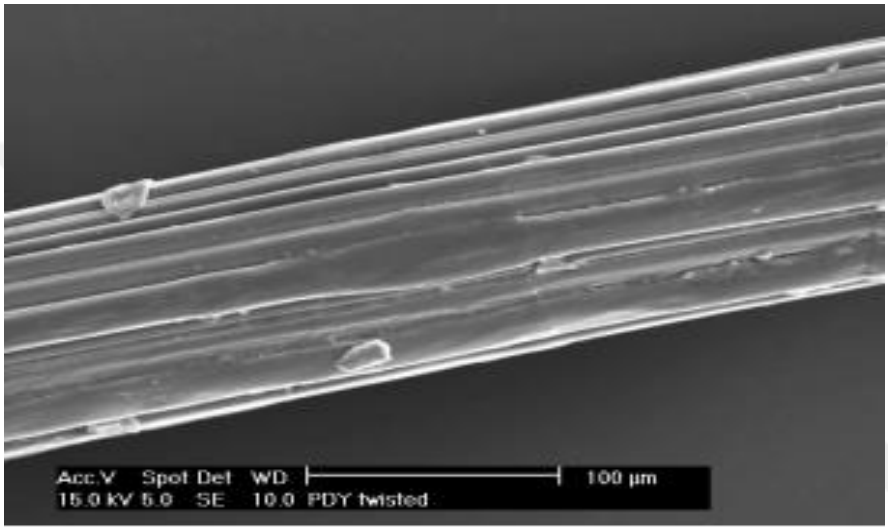

Figure 1.11 : SEM micrograph of UHMWPE fiber [18].

Due to the high molecular weight, morphological structure and chemical resistance of UHMWPE, it was difficult to find suitable solvents. To obtain high strength, orientation in the fiber must be provided along the fiber axis, which can be achieved with the low viscosity. The two most common solvents of UHMWPE are decalin and xylene, but when previous studies are examined, it is difficult to dissolve at concentrations due to the definite increase in viscosity. Decalin is known as colorless and odorless and is a suitable solvent for polyolefins. One of the reasons why it is widely used for UHMWPE is its high volatility. On the other hand, high volatility is limiting at high spinning speeds, making it difficult to impart high strength to the fiber. Another common solvent used is paraffin oil. Thanks to its low volatility and flammability properties, it provides an advantage at the point of combining with PE. On the other hand, since its structure is non-volatile, it requires an extra volatile chemical supplement such as hexane. In the gel drawing method, the UHMWPE and solvent suspension are mixed homogeneously under heat and pressure [7,9,10].

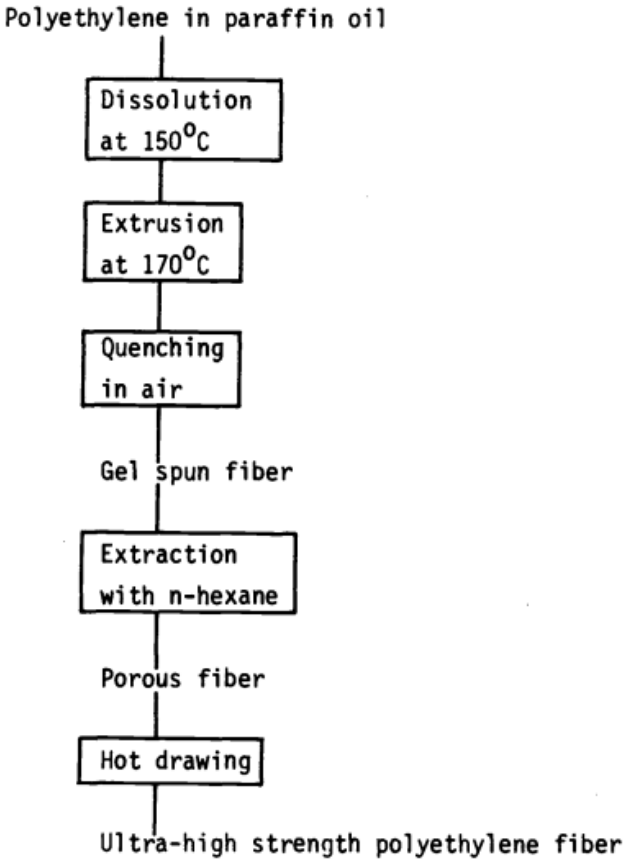

Figure 1.12 : Schematic diagram of UHMWPE fiber spinning [9].

A major breakthrough was achieved by using a co-rotating twin-screw extruder to obtain homogeneous solution. The gel spinning process is now confined to measurements in between the co-rotating screws and the barrel and that worked well in twin-screw extruders with a specific length/diameter ratio, typically L/D > 40.

1.2.3.2 Hansen solubility parameter

Hansen solubility parameters were developed by Charles M. Hansen to predict the probability of a material being dissolved in a solution [13]. This concept is based on the principle that substances with similar properties tend to dissolve in each other. Permanent dipole-permanent dipole forces (δ_p), hydrogen bonding (δ_h) and dispersion (δ_d) are the three main portions of the Hansen solubility parameters (Figure 1.13). The symbol δ is defined as the total dissolution parameter, and the relationship between total dissolution and subparameters is shown in equation 1.1

$$\Delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \qquad (1.1)$$

It is defined as the seperation between two points in R_a Hansen space. The relation between R_a and the main solubility parameters is given in equation 1.2.

$$(R_a)^2 = 4(\delta_{d2} - \delta_{d1})^2 + (\delta_{p2} - \delta_{p1})^2 + (\delta_{h2} - \delta_{h1})^2 \quad (1.2)$$

The interaction radius of polymers in Hansen space is defined as R_o. Solvents in this range in the defined space swell or dissolve the polymer of interest and to define and predict this interaction, the relative energy difference (RED) value is defined. In the case of relative energy difference > 1, since there will be no interaction between the solvent and the polymer, it will not act as a solvent against the polymer. When the relative energy difference ≤ 1, it means that the cohesion energy difference is low, so the solvent will interact with the polymer to dissolve or swell the polymer. The relation describing R_o, R_a and the relative energy difference is given in equation 1.3.

$$RED = R_a / R_o \quad (1.3)$$

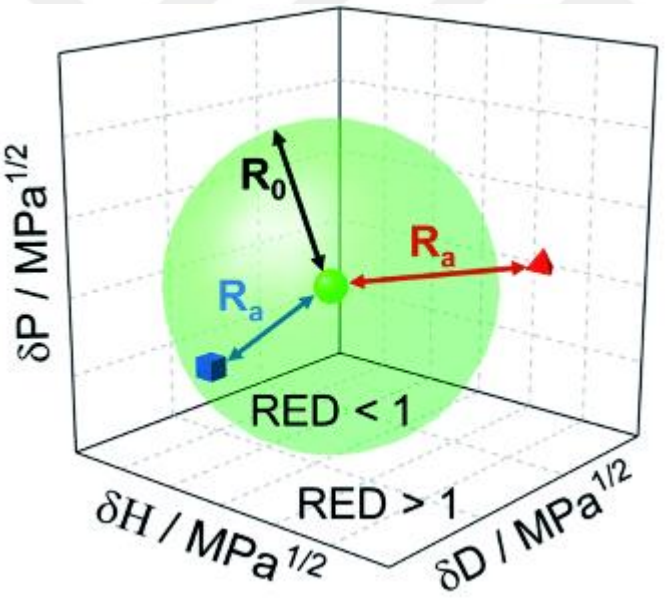

Figure 1.13 : Schematic illustration of hansen space [13].

According to the relative energy difference calculated from Hansen parameters, the difference between wet spinning and gel spinning can be explained. In the two spinning methods, the chemical-polymer interaction in the extraction bath is expressed by different RED values. In wet spinning method, the relative energy difference always takes a value less than 1. In wet spinning, the chemical in the extraction bath dissolves or swells the polymer, where bidirectional diffusion occurs. In gel spinning, the relative energy difference in the extraction bath is always greater than 1. Dissolution

does not occur between the polymer and the chemical, so one-way diffusion takes place from the solvent to the coagulant. The diffusion directions in the two spinning systems are shown in Figure 1.14 [19].

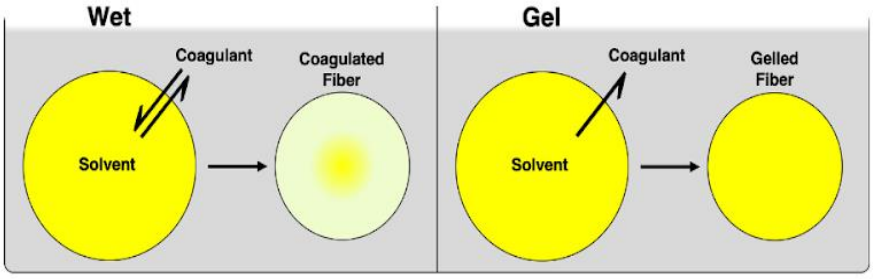

Figure 1.14 : Diffusion directions of wet vs gel spin in the coagulation bath [19].

1.2.4 Surface functionalization of fibers

High performance fibers are used in large areas such as ballistic materials, medical fields and rope making, so the demand for these fibers is increasing day by day. In this way, fiber reinforced composite materials are becoming more significant recent days. Composite reinforcement consists of fiber and matrix. In the case of impact, martix transfers the loads to the fibers. Different mechanical properties can be obtained according to the tensile properties, volume ratio, direction and length of the fiber. When interaction forces between fiber and matrix is over a threshold, fibers acts as a reinforcing element to carry the loadswhile the polymer matrix acts as a transfer medium Although the limited capacity of polyethylene polymer to form an adhesive bond limits its application areas, it has a great application area in composites due to its lightweight characteristics, easy processing and versatility. Ultra-high molecular weight polyethylene (UHMWPE) fibers are unique among reinforcing fibers thanks to its low moisture absorption resistance, high abrasion resistance, low density, high chemical resistance, mechanical properties and high impact resistance. The effect of surface modification on the interface properties was revealed by modification techniques [20]. Inadequacy of polar groups in polymeric materials with low adhesion properties results in poor surface energy. Adhesion takes place when the fiber is wet, and wettability takes place when the reinforcing fiber’s surface energy is higher than that of the matrix polymer. The wettability of the fiber mainly depends on the surface energy. When a polymer diffuses the surface irregularities of the matrix and settles there, adhesion occurs, which is called mechanical interlocking [21], [16]. There are

approaches to improve adhesion properties. For instance, the amount of mechanical interlocking can be increased with improved surface roughness and increased reactive locations, and the intermolecular interaction can be changed by adding different functional groups to the surface of fiber.

1.2.4.1 Wet methods

Chemical etching

In the chemical etching method, the fiber surface is chemically activated with strong oxidative agents and roughened by abrasion, so that the fiber surface becomes physically and chemically modified [12,23]. In a study, UHMWPE fibers was etched with various chemicals (chromic acid, hydrogen peroxide and potassium permanganate). It was found that chromic acid improved surface roughness and provide the better surface tension, but the surface roughness was low in the treatment with potassium permanganate and hydrogen peroxide [24]. In another study, the wear between polyethylene matrix and chromic acid-treated UHMWPE fibers was examined. The tensile properties of the fiber increased in 30 seconds, good surface roughness was obtained in 10 minutes of processing, and it was came out that the polyethylene- fiber composite's interface properties developed by ~330% [25] . In another study on chromic acid treated UHMWPE fiber, fibers showed improved tensile and tear strength than untreated fibers [26]**.** On the other side the improvement in tear strength of potassium permanganate-treated UHMWPE fiber composites was lower than that of chromic acid-treated UHMWPE composites [27]. One of the studies on UHMWPE fiber treated with potassium permanganate on epoxy compozites focused on its mechanical properties According to the results of the study, the process enhanced the interface properties approximately 26%, but when compared to pure epoxy it caused a decrease in tensile strength [28].

