GAZİANTEP UNIVERSITY GRADUATE
SCHOOL OF NATURAL & APPLIED SCIENCES

ELECTROSPINNING OF THERMOPLASTIC POLYURETHANE (TPU) FOR PRODUCING NANOFIBERS

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IN
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MEHMET DAŞDEMİR
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Electrospinning of Thermoplastic Polyurethane (TPU) for Producing Nanofibers

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ABSTRACT

ELECTROSPINNING OF THERMOPLASTIC POLYURETHANE (TPU) FOR PRODUCING NANOFIBERS

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Fibers are the main building blocks of all textile structures. Fabrics, yarns, and other textiles are constructed by fibers which directly affect the finished products in functionality and performance. Fine fibers have increasingly been used in textile products due to the fact that the handling and performance of yarns and fabrics constructed by fine fibers are more preferable than the coarse fibers. In terms of fibers, "*nano*" refers to the diameter of the fiber. Generally speaking, nanofibers have diameters less than one micron and cannot be seen without visual amplification. In the nanometer range, electrospinning technique has been proved to be convenient, effective and has been used for processing many fibers.

In this study, solution electrospinning and melt electrospinning setups were established in order to produce nanofibers from thermoplastic polyurethane (TPU). In solution electrospinning process solution concentration, applied voltage and distance from tip of the needle to collector were used as experimental parameters while in melt electrospinning process processing temperature, applied voltage and distance from spinneret exit to collector were used. The electrospinning processes of TPU fibers obtained in two different setups have been observed. Finally the results obtained by evaluating samples which were formed by two different electrospinning setups are discussed visually and statistically.

Key words: Electrospinning, nanofiber, thermoplastic polyurethane (TPU)

ÖZET

ELEKTRO-ÜRETİM YÖNTEMİ İLE TERMOPLASTİK POLİÜRETANDAN (TPU) NANOLİF ELDESİ

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Lif, tekstil malzemelerinin oluşturulması için gerekli temel yapı birimidir. Kumaşları, iplikleri ve diğer tekstil malzemelerini oluşturan lifler, son ürünün işlevsellik ve performans özelliklerini belirleyici bir rol oynar. Bu tekstil malzemelerinde, yumuşak tuşe ve yüksek kullanım performansları istenildiğinde ise çoğunlukla ince lifler tercih edilir. Bu ince lifler, mikro ve nano çaptaki liflerdir. Mikro çaptaki lifler günümüzde birçok üründe yaygın olarak kullanılmaktadır. Nanolifler, bir micron ve altındaki çapa sahip olan lifler olup insan gözü ile görülmesi çok güçtür. Nanolif eldesi için kullanılan en güvenilir ve etkili yöntem ise elektro-üretim (electrospinning) yöntemidir.

Bu çalışmada, termoplastik poliüretandan (TPU) nanolif elde etmek için solüsyon elektro-üretim düzeneği ile eriyik elektro-üretim düzeneği kurulmuştur. Solüsyon elektro-üretim düzeneğinde TPU konsantrasyonu, uygulanan voltaj ve iğne ucu ile toplayıcı arası uzaklık değerleri deney değişkenleri olarak kullanılmıştır. Eriyik elektro-üretim düzeneğinde ise işlem sıcaklığı, uygulanan voltaj ve düze ile toplayıcı arası uzaklık deney değişkenleri olarak kullanılmıştır. İki farklı düzeneğin kullanıldığı TPU liflerinin elektro-üretimi gözlemlenmiştir. Sonuçlar, bu sistemlerle üretilmiş örneklerin ve örneklerden alınan taramalı elektron mikro fotoğraflarının (SEM = Scanning Electron Micrographs) incelenmesi ile, görsel ve istatistiksel olarak yorumlanmıştır.

Anahtar Kelimeler: Elektro-üretim, nanolif, termoplastik poliüretan (TPU)

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LIST OF ABREVIATIONS

AC	Alternative current
CA	Cellulose acetate
CNT	Carbon nano tubes
DC	Direct current
DMF	Dimethylformamide
DSC	Differential scanning calorimetry
ES	Electrospun
FESEM	Field emmission scanning electron microscope
GNF	Graphite nanofibers
HFIP	Hexa-fluoro-isopropanol
MB	Meltblown
Mt	Montmorillonnite
nm	Nanometer
NSF	National Science Foundation
OAUGDP	One atmosphere uniform glow discharge plasma
PA	Polyamid (nylon)
PAN	Polyacrylonitrile
PC	Polycarbonate
PCL	Polycaprolactam
PE	Polyethylene
PEN	Polyethylene naphthalate
PEO	Polyethylene oxide
PET	Polyethylene terephtalate
PP	Polypropylene
PU	Polyurethane
PVA	Polyvinyl alcohol
PVC	Polyvinylchloride
SEM	Scanning electron micrograph
TGA	Thermogravimetric analysis
THF	Tetrahydrofuran
TPU	Thermoplastic polyurethane
US	United States
µm	Micrometer

CHAPTER 1
INTRODUCTION

1.1. Introduction

Since the existence of human beings, the textiles have been indispensable for people. At the beginning, people began to wear simple clothes for the purpose of covering and preventing themselves. Then, people wore the fabrics produced with natural fibers, which had good appearance. The fibers based on modified cellulose made by Chardonnet in 1885 was known as the first synthetic fiber. Especially, the invention of nylon, by Dupont in 1935, propelled a rapid development in the textile industry.