Surface coating

Coating refers to the process of applying thin layers of coating films onto a surface. This can be achieved by either allowing the monomer to self-polymerize on the surface of the fiber or by depositing a suitable functional layer onto the substrate material [20]**.** In a study researched by L. Shanmugam et al, multi-walled carbon nanotubes (MWCNTs) that have been functionalized were added to the PDA solution to improve the adherence of the UHMWPE fiber to the thermoplastic matrix and showed that it enhanced the fiber-matrix bond strength by ~42.50% [29]**.** In another study researched

by Wang et al, reduced graphene oxide (rGO) was deposited on the UHMWPE fiber with PDA coated to make the UHMWPE surface conductive and it was characterized using XPS, FTIR and SEM methods. UHMWPE-PDA-rGO retained tenacity better than UHMWPE-PDA-Ag, with excellent tenacity retention of 84.8%-93.2% as opposed to 69.6%. The procedure of in situ reduction and deposition only partially decreased GO, according to calculations made with TGA data and linear density. [30]**.** In the processing stage, graphene oxide underwent a reduction process to become reduced graphene oxide (rGO) after being dispersed in water to create a consistent suspension. This rGO was then coated onto UHMWPE fibers that were previously coated with PDA. Consequently, the UHMWPE fiber demonstrated decreased resistance, indicating an enhancement in conductivity.

Another coating method is the oxidative polymerization of pyrrole. X. Jin et al studies on coating of PPy (Polypyrrole) over UHMWPE (Ultra-High Molecular Weight Polyethylene) fiber, resulting in a significant increase of 280% in the tensile shear strength. [31]**.** The enhanced mechanical interlocking and improved adhesion are attributed to an increase in the roughness of the fiber's surface. In a comparable investigation, researchers conducted studies aimed at enhancing the interfacial adhesion and compression performance of polymer composites reinforced with UHMWPE fiber. To improve the compressive strength of epoxy-UHMWPE fiber composites, after undergoing plasma treatment, the fibers were subsequently coated with PPy [32]**.** It was found by Y. L. Tian and L. M. Guo, that the application of plasma treatment alone did not lead to an increase in the compressive strength of reinforced polymer composites with UHMWPE fiber. However, when plasma treatment was combined with coating processes, a substantial enhancement of approximately 54% in compressive strength and approximately 848% in interfacial adhesion was observed. UHMWPE fiber was coated with Polyethylene wax grafted maleic anhydride (PEW-g-MAH), which has a molecular structure similar to UHMWPE. Tensile testing revealed that after being coated with 9% by weight of PEW-g-MAH, the UHMWPE fibers exhibited 53.59% increase in tensile strength compared to the original, untreated fibers, in another study [33]**.** UHMWPE fiber was coated with tannic acid (TA)-Na+, which has a phenolic hydroxyl group and can form a nanofilm on the surface of substrate, although the average breaking strength of the fibers remained unchanged, there was a noticeable increase in the tensile strength by 28.0% and the tensile modulus

by 49.4% in the macro composites [30]**.** This proves that the properties of composites can be improved without compromising integrity of fiber. Schematic of tannic acid coating given in Figure 1.15.

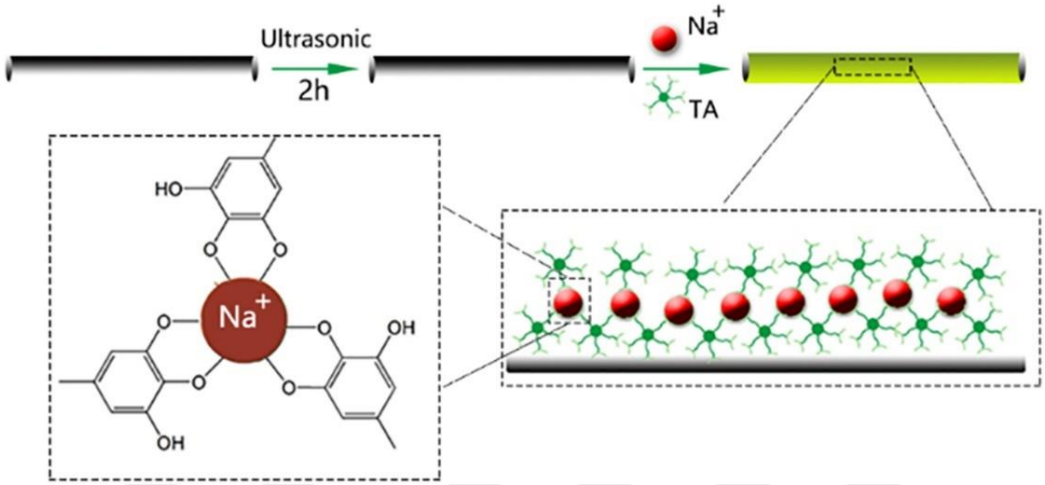

Figure 1.15 : Schematic of tannic acid coating [30].

1.2.4.2 Dry methods

Corona discharge

Corona discharge is a technique utilized to induce surface oxidation of materials by ionizing plasma through high-frequency discharges applied between grounded metal coil and electrodes**.** In this process, the sample is positioned within the between-electrode space, where oxidants interact with the sample's surface, resulting in the formation of oxidizing groups. This system is showed in Figure 1.16. This leads to an enhanced bonding and interaction between the fibers and the polymer matrix, while also causing physical and chemical changes to the fiber surface. For instance, it is widely acknowledged that corona discharge processing results in the formation of micropits and the introduction of oxygen functional groups on the fiber surface [34]**.** In corona discharge, different processing times and strengths and interfacial properties of composites can be modified in many different variations. In a research studied by Z. Zheng et al, the impact of corona discharge treatment on UHWMPE fiber was examined. Different levels of processing power and time were applied to investigate the effects on the fiber. SEM images clearly indicated that micropits increased as the power of the corona discharge increased. However, it was also found that the fiber strength decreased as the corona power increased. According to the study's findings, the peel strength reached its maximum value at 0.1 second during corona application,

after which the tensile strength decreased as the power increased [34]**.** In an alternative investigation, the corona discharge technique was employed to enhance the interfacial shear strength between UHMWPE fiber and HDPE film. The findings were presented through multivariate regression analysis.

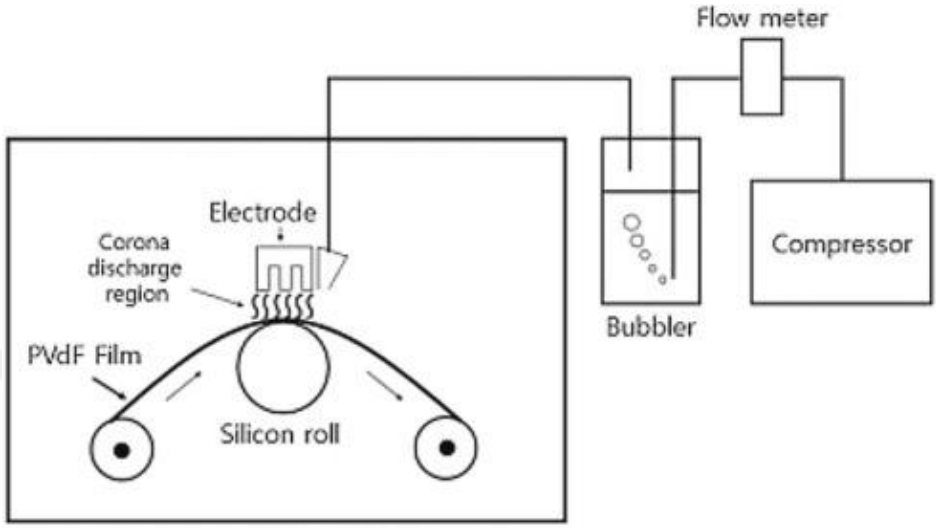

Figure 1.16 : Schematic of corona discharge [33].

According to analysis by Z. Zheng et al, HDPE-treated UHMWPE fiber, it has been reported that functional groups have an effect of 50% and surface roughness has a 50% effect on the interfacial shear strength [35]**.**

Plasma treatment

In this process, the sample is positioned within the between-electrode space, where oxidants interact with the sample's surface, resulting in the formation of oxidizing groups which illustrated in Figure 1.17. This leads to an enhanced bonding and interaction between the fibers and the polymer matrix, while also causing physical and chemical changes to the fiber surface. For instance, it is widely acknowledged that corona discharge processing results in the formation of micropits and the introduction of oxygen functional groups on the fiber surface [35]**.** In corona discharge, different processing times and strengths and interfacial properties of composites can be modified in many different variations. In a research study, the impact of corona discharge treatment on UHWMPE fiber was examined. Different levels of processing power and time were applied to investigate the effects on the fiber. SEM images clearly indicated that micropits increased as the power of the corona discharge increased. However, it was also found that the fiber strength decreased as the corona power increased. According to the study's findings, the peel strength reached its maximum

value at 0.1 second during corona application, after which the tensile strength decreased as the power increased [34]. In an alternative investigation, the corona discharge technique was employed to enhance the interfacial shear strength between UHMWPE fiber and HDPE film. The findings were presented through multivariate regression analysis. According to analysis of HDPE-treated UHMWPE fiber, it has been reported that functional groups have an effect of 50% and surface roughness has a 50% effect on the interfacial shear strength [36].

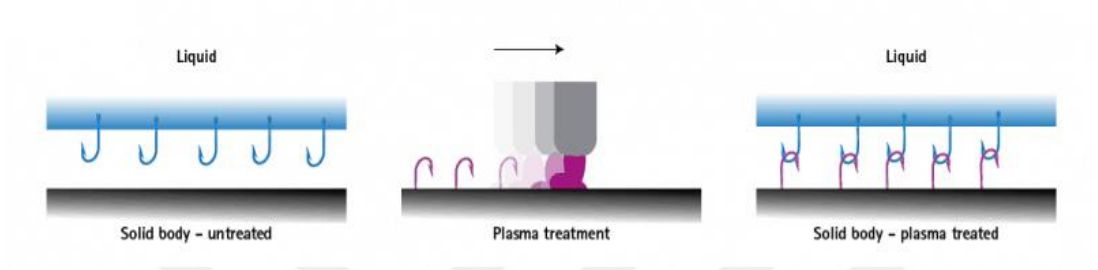

Figure 1.17 : Plasma treatment illustration [32].

Polar functional groups are routinely added to the surfaces of fibers using the extremely adjustable surface treatment technique known as plasma treatment . Plasma treatment can give textile fibers a variety of surface alterations, including sensitivity to adhesion, wettability, maintaining air permeability, and inert. A desired gas and an electric field interact in a vacuum container to form the medium known as plasma, this gas can be oxygen, nitrogen, helium, air and many different gases. This plasma contains free electrons consisting of molecular, ionic, atomic, and radical species [37]. When gas ions are released, they interact with the surface and cause changes in its chemical structure. This interaction involves the breaking of chemical bonds and the generation of free radicals. Once the surface entities are activated, they can undergo crosslinking or join together with excited ions.

After plasma treatment, the adhesion of epoxy resin-UHMWPE fiber enhanced by minimum 4 times in the research [30]. In another study conducted with FTIR-ATR, LRS, XPS, SEM, and contact angle measurements, it was observed that chemical bonding, mechanical interlocking effects had significant effects on adhesion [35]. Oxygen and nitrogen plasma exhibit different behaviors, with oxygen plasma being more efficient in providing oxygen-rich functional groups. Consequently, fibers treated with nitrogen plasma primarily rely on mechanical interlocking for adhesion, while fibers treated with oxygen plasma benefit from both mechanical interlocking and

chemical interactions for adhesion. In a different study, studied by S. Wang et al, argon plasma was applied to vinylester resin - UHMWPE fiber and its effects on interfacial adhesion were investigated [30]**.** By subjecting UHMWPE fibers to argon plasma treatment, the adhesion between the fibers and vinylester resin is enhanced. This is achieved by inducing roughness and creating cavities on the fiber surface. Additionally, the treatment renders the UHMWPE fibers chemically inert, further contributing to adhesion. However, it was observed that the adhesion decreased as the treatment time was prolonged in argon plasma. This can be attributed to a reduction in the concentration of functional groups with a large amount of oxygen over time, leading to a more intertwined fiber surface. Figure 1.18 shows, an example of plasma treated fiber [20].

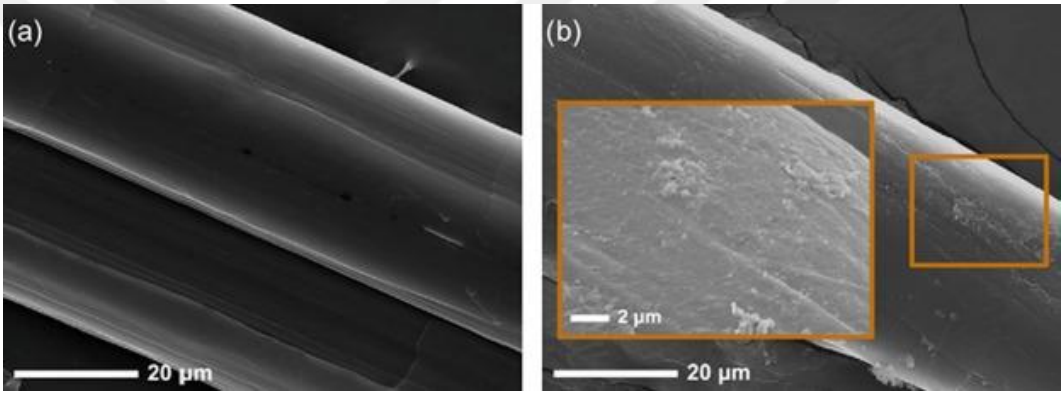

Figure 1.18 : Plasma treated fiber [20].

1.3 Hypothesis

High performance UHMWPE fibers would be achievable, but as observed from the literature the inert nature of PE does not allow high performance on composites produced thereof. For that reason, in this study surface of UHMWPE was modified using physical and chemical approaches and cross-linking between fiber and matrix polymer can be obtainable. UHMWPE has very high molecular weigth such as $5x10^6$ g/mol. So, it has a very high melt viscosity, solution processing would seem to be the best option. Gel spinning of UHMWPE with paraffin oil can be achievable with counter rotating twin screw extruder and mechanical properties are enhancable with post drawing. Chemical interface agents that can enhance the covalent and various intermolecular interactions between the surface-activated fibers and the matrix resin.

2. EXPERIMENTAL

2.1 Materials

In this study, UHMWPE in powder form having a molecular weight of $5,5x10^6$ g/mol POLIMAXX U511 was used. Industrial paraffin oil and n-hexane were purchased from Bluchem (Istanbul) to be used as solvent and extraction agent. Zinc Stearate is a completely non-toxic zinc compound that finds wide-ranging industrial applications, hereby it is aimed to be used as processing agent provided by BASF and antioxidant Irgafos 168 provided by Zirve Polimer. UHMWPE, solvents and processing aids were used in combination for fiber formation.

For the enhancement of surface adhesive characteristics of the fiber, various approaches were applied. Gluteraldehyde was benefited for its stabilizing and cross-linking behavior, it was supplied from Labor Teknik. The UHMWPE fibers were also treated by nitric acid ($C_6H_8O_7$) and sulphuric acid (H_2SO_4) for etching. Etching solution consisted of aqueous solution of etching agents (nitric acid and sulphuric acid). Epoxy resin was selected to be the matrix compound of fiber reinforced composites. It purchased from Evonik. Standard composite tensile test specimen was casted in silicone mold, for which RTV2 molding silicone was purchased from Kompozit Akademisi.

2.2 Production of UHMWPE Fiber via Gel Spinning

The production of UHMWPE fibers was accomplished in three stages. First stage involves the preparation of spinning suspension and its gel spinning. Second step deals with the extraction of the solvent used. Finally, the third step aims to further orient the fibers in a post treatment.

2.2.1 Dry jet-wet spinning of UHMWPE

In this experiment the suspension containing 8 wt.% UHMWPE were used to prepare gel fiber. The ratio of ultra-high molecular weight polyethylene (UHMWPE) raw

materials and the concentration of the solvent significantly affect the preparation of UHMWPE fiber. This ratio determines the dissolution behavior of UHMWPE and influences rheological behaviour of the spinning solution. Optimum ratios and solvent concentrations are needed to be carefully considered to achieve successful preparation of UHMWPE fiber with desired properties. The concentration of the spinning solution plays a critical role. The presence of molecular entanglement points affects the fiber spinning and drawing effect, which in turn effect the properties of the fiber. Therefore, the concentration of the spinning solution is a critical parameter that influences the fiber's characteristics and performance. When the spinning solution concentration is high, it leads to an increased number of macromolecular entanglement points. This results in higher tensile resistance, making it challenging to achieve a high draw ratio for the fiber. Additionally, an excessively high spinning solution concentration may inhibit the complete dissolution of polyethylene, in this way negatively affecting the performance of the resulting frozen gel. It is important to find the optimum spinning solution concentration for balancing these factors and achieve the desired fiber properties.

The suspension was initially tried to be delivered to the spinning system via a heated piston pump of 1 liter solution capacity was used. The piston pump experiment was abandoned due to the flammability of the paraffin oil under pressure. For the continuity of the experiments, the suspension was fed to the counter rotating twin screw extruder with L/D 50. The twin screw extruder is demonstrated in Figure 2.1. Prior to feeding to the extruder, UHMWPE paraffin oil, zinc stearat and antioxidant were mixed in a container by mechanical stirring to preserve the suspended state. The filament was extruded using a monofilament spinneret with a diameter of 1.75 mm. A constant take-up speed of 24 m/min was used for production. The twin-screw extrusion rate has a significant impact on the shear force applied on polyethylene molecules and affects the dissolution process. When the twin-screw rate is too low, the shear force on the polyethylene molecules is insufficient, resulting in inadequate mixing and dissolution in the paraffin solvent. This leads to prolonged residence time, causing molecular weight degradation. Moreover, insufficient shear force fails to untangle the molecular chains, making the fiber prone to breakage during subsequent drawing processes. On the other hand, if the twin-screw extrusion rate is too high, it can damage the molecular structure of polyethylene, causing molecular degradation. It can also result in

inadequate entanglement, which affects the production efficiency. Therefore, finding the appropriate twin-screw extrusion rate is crucial to ensure effective dissolution, to maintain molecular integrity, and to optimize production efficiency.

The filament was quenched into a 1.5 meter long cold water bath of 20 ^{o}C to form gel fiber. The temperature profile from feed zone to spinneret was shown in Table 2.1. Cold water bath located 25 mm under the spinning hole.

Table 2.1 : Temperature profile of the extruder.

Feed Zone (^{o}C)	Extruder II (^{o}C)	Extruder III (^{o}C)	Extruder IV (^{o}C)	Spinneret (^{o}C)
120	140	160	195	175

The fiber diameter decreases to as low as 0.9 mm from the exit of the nozzle to the the bath entrance. In this air gap, orientation is crucial to be as optimal as possible.

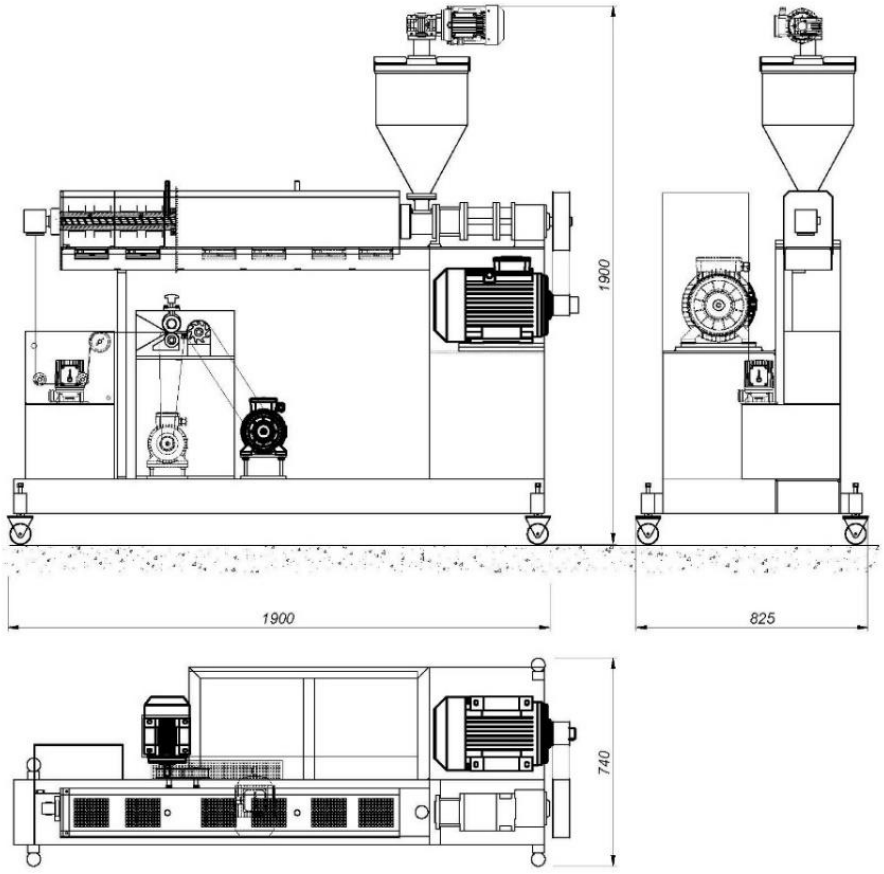

Figure 2.1 : Technical drawing of counter rotating extruder.

Table 2.2 : Technical properties of extruder.

Part of Machine	Property
Screw Diameter	25 mm
Screw L/D	50
Screw Rate	Max. 350 rpm
Enginer Power	5,5 kW

Gel spun fibers were wound on to a spool. After gel spinning, the as-spun gel fibers were placed into the n-hexane bath in orderto perform extraction of paraffin oil during 6h. Table 2.2 shows technical properties of extruder.

2.2.2 Post treatment by hot drawing

Post drawing techniques have also been applied to the samples that achieve superior mechanical results from hot drawn samples. During the hot drawing process, the fiber is typically heated to a controlled temperature and then subjected to tension or pulling. As the fiber is stretched, the polymer chains within the fiber rearrange, resulting in a preferred alignment of the molecular chains along the fiber's axis. The extracted fiber samples were subjected to a post-operational hot drawing via a home-made custom designed device which has a semi-closed 30 cm tunnel surrounded by heaters. The post drawing is shown in Figure 2.2. In this tunnel, which is heated to a set temperature of 115 ^{o}C, the fiber is drawn between 2 cylinders. The speed of the first cylinder is 220 mm/min, while the speed of second cylinder is 440 mm/min to achieve a constant drawing rate. To reduce the diameter and enhance the orientation, the fibers were subjected to five cycle drawing processes. After the fifth drawing process, the drawing ratio reached to 43.75, fiber breakage occurred. Increasing the temperature resulted in even more breakage, and the diameter could be reduced to a maximum of 40 microns. Zone annealing and drawing, despite of being older methods, offer significant advantages in the hot drawing technique. These methods help stabilize the newly formed chain structure, enhance the crystallinity of the precursor groups, prevent the back folding of the extruded polymer chain, and minimize thermal degradation of the

fiber. In the design of the hot drawing study, it is aimed to improve the performance of the orientation related properties as in mechanical and thermal performance.

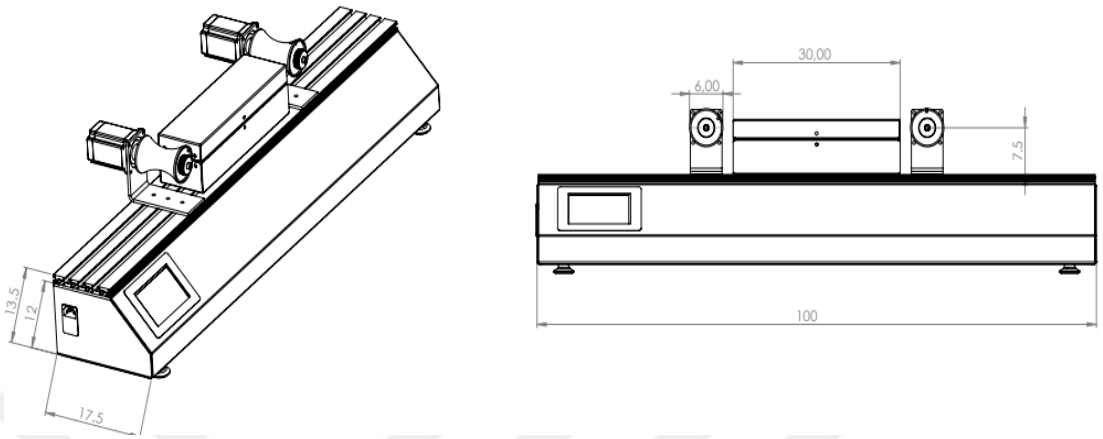

Figure 2.2 : Hot drawing unit.