Fibers are main building blocks of textiles. Fabrics, yarns, and other textiles are constructed by fibers which directly affect the finished product in the functionality and performance.

Fine fibers have increasingly been used in textile products due to the fact that the handling and performance of yarns and fabrics constructed by fine fibers are more preferable than the coarse fibers. They have good handling, better appearance, increased stain resistance and improved wrinkle resistance. For instance, the fabrics made by cotton having low micronaire value (very fine) that have high selling prize, are more comfortable. Additionally, the clothes produced with synthetic microfibers, which have a function of resistance to hard weather conditions, are light and comfortable.

Production of fine synthetic fibers with limited fineness can be realised by the conventional fiber processing methods, such as melt spinning, dry spinning and wet spinning. Especially, melt spinning is widely used to produce very fine fibers which have a diameter of several micrometers. However, spinning and drawing of the molten polymer in melt spinning process can process in a limited range.

Within the past decade, the industry has rediscovered and continued to develop technologies that enable production of extremely small fibers “*nanofibers*” using a process called "*electrospinning*" [1]. With regard to fibers, "*nano*" refers to the diameter of the fiber. Generally speaking, nanofibers have diameters less than one micron and cannot be seen without visual amplification. In the nanometer range, electrospinning technique has been proved to be convenient, effective and has processed many fibers. Moreover, long and continuous nanofibers can be produced in a simple manner by the process of electrospinning.

Nanofibers are able to form a highly porous mesh and their large surface-to-volume ratio improves performance for many applications. Electrospinning has the unique ability to produce nanofibers of different materials in various fibrous assemblies. The relatively high production rate and simplicity of the setup makes electrospinning highly attractive to both academia and industry. A variety of nanofibers can be made for applications in energy storage, healthcare, biotechnology, environmental engineering, and defense and security [2].

In electrospinning, electrostatic forces are used in addition to mechanical forces to drive the fiber forming process [3]. Simply stated, electrospinning is a process that uses the electrostatic attraction between a charged polymer and a grounded or oppositely charged collection plate to produce extremely fine fibers ranging in diameter from less than 10 nanometers (nm) to several micrometers. Recent developments have shown it can be performed on polymers both in the molten state and in solution [1].

The commercialization of electrospinning has not been come off yet, however more than 100 patents for electrospinning polymer melts and solutions have been filled in the past 70 years. Therefore, many institutions and researchers have been studying to improve the process and design a commercial electrospinning machine.

1.2. Objective of Thesis

The first objective of this work is to explore the processing of electrospinning in the production of nanofibers. Electrospinning of polymers, in both melt and solution, was investigated on the experimental set up that was designed to achive this goal.

The second objective is to produce nanofibers with thermoplastic polyurethane (TPU) polymer in solution and melt state by using electrospinning technique.

Furthermore, special designed apparatus for processing TPU were used to compare and contrast the processes of melt and solution electrospinning.

The last objective is to characterize the electrospun fibers qualitatively and quantitatively using scanning electron microscopy (SEM).

In addition to these, the main objective of this study is to produce nanofibers from TPU polymer for taking advantages of this polymer in textile industry. Hence, it has high stretchable ability and soft handling.

1.3. Structure of Thesis

Chapter 2 is named as “Nanofibers”. The main purpose of this chapter is to give basic information about nanofibers. In this chapter, the term of nano is explained firstly. Then nanotechnology and nanotechnology in textiles are discussed. Finally, nanofibers, production methods of nanofibers, and application areas of nanofibers are explained in detailed form.

Chapter 3 is named as “Electrospinning Process”. This chapter gives a detailed description about electrospinning process. Historical background and theory of the process are given in detailed form. In addition to these, the literature survey on electrospinning of polyurethane is mentioned.

Chapter 4, “Materials and Methods” includes the explanation of the apparatus and parts of the experimental set-ups which were used in the experiments. Also, the laboratory test equipments used in the characterization of nanofibers are presented.