2.3 Surface Treatment of UHMWPE Fiber

2.3.1 Chemical etching

The UHMWPE fibers were treated by nitric acid and sulphuric acid. The nitric solution was a compound of $C_6H_8O_7$, H_2SO_4, and H_2O. Drawn UHMWPE fibers were immersed in a nitric acid solution for about 5 min at 25 ^oC and then rinsed with distilled water 3 times. The treated fibers were dried in a vacuum oven at room temperature for 24 h. After chemical etching the fibers were further treated with gluteraldehyde. The fibers were then kept in an oven at 80 °C for 4 hours and left to dry.

2.3.2 Corona discharge

The use of the corona discharge method was chosen to develop adhesion characteristics of fiber samples. High frequency discharges delivered across electrodes and grounded metal rolls are the main components of corona treatment. The SIMCO ION TM CM5 device, working in a system with air at the room condition, was used to carry out corona application. The air gap between the copper electrodes and the test sample in the corona system was fixed at 2 mm. The UHMWPE fibers were exposed to discharge below 12 kV and 10 kV during 5 and 10 minutes (Table 2.3). The fibers exposed to corona discharge were subsequently passed through a glutaraldehyde bath. The fibers were then kept in an oven at 80 ^oC for 4 hours to dry.

Table 2.3 : Corona discharge treatment parameters.

Sample	Distance (mm)	Voltage (kV)	Time (min)
UHMWPE	2	10	5
UHMWPE	2	10	10
UHMWPE	2	12	5
UHMWPE	2	12	10

2.3.3 Production of UHMWPE fiber reinforced epoxy resin

The UHMWPE fibers were untreated, treated and grafted with gluteraldehyde, placed manually into molds prepared in 50x10x3,5 mm dimensions. Bisphenol A diglycidyl ether (DGEBA) epoxy resin and Isophorondiamine (IPDA) hardener were used. The samples prepared with resin hardener at a ratio of 2:1 and cured at room temperature for 36 hours. Like other amines, it serves as a curing agent for epoxy resins. Epoxy and curing agent is illustrated in Figure 2.3 and 2.4.

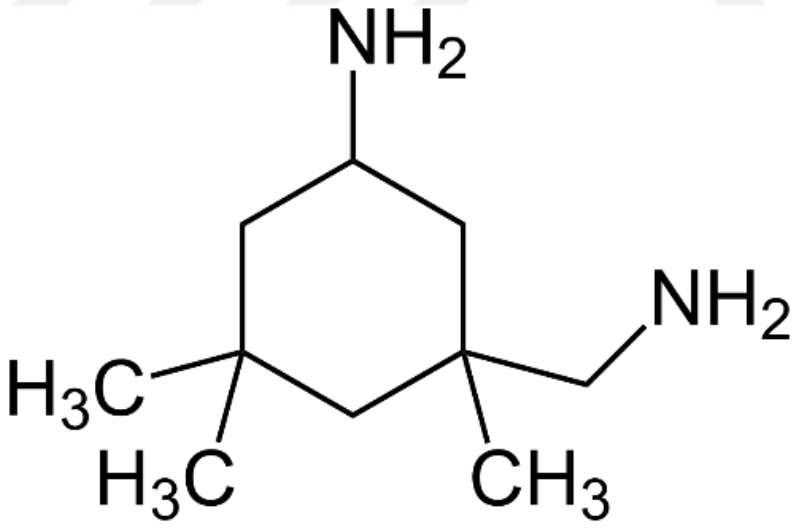

Figure 2.3 : Chemical structure of IPDA [6] .

In our experiment mechanical strength is crucial, so IPDA was chosen for curing agent. DGEBA is a liquid epoxy resin, which is an organic compound. It is typically a colorless viscous liquid. DGEBA serves as a vital ingredient in various epoxy resin formulations.

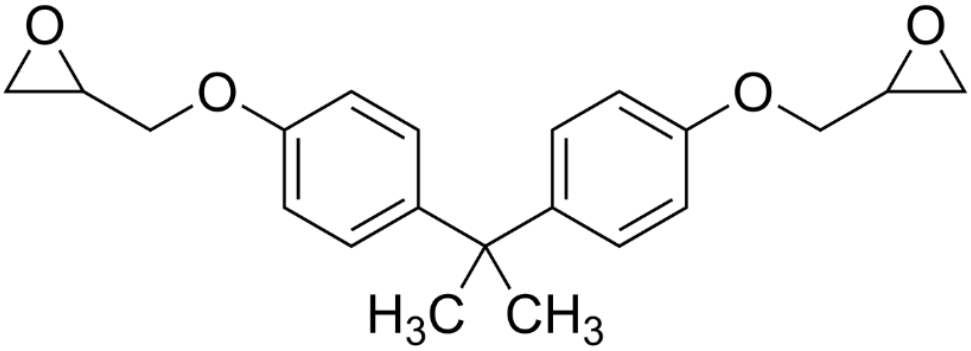

Figure 2.4 : Chemical structure of DGEBA [6].

In the production of advanced composite materials, where performance is the crucial criteria, the higher cost is less critical. The remarkable qualities of UHMWPE fiber-reinforced composite have attracted a lot of attention. But the straightforward methylene structure results in an inert chemical surface, making it challenging for the fiber to react with epoxy resin. In Figure 2.5, curing mechanism of epoxy is illustrated.

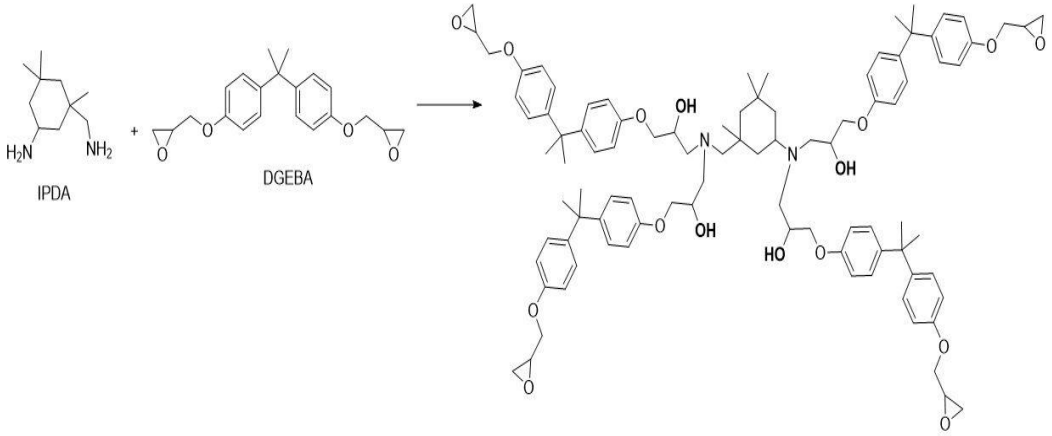

Figure 2.5 : Curing mechanism of epoxy resin [6].

2.3.4 Gluteraldehyde grafting

The fibers were treated with glutaraldehyde bath to impart surface functionality after corona and acid treatment. At this point, it is believed that the hydroxyl group on the fibers will react with the carboxyl group on glutaraldehyde. When the grafted fibers are incorporated into a composite structure with epoxy, a cross-linking reaction takes place between the functional groups on the fiber surface and the epoxy resin. This cross-linking process involves the formation of covalent bonds, resulting in the establishment of a three-dimensional network within the composite material.

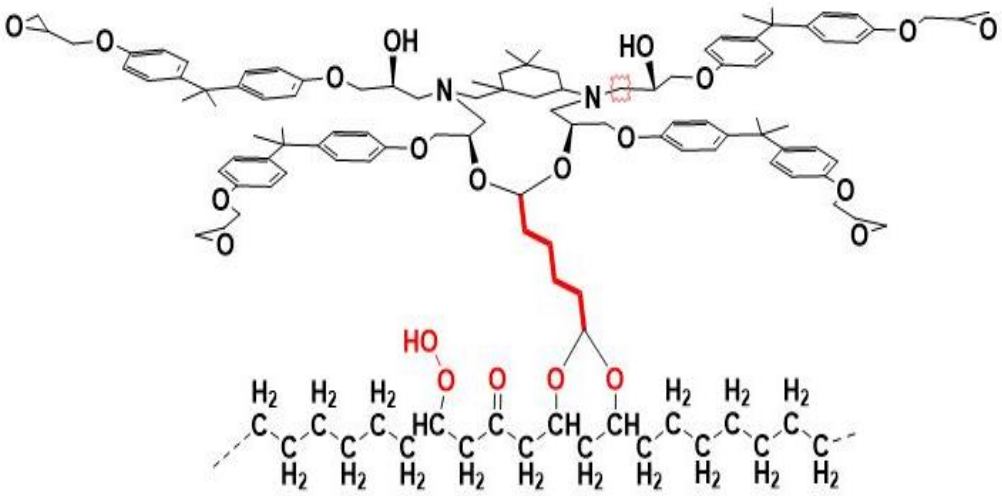

Figure 2.6 : Crosslinking mechanism of UHMWPE fiber and epoxy resin [6].

The cross-linking enhances the mechanical strength, durability, and thermal stability of the composite by improving the load transfer and interfacial adhesion between the fibers and the epoxy matrix. This leads to an overall improvement in the performance and properties of the composite material. The treated fibers are then placed in an oven for drying. Figure 2.6 shows, crosslinking mechanism of UHMWPE and epoxy resin.

2.4 Characterization of UHMWPE Fibers

2.4.1 Optical and polarized light microscopy

The samples were analyzed by a Nikon Eclipse 50i optical microscope to quantify the average fiber diameter. The resulted diameters were used for plotting of the stress-strain curve.

2.4.2 Mechanical test

2.4.2.1 Tenstile testing

For evaluation of mechanical performance of fibers, tensile testing was carried out. Randomized samples were analyzed using optical microscope, and their average diameter was calculated. An optical microscope (Nikon Eclipse 50i) was used to determine the average diameter. Tensile testing was carried out by a Zwick Roell Proline Universal Tensile Tester equipped with a 2 kN load cell. For the fiber testing specimen, gauge length was fixed to be 25.4 mm with a holder shown in Figure 2.7

and, a constant jaw speed of 15 mm/min was applied to fiber samples. All tensile tests were repeated on 5 samples and were performed under ambient conditions.

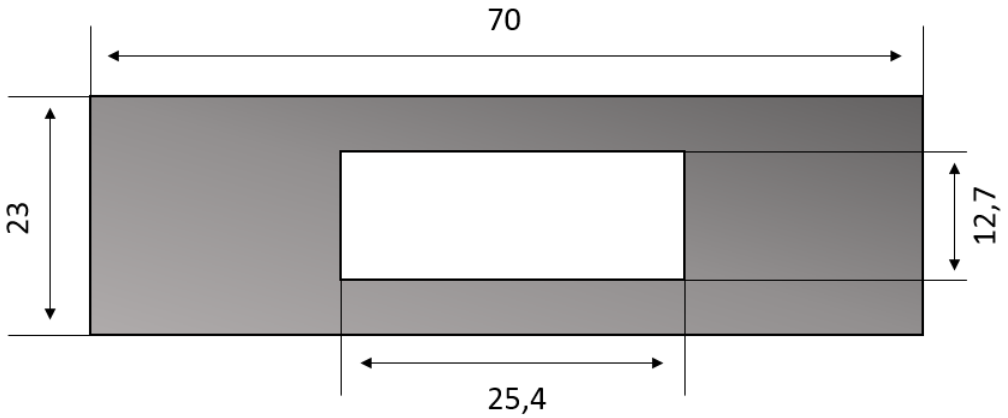

Figure 2.7 : Scheme of tensile test specimen holder.

For composite testing, tensile bars formed by epoxy casting were used. Tensile testing was conducted on three different samples. These were pure epoxy, untreated fiber reinforced epoxy and gluteraldehyde grafting fiber epoxy composite. 3 sets of samples were tested from each group of composites. Gauge length was determined to be 25 mm and constant jaw speed of 100 mm/min was applied the composite samples.

2.4.3 Scanning electron microscopy

The TESCAN VEGA 3 SEM device was used to analyze the fiber and composite morphology. In order to ensure conductivity, Au/Pd coating was applied on the surface for 165 seconds. Samples were scanned in the magnification range of 500x to 1,5 kx.

2.4.4 Thermal analysis

TA Instrument was used to determine the thermal behaviours of yarn, such as crystallyzation, glass transition and melting temperatures. The yarn samples of about 3.5 mg were comprised in a non-volatile aluminum container and heated to 170 ^{o}C with the heating rate of 10 ^{o}C /min under nitrogen gas flow. 3 different samples tested; gel state fiber, undrawn extracted fiber and drawn extracted fiber.

3. RESULTS AND DISCUSSION

3.1 Mechanical Properties

3.1.1 Mechanical properties of fiber

Dissolution of UHMWPE, extrusion, spinning as in form of mono- or multiflament, extraction, drying and obtaining the final product are the main steps of the gel spinning method. Achieving the fast and efficient dissolution of UHMWPE powders in paraffin oil solvents is a complex task primarily due to the material's high molecular weight, viscosity, and entanglement. However, the dissolution process is crucial for achieving the desired performance properties. The UHMWPE fibers produced at 24 m/min spinning speed and gel fibers were extracted with n-hexane and subjected to different cycles of hot drawing.

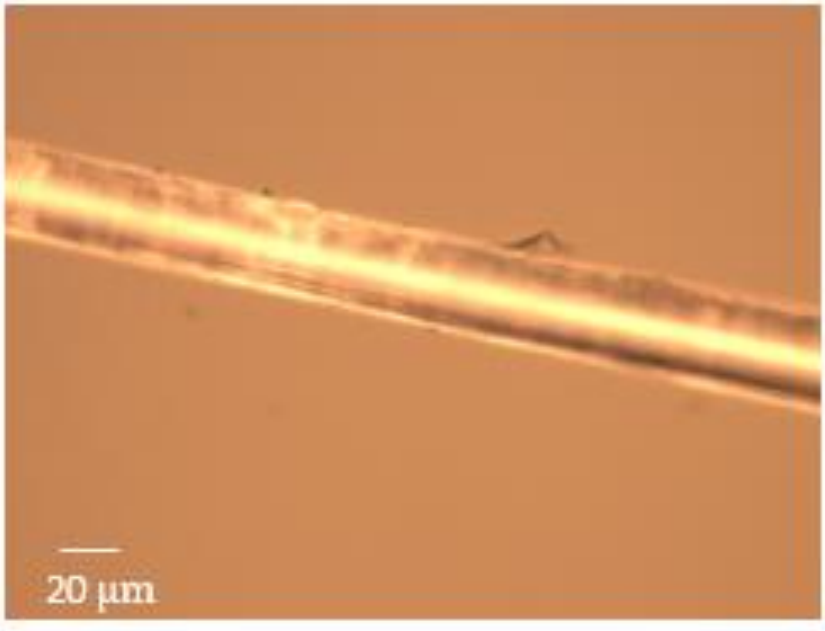

Figure 3.1 : Optical microscope image of produced UHMWPE fibers.

UHMWPE fibers have acquired a highly oriented and crystalline structure after being drawn at a specific temperature. It can be observed from that with the increase of DR (drawing ratio), the linear density of fibers decreased, and the strength increased. Table 3.1 shows the gradual improvement of the fiber mechanical properties. As it can be

seen, at the end of the fifth drawing cycle enhanced strength and modulus properties of the fibers obtained from UHMWPE gels. Obtained tensile strength at 3 GPa levet indicates that UHMWPE gel is suitable for high strength and modulus fiber formation.

Table 3.1 : Mechanical properties of UHMWPE fiber.

Number of Drawing Cycle	Drawing Ratio	Thickness (μ)	Tensile Strength (MPa)
2	17.50	100.0 ± 6.12	713 ± 278.24
3	22.48	77.8 ± 5.11	1565 ± 328.67
4	29.60	59.1 ± 1.44	2036 ± 601.02
5	43.75	40.3 ± 0.57	3016 ± 250.06

Table 3.1 and Figure 3.1 demonstrate the tensile performance of UHMWPE fibers produced at various draw ratios. A study has found that mechanical strength and orientation of polyethylene improve during the stretching process, along with an additional hot drawing process applied after stretching [4]. It was discovered that the tensile strength increases as the UHMWPE chains' orientation along the fiber axis increases because the orientation makes the molecular chains more aligned, which increases the tensile strength. Maximizing orientation can lead to stronger and better mechanical qualities and improved strength. Increasing the hot-drawing ratio (DR) from 15 to 40 continuously improves the mechanical properties of UHMWPE fiber samples. This improvement is associated with a reduction in the lateral size of the lamellar structure and an increase in the long period. Higher drawing ratios generate axial stress, leading to the development of an internal microfibril structure within the fibers. It is significant to note that the process of crystallization in fibers at high temperatures is a relatively slow process [15,38]. Considering the two cases where the stretching ratio is too high and too low, when the ratio is excessively high, the fiber may not enter the stretching direction and its crystallization will be adversely affected [36]. In case the ratio is too low, the fiber is damaged due to exposure to high temperature. It is important to control the temperature parameter in order not to permanently damage the fiber during the process and to obtain improved fiber. In case the temperature is too high, the fiber may be damaged, due to the damage that may

occur in the molecular structure. If the temperature is too low, fiber stretching, and molecular orientation cannot be achieved adequately. Figure 3.2, Table 3.2 and Figure 3.3 shows mechanical behaviour of produced UHMWPE fibers.

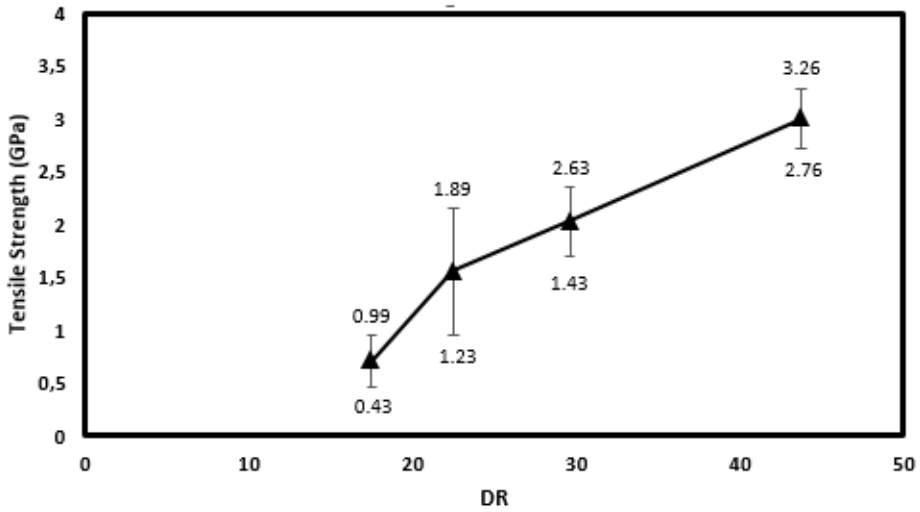

Figure 3.2 : Mechanical strength of UHMWPE fiber.

When UHMWPE fibers are subjected to specific temperatures during the drawing process, they undergo a transformation that leads to a crystallized and highly oriented structure. This transformation occurs predominantly at higher temperatures, where the mobility of PE chains within the fibers increases, resulting in a more compact fiber structure. By reducing the entanglements between polymer chains and minimizing their interactions, it becomes possible to achieve high draw ratios, which in turn enhance the molecular orientation of the fibers and improve their strength and modulus. As the drawing ratio increases, certain structural elements within the fibers undergo changes.

Table 3.2 : Elongation values of UHMWPE fiber.

Number of Drawing Cycle	Drawing Ratio	Thickness (μ)	Elongation (%)
2	17.50	100.0 ± 6.12	10.52 ± 2.62
3	22.48	77.8 ± 5.11	6.67 ± 1.69
4	29.60	59.1 ± 1.44	5.34 ± 1.01
5	43.75	40.3 ± 0.57	3.26 ± 0.14

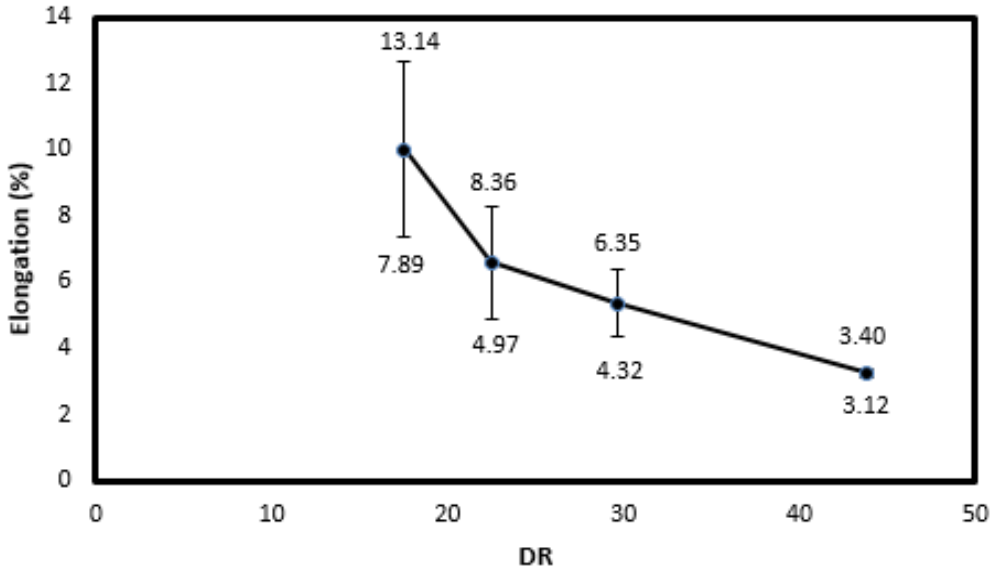

Figure 3.3 : Elongation values of UHMWPE under different drawing ratios.

The amorphous chains shaped shish structure. The mechanism behind the high orientation and strength of the fibers can be explained by the theory of crystallization under extension. During the drawing process, oriented chain segments penetrate the amorphous regions of the fibers, leading to increased mechanical strength and orientation. The optimal drawing temperatures for gel-spun UHMWPE fibers typically fall between 80 and 148 °C. During the drawing process, it has been discovered that these temperatures make it easier to achieve the necessary molecular orientation and mechanical properties. To maximize the strength and other performance qualities of gel-spun UHMWPE fibers, it is essential to carefully regulate and alter the drawing temperature within this range [22].

3.1.2 Mechanical properties of UHMWPE fiber reinforced composite

Polymer composites reinforced with fiber such as carbon fiber, glass fiber, aramid fiber, and ultrahigh-molecular-weight polyethylene (UHMWPE) fiber are extensively utilized due to their remarkable properties, such as lightweight design and high specific strengths and moduli [32]. Fiber-reinforced composite with UHMWPE mechanical properties are greatly influenced by the interface between the UHMWPE fiber and the matrix material. This is because an effective interface allows for efficient load transfer, which enhances mechanical properties like strength and stiffness. A weak or poorly bonded interface can lead to decreased mechanical performance and compromised integrity of the composite, as the contact and adhesion between the fiber and matrix

directly influence the transmission of stress and load between the two components. To achieve superior mechanical properties in UHMWPE fiber composites, it is essential to enhance the interface properties by suitable surface treatments or interfacial modifiers. Numerous methods to enhance the surface properties of UHMWPE fiber have been proposed [36]. These methods include corona discharge treatment to enhance the T-peel strength of composites, chemical grafting to make UHMWPE fibers wettable or capable of reacting with the matrix, and acid etching to roughen the surface and improve wettability.