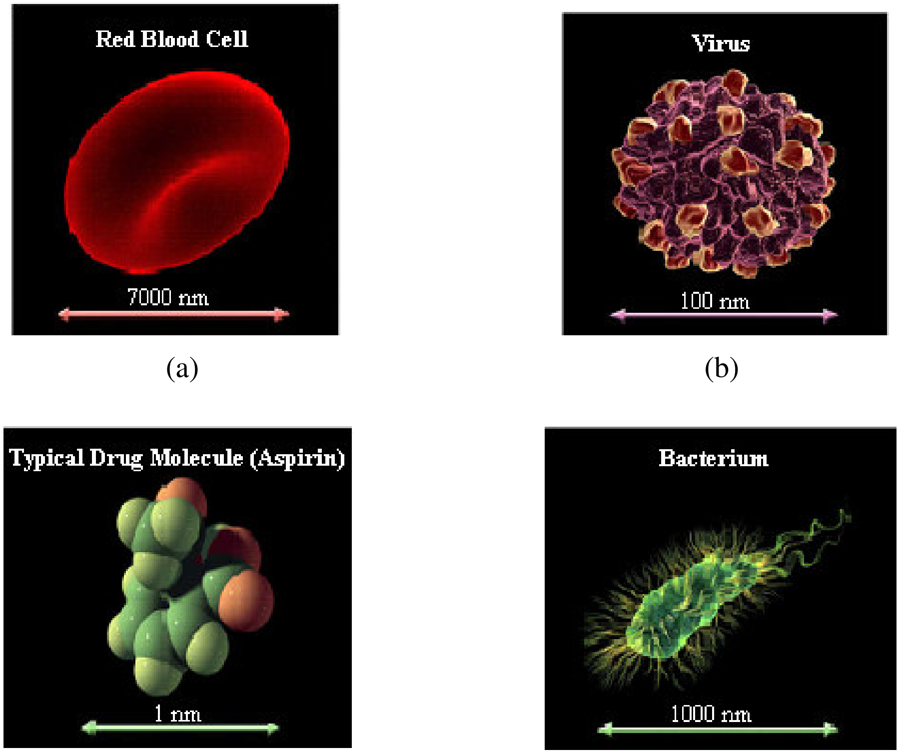
Experimental observations and results are given in Chapter 5 as “Results and Discussions”. Moreover, discussions of the results are included in this chapter.

The conclusion of the thesis and recommendations on the experimental set-up for further studies are given in Chapter 6 as “Conclusions and Recommendations For Further Work”.

CHAPTER 2
NANOFIBER

2.1. Introduction

The word ‘nano’ meaning ‘dwarf’ in Greek language refers to dimensions on the order of magnitude of 10^{-9} [4]. A “nanometer” (nm) equals one billionth of a meter. One human hair is about 80,000 nanometers thick. It takes ten atoms of hydrogen side-by-side to equal one nanometer. A DNA molecule is about 2.5 nm wide. A red blood cell is vast in comparison: about 7,000 nm in diameter. Everything on the nano-scale is invisible to the unaided eye and even to all but the most powerful microscopes [5]. To illustrate, some microscope images are shown in Figure 2.1.



(a) (b)

(c) (d)

Figure 2.1 Microscope images of (a) A red blood cell, (b) A virus, (c) An aspirin, (d) A bacterium [6]

2.2. Nanotechnology

Nanotechnology is usually thought as “engineering at the atomic scale”. The term of “nanotechnology” refers to engineered structures, devices, materials and systems that have a length of submicron. At this length, materials begin to exhibit distinct properties that affect their physical, chemical and biological behavior. The physical, chemical, and biological characteristics of materials differ in basic and functional ways from the properties of individual atoms and molecules or bulk matter. Therefore, nanotechnology is a multidisciplinary science including chemistry, physics, material, medicine, textiles, etc. Additionally, it encompasses engineering and technology that involves imaging, measuring, modeling, and manipulating at the nano scale.

The nanometer length scale is unique because it makes it possible to change the fundamental properties of materials without altering their chemical composition. Particles at the nano scale, or nano particles, have very high surface areas, and their behavior and mobility can be changed. This creates unlimited possibilities for products and applications [7].

Many scientists and experts believe that the nanotechnology will be the next industrial revolution and the key to a future enabling new opportunities and applications.

In the past fifteen years, global attention and worldwide investment in nanotechnology have been remarkably rising. Thus, research and development studies have increased sharply. For instance, United States Federal Funding for nanotechnology research and development has increased substantially since inception of the NNI, from $464 million in 2001 to an estimated $1,081 million in 2005 [8].

The United States is not the only country to recognize the tremendous economic potential of nanotechnology. While difficult to measure accurately, some have estimated that worldwide government funding has increased to about five times what it was in 1997, exceeding $2 billion in 2002. Asian countries, including Japan, China and Korea, as well as several European countries, have made leadership in nanotechnology national priorities [8].