In this experiment, we utilized corona discharge and chemical etching techniques to enhance the adhesion of the fibers. By analyzing Fourier-transform infrared (FTIR) results, it was determined that chemical etching was more aligned with the aim of this study. After the surface treatment, three different epoxy composite samples of certain sizes were prepared for the experiment. Tensile tests were conducted on the samples that are pure epoxy, untreated fiber-reinforced epoxy, and epoxy treated with chemical etching and glutaraldehyde grafting [30].

Table 3.3 : Mechanical properties of composites.

Sample	Tensile Stregth (MPa)
Pure Epoxy	30,9 ± 0,70
Untreated Fiber Reinforced Epoxy	53,2 ± 2,06
Treated Fiber Reinforced Epoxy	61,6 ± 1,43

In comparison to the original UHMWPE fiber-reinforced composite, the surface modification procedures used on the UHMWPE fiber produced a slightly increased tensile strength, as shown by the data in Table 3.3 and Figure 3.4. Findings point out that the surface treatments have a positive effect on the mechanical properties of the composite material reveal the potential in this field. However, it appears that the increase in tensile strength may be relatively limited. Further analysis and evaluation is needed to determine exactly how important these improvements are and what implications they might have in practical applications. According the tensile test results, gluteraldehyde grafted fiber enhanced 99.35%.

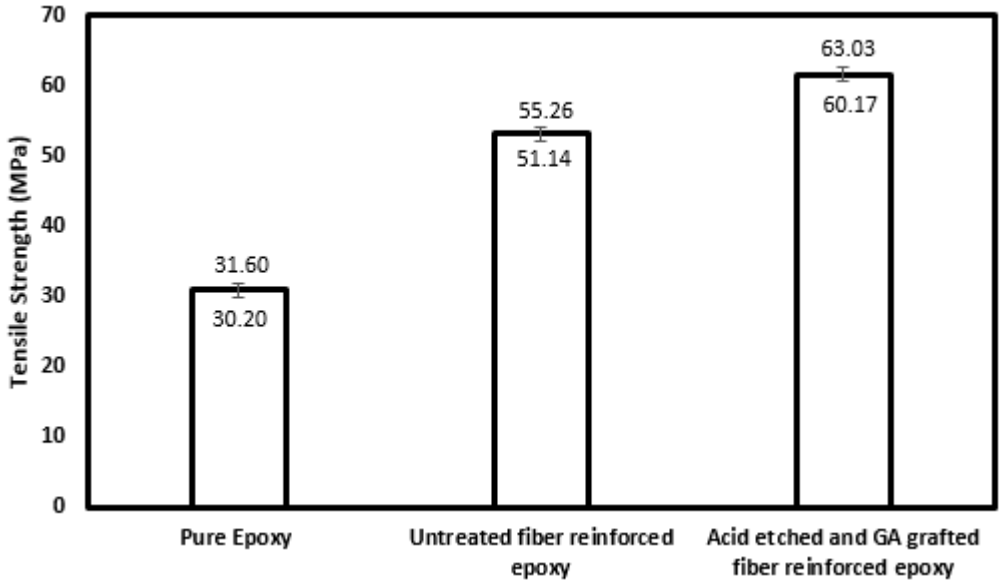

Figure 3.4 : Mechanical properties of produced composites.

3.2 Thermal Analysis of UHMWPE Fiber

The crystalline structure of UHMWPE fibers can be illustrated by their melting behavior. Figure 3.5 shows us 3 different state materials DSC data that are gel state fiber, extracted undrawn fiber and extracted drawn fiber. Our experimental gel fiber contains a large amount of paraffin oil and the paraffin oil doesn't crystallize, so the melting peak of gel fiber smaller than the extracted drawn and undrawn fibers. Since the polyethylene crystal grows more regularly as a result of paraffin oil extraction, the melting point of extracted fiber is higher than that of gel fiber. Specifically, the extracted drawn fiber exhibits a melting temperature of 140.7 °C. If the right temperature and drawing ratio are used during the hot drawing process, crystallinity can rise as chain orientation increases. The peak temperature associated with the melting endotherm shows an increasing trend as the drawing ratio (DR) increases.

Interestingly, when the DR values approach 40, two smaller melting endotherms become apparent at temperatures around 151.1 °C and 156.2 °C. Additional endotherms are observed to the right of the main melting endotherms of the drawn UHMWPE fiber samples [39]. Orthorhombic-hexagonal transition occurs as a result of changes in the positions of atoms due to factors such as temperature, pressure, and other external influences, leading to the material acquiring a new crystal structure. An orthorhombic structure is a prism-like crystal structure with three unequal edges and angles, while a hexagonal structure resembles a hexagon with six equal edges.

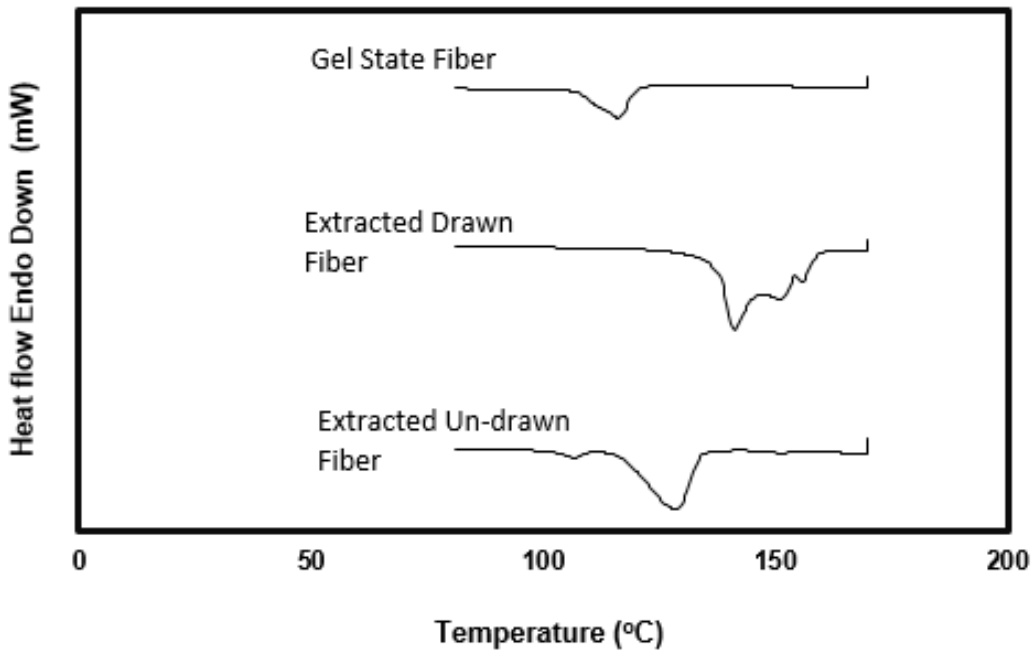

Figure 3.5 : DSC thermograms of 3 different state fibers.

As the drawing ratio (DR) values increase, the peak of melting temperatures of the UHMWPE fibers also rise, accompanied by the emergence of new endotherms. This phenomenon suggests a structural modification within the fiber that contributes to the observed changes in melting behavior. During thermal scanning, the strained orthorhombic crystals undergo a transformation into hexagonal or pseudo-hexagonal crystal phases, leading to the appearance of endotherms with a melting point of approximately 151 °C [10]. However, this orthorhombic-hexagonal phase shift is not evident in the DSC data of the recovered undrawn fibers and gel state fibers. This observation indicates that the presence of branched chains significantly hinders or even prevents this phase transition [39].

3.3 Morphological Analysis

3.3.1 Morphological analysis of fibers

Scanning electron microscopy was used for the investigation of the morphological features. The SEM image of the UHMWPE fiber in form of extracted drawn sample, indicates a smooth surface, round shape and defects. During the drawing process, the as-spun fiber undergoes a transformation into an elongated structure oriented along the axial direction.

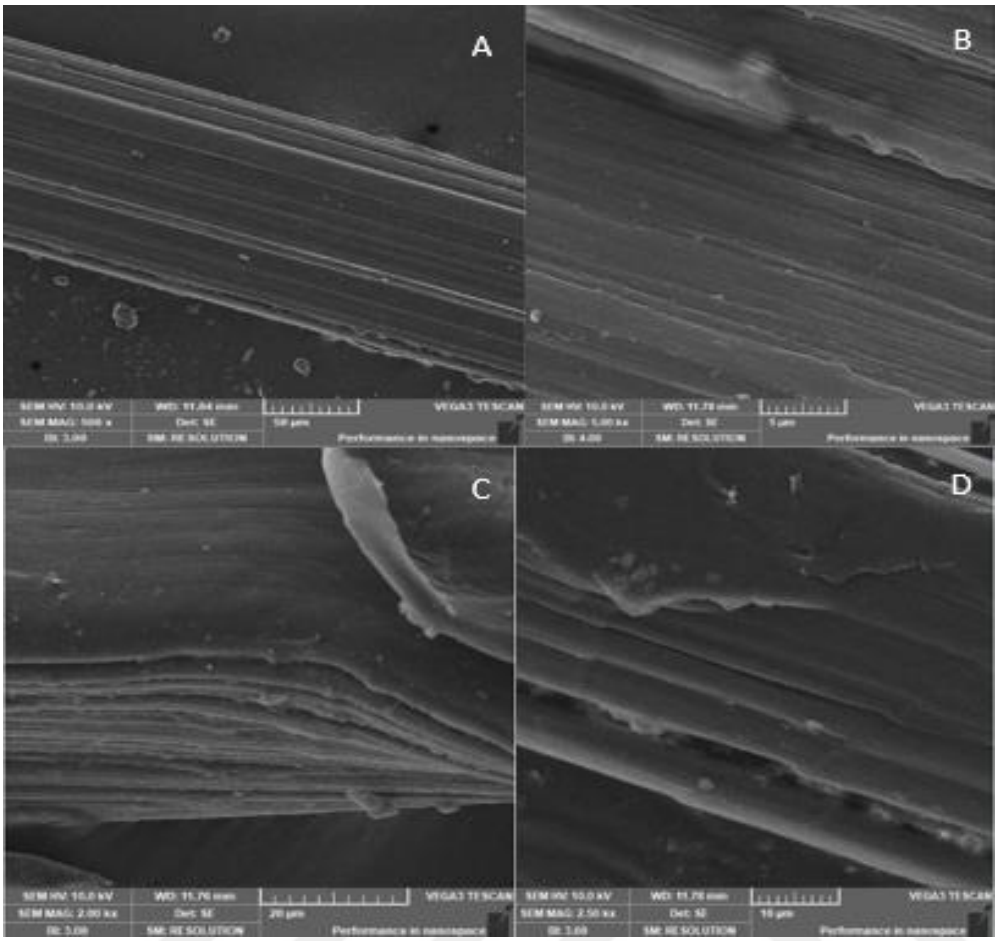

Figure 3.6 : SEM micrograph of extracted drawn UHMWPE fiber.

Continued drawing resulted in a further transformation of the fiber, leading to a more oriented surface structure and a noticeable improvement in surface smoothness. This demonstrated that ultra-high drawing created defects on the surface of the fiber as well as chain segment slip and crystal structure fracture. This defects and microfibril structure can be seen in Figure 3.6. The microfibrillate structure of UHMWPE is characterized by long, thin, and closely packed fibrils. These fibrils have a high aspect ratio (length to width ratio) and are aligned parallel to each other. The alignment of the fibrils gives UHMWPE its exceptional mechanical properties, such as high tensile strength and impact resistance. Simultaneously, subjecting the fiber to an elevated drawing temperature near the melting point of UHMWPE caused partial melting of the surface structure, resulting in prominent cracks and smearing effects which shown in the SEM photograph. During the drawing process, the transformation of the fiber into an axially ordered structure signifies the reorientation and alignments of the polymer chains. This structural transformation plays a crucial role in enhancing the mechanical

properties, including tensile strength and modulus, of the UHMWPE fiber. It significantly contributes to the overall performance improvement of the fiber [30] [15].

3.3.2 Morphological analysis of UHMWPE fiber reinforced composite

The acid treatment and gluteraldehyde grafting, ensures improved bonding between the fiber and the epoxy resin matrix, leading to better adhesion. The treatment also serves to protect the fiber, reduce friction during processing, and address compatibility issues between the fiber and the resin. Overall, the treatment facilitates optimal contact and bonding between the treated fiber and the epoxy resin. UHMWPE fibers are randomly dispersed in the epoxy matrix. The system initially exposed the fibers to a 12 kV corona discharge and acid etching, and the effects of these methods were examined. According to the results, the acid etching method was found to be more effective. SEM images were obtained from three different composite materials. These are untreated UHMWPE fiber reinforced composite, acid etching and acid etching gluteraldehyde grafted UHMWPE fiber reinforced composite.

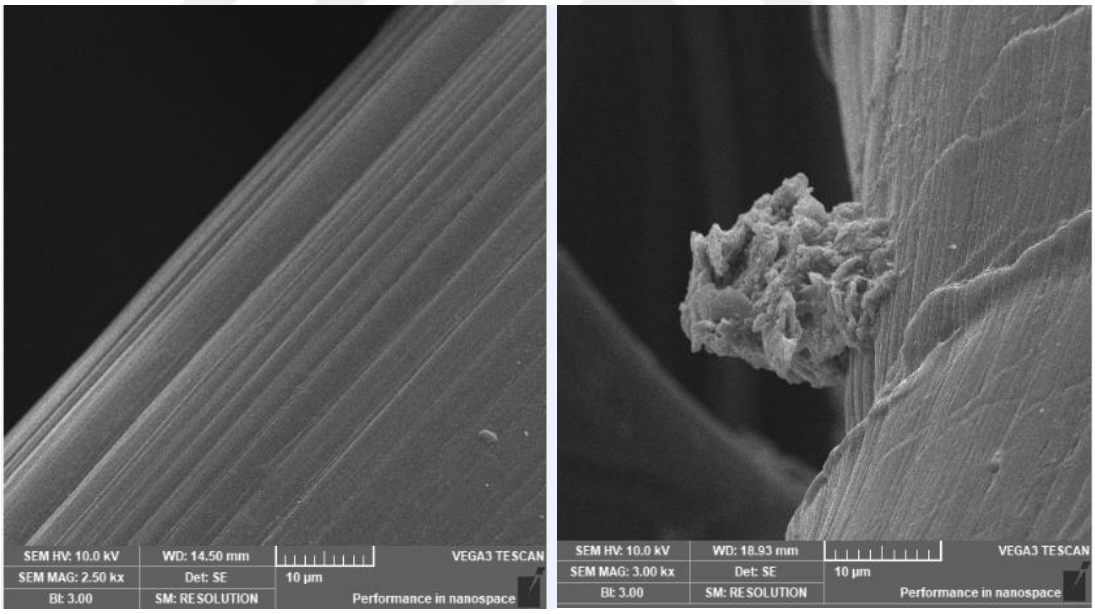

Figure 3.7 : Untreated fiber and acid etched gluteraldehyde grafted fiber.

In order to evaluate the adhesion properties between the matrix and UHMWPE fibers modified by GA, composite was fabricated. Tensile tests were conducted to obtain the average values of the interfacial shear strength (IFSS) as a parameter for adhesion characterization. The average value of the IFSS (interfacial shear strength) represents the adhesion strength between the modified UHMWPE fiber and the matrix material.

It provides an indication of how well the fiber is bonded to the matrix, reflecting the effectiveness of the GA modification in enhancing the interfacial adhesion between the fiber and the matrix. Figure 3.7 shows, untreated and acid treated fiber's SEM micrographs.

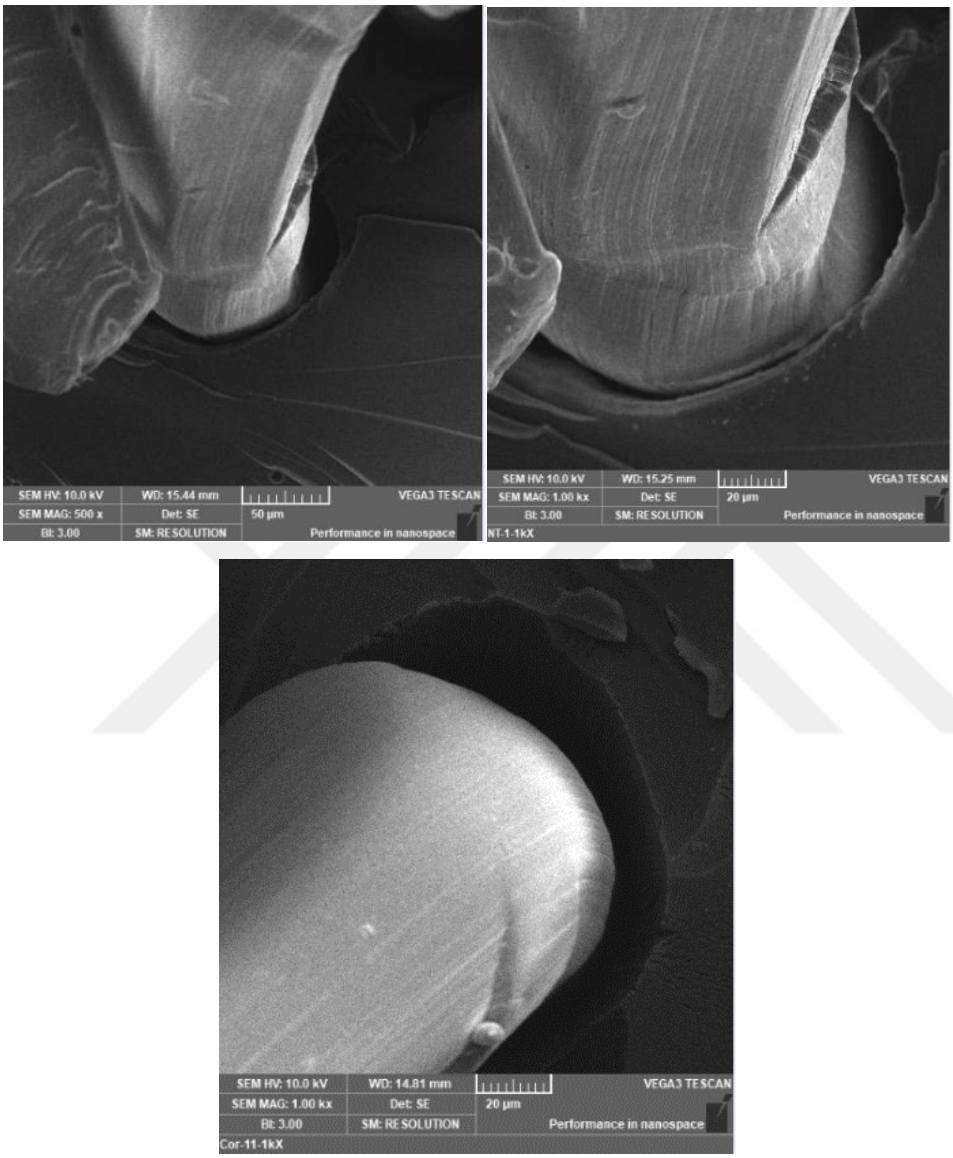

Figure 3.8 : SEM micrographs of untreated fiber/epoxy composite.

Morphological interlocking between fiber and epoxy should be observed for the composite to exhibit superior loading and impact performance. The corona discharge exposed sample indicate that there is poor interaction between the UHMWPE fiber and the epoxy resin. The poor interaction observed could be due to several reasons. One possible reason is the inert nature of UHMWPE, which has low surface energy and limited reactivity with other materials .This can make it difficult for the epoxy

resin to form a strong bond with the UHMWPE fiber. The corona discharge treatment might not have been sufficient to introduce the necessary functional groups or alter the surface chemistry of the UHMWPE fiber effectively. More rigorous corona discharge parameters, is voltage, current might be required to achieve better adhesion between the fiber and the epoxy resin [40]. After the acid etching and gluteraldehyde grafting, we can see on the SEM mirographs which enhance the interlocking and this interlocking can be seen in Figure 3.9. In Figure 3.8, untrated fiber failed to succeed mechanical locking.

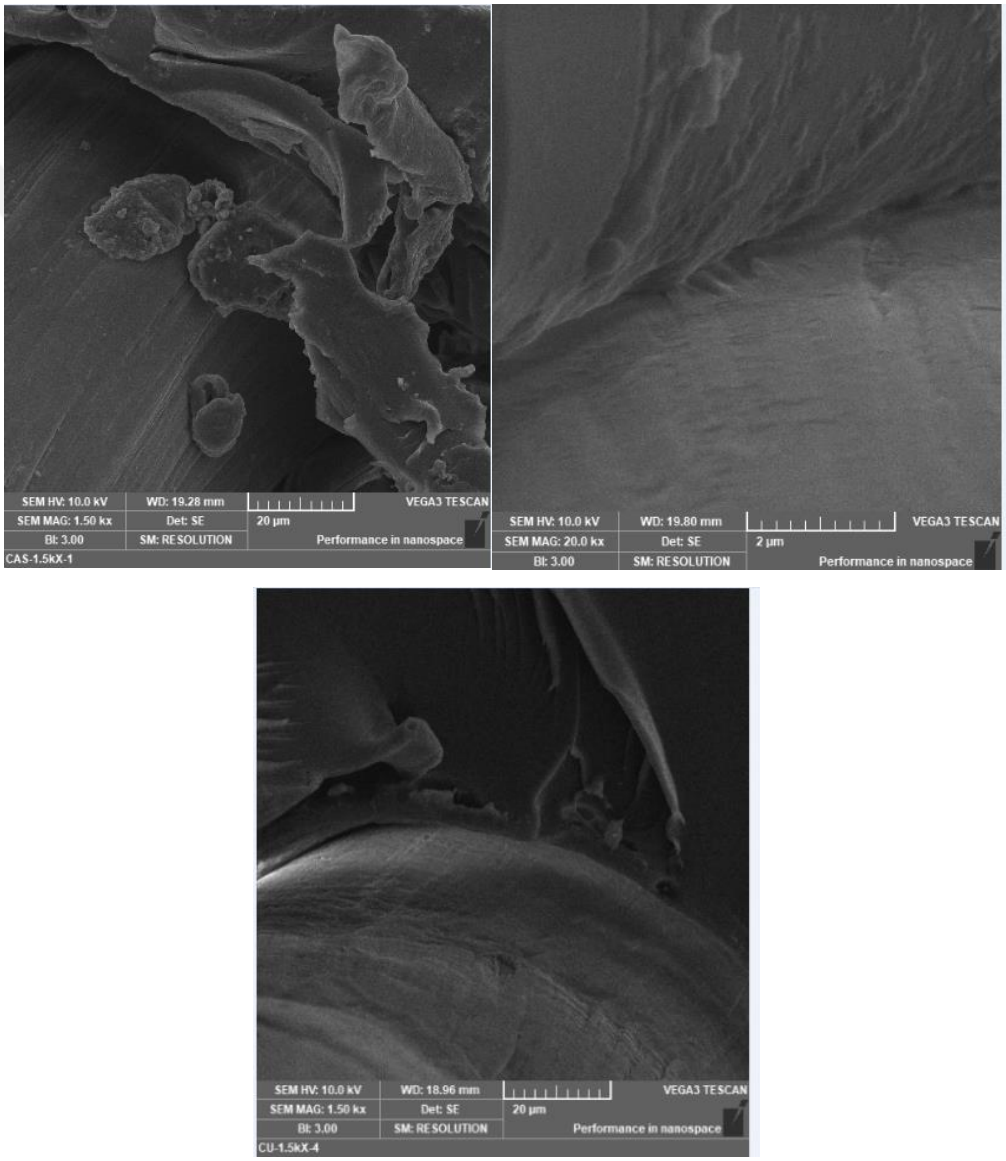

Figure 3.9 : SEM micrographs of acid treated and GA grafted composites.

3.4 FTIR Analysis

The attenuated total reflection fourier transform infrared (ATR-FTIR) test was used to evaluate changes in the UHMWPE fiber surface. The FTIR spectra allow the examination of any changes brought about by the surface treatment procedure through a visual depiction of the molecular vibrations and chemical bonds existing on the fiber surface. When the spectra before and after processing are compared, precise changes in the surface of the UHMWPE fiber can be observed and evaluated.

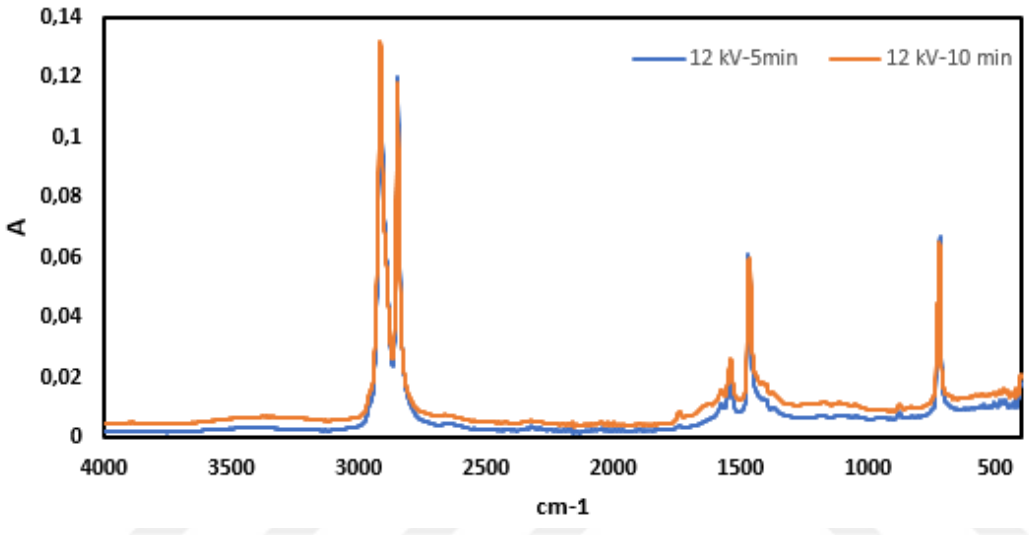

Figure 3.10 : FTIR spectra obtained by different corona discharge time.

Figure 3.10 shows, 12 kV voltage and 10 minute is the best parameter for dry method which we use. The associated spectrum, which shows discrete peaks at particular frequencies, makes it possible to see the distinctive qualities of UHMWPE fibers. The surface chemistry UHMWPE fibers can be observed using the these peaks which corresponds to various molecular motions under IR illumination. ATR method provides chemical structural information about the fiber surface rather than bulk properties. The stretching vibration of the -CH_2 groups in the UHMWPE fiber is shown by the peak at wavelengths of 2910-2850 cm^{-1}. This vibration is related to the motion of the carbon-hydrogen (C-H) bonds in the polymer chain's methylene (-CH2-) units. A second peak, which is associated with the asymmetrical bending vibration of the -CH2 groups, is seen at 1464 cm^{-1}. The bending motion of the carbon-hydrogen (C-H) bonds in the methylene units of the UHMWPE fiber is responsible for this vibration [41]. The treated UHMWPE fiber spectrum may exhibit three new bands not found in the pristine UHMWPE fiber spectrum. These new bands demonstrate how surface

treatment has altered the structure or molecular composition of UHMWPE fibers. Therefore, valuable information about the results of applying specific modifications or functional groups to the UHMWPE fiber surface can be obtained by examining the precise positions and intensities of the bands. Further research and comparison of treated and untreated spectra can help in understanding the effect of surface treatment on the molecular properties of UHMWPE fibers. By using acids to dissolve a tiny layer of material from the UHMWPE fiber's surface, acid etching produces a surface that is rougher and more reactive. Acid etching results in a roughened surface that increases the fiber's surface area and improves surface energy [27]. This inducement improved wetting and adhesion properties between the fiber and the epoxy resin matrix.

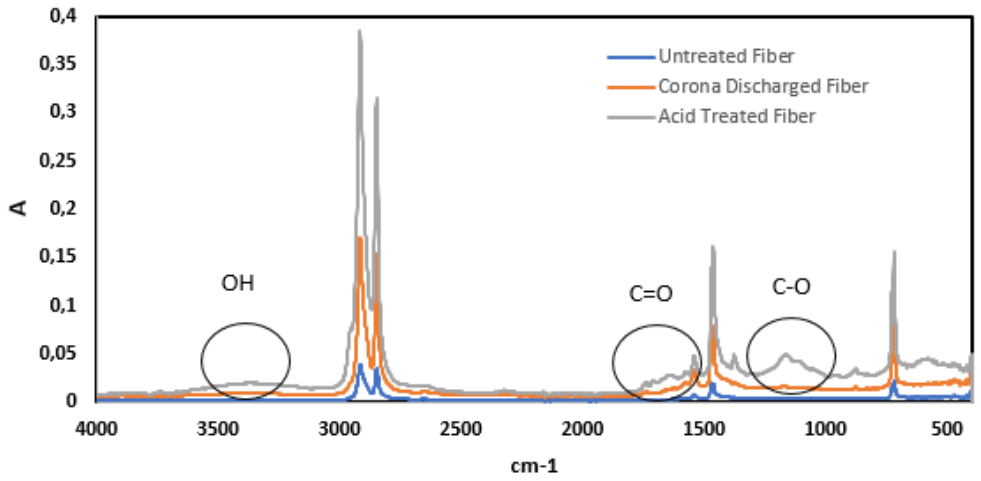

Figure 3.11 : FTIR spectra of untreated, corona treated and acid treated fibers.

The increased surface energy and roughness provide more active sites for chemical reactions and simplify better interfacial bonding with the resin. On the other hand, corona discharge treatment involves subjecting the UHMWPE fiber to high-energy plasma. While corona discharge can modify the surface properties to some extent, it may not produce the same effect of surface functionality as acid etching. The plasma treatment in corona discharge can increase the surface energy to some degree, but it can not create as rough a surface as acid etching. Corona treated samples were evaluated among each other, and the most promising sample set was selected to be the one treated at 12 kV for 10 minute. The FTIR spectral graph belonging to these samples is given in the comparative Figure 3.11. In summary, acid etching is often preferred over corona discharge for achieving better surface functionality, enhanced adhesion, and improved bonding between UHMWPE fibers and epoxy resins through

providing both suface roughness and functional groups [35]. Figure 3.11 shows, acid etching results in better surface functionalization in comparison with corona discharge treatment.

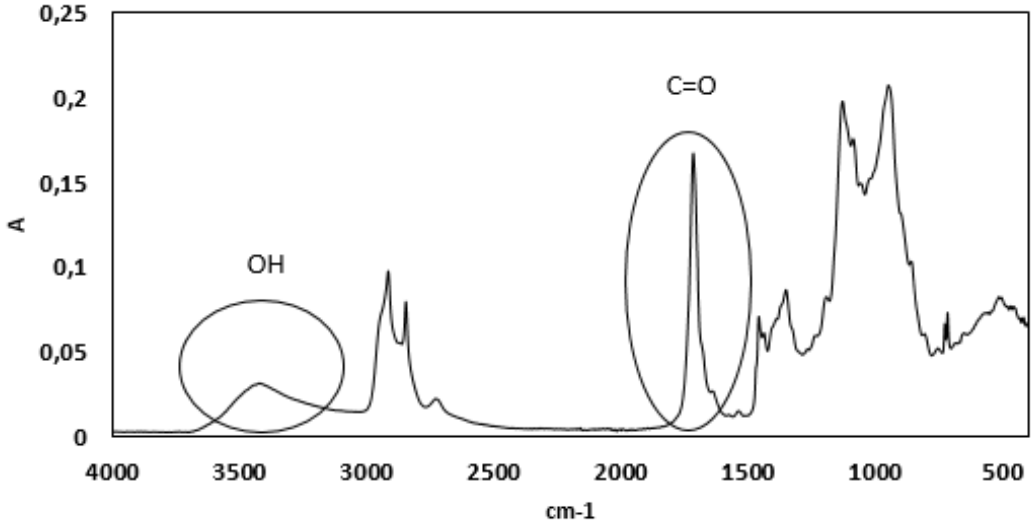

Figure 3.12 : FTIR spectra of pure gluteraldehyde.

Figure 3.13 shows, acetal bridges created as a result of hydroxyl on the fiber and carboxyl on the gluteraldehyde reaction. So C-O-C bonds obtained. This improve the compatibility and adhesion of the treated UHMWPE fibers with other components in composite systems.

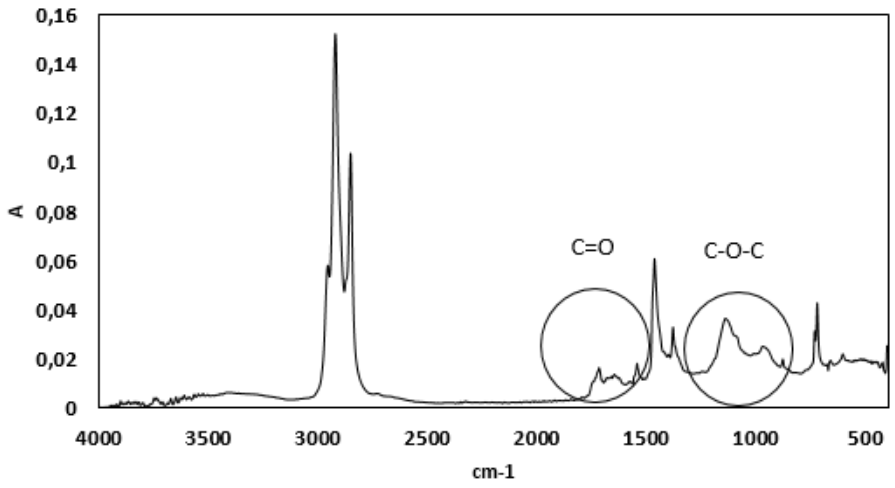

Figure 3.13 : FTIR spectra of gluteraldehyde grafted UHMWPE fiber.

Additionally, the treated UHMWPE fibers exhibit peaks in the FTIR spectrum between 1295 and 1190 cm^{-1}, corresponding to the stretching vibrations of C-O-C bonds. These results imply that the UHMWPE fibers and glutaraldehyde engaged in an acetalization

reaction that produced acetal bridges. The existence of these additional bands is evidence that the surface of the UHMWPE fibers goes through a chemical change during the surface treatment procedure [42]. Figure 3.12 shows, pure gluteraldehyde FTIR spectra. Improved bonding between these surfaces can lead to superior performance and properties of the treated UHMWPE fibers, ultimately improving the overall quality and functionality of the composite. It can specifically support improved strength and stability in particular areas of the fiber. As a result, gluteraldehyde grafted UHMWPE fibers' carboxyl groups on surface were enhanced [43].

4. CONLUSION

• In this thesis, the production of high-performance polyethylene fibers was accomplished using counter rotating twin screw extruder. After paraffin oil extraction, the samples were treated in a hand-made hot drawing unit at a certain temperature, resulting in a important enhancement in mechanical strength.

• The sample showed a tensile strength of 3 GPa when the thickness of sample reduced 40 microns. This reveals that amorphous parts were stretched and most probably oriented. An extensive study on molecular orientation of high performance PE fibers will be performed in our future studies.

• It was observed that the microfibril structure developed with the increase in the drawing ratio. A high rate of oriented and microfibrillated structure was observed in the structure of the UHMWPE fiber, which was drawn at a certain temperature.

• Two smaller but recently formed endotherms were discovered to the right of the primary melting endotherm at temperatures about 151.1 °C and 156.2 °C for extracted and drawn UHMWPE fiber samples about drawing ratios close to 40.

• While chemical etching and corona discharge is the commonly used methods to improve the interaction between fibers and epoxy resin, chemical etching method has been more successful in forming functional groups. Glutaraldehyde was grafted to the acid treated fiber. It appeared from the SEM images and mechanical test results that the interface adhesion was improved. According to the tensile test results, untreated fiber and epoxy resin composites tensile strength increased by 72.16%. When glutaraldehyde grafting was applied to the fiber, the tensile strength was increased by 99.35%.

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