Nanotechnology has the potential to profoundly change our economy and to improve our standard of living, in a manner not unlike the impact made by advances over the past two decades by information technology. While commercial products are starting to come to market, some of the major applications for nanotechnology are five to ten years out. Private investors look for shorter-term returns on investment, more in the range of one to three years. Consequently, government support for basic research and development in its early stages is required in order to realize nanotechnology's full potential and to maintain a competitive position in the worldwide nanotechnology marketplace [8].

Global market for nanotechnology applications in the life sciences by technology type in 2004, 2005, and 2010 is given in Figure 2.2. When the graph is examined, it is clear that there is a huge increase in global market for nanotechnology applications. For instance, while solid nano particles had a market of $180 million in 2004, they had a market of $360 million in 2005. It is estimated that the global market of solid nano particles will be $1350 million in 2010 [5].

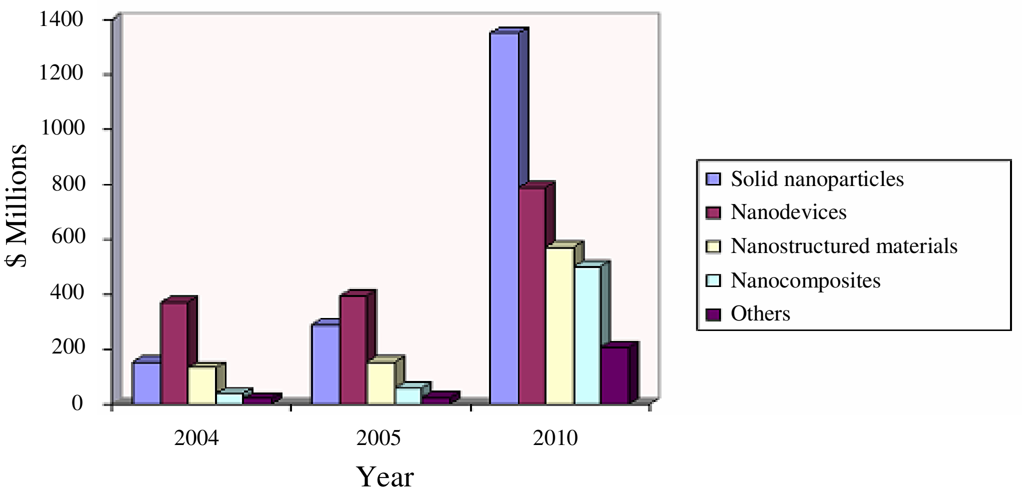


Figure 2.2 Global market for nanotechnology applications in the life sciences by technology type, 2004, 2005 and 2010 ($ Millions) [5]

According to the current estimates, about 20,000 researchers in worldwide are working in nanotechnology research and development, which is directed toward understanding and creating improved materials, devices, and systems that exploit new properties [8].

2.3. Nanotechnology in Textiles

The innovations in the textile industry contains the development of recent products to deal with present consumer demand as well as process innovation that provides lower costs, higher capacity and better quality. Nanotechnology in textile industry aims to create smaller materials and to produce products with them, which have excellent properties such as high performance, a variety of functionality, and better quality. In addition, nanotechnology enables to increase the value of the textile products.

The textile industry could be affected quite significantly by nanotechnology, with some estimates talking of a market impact of hundreds of billions of dollars over the next decade [9]. The market for textiles making use of nanotechnologies nano-textiles will reach $13.6 billion by 2007, climbing dramatically to reach $115 billion by 2012. Highest growth rates will be seen outside the traditional apparel and home applications, where demand for performance improvements rather than cost reduction will drive the rapid adoption of nanotechnologies [10].

Nano science has already produced stain and wrinkle resistant clothing, and future developments will focus on upgrading existing functions and performances of textile materials and developing “smart” textiles with unprecedented functions such as;

- Sensors and information acquisition and transfer.
- Multiple and sophisticated protection and detection,
- Health-care and wound-healing functions,
- Self-cleaning and repair functions [9].

US Company Nano-Tex [11] is already marketing its NanoCare stain and wrinkle resistant technology, and NanoFresh (to freshen sports clothing) is expected soon. Scientists at the Hong Kong Polytechnic University have built a nano layer of particles of titanium dioxide, a substance that reacts with sunlight to break down dirt and other organic material. This layer can be coated on cotton to keep the fabric clean. Clothes simply need to be exposed to natural or ultraviolet light for the cleaning process to begin. Once triggered by sunlight, clothing made out of the fabric will be able to get rid itself of dirt, pollutants and micro-organisms. The whole laundry industry would be affected if the technology proves to be economically viable [9].

One of the applications in textiles is freshness of textiles. A company, named Ciba [12], modifies fibres on the basis of nano container microcapsules that either prevents bacterial growth by releasing antimicrobiotics or by absorbing odors. The fabric on the right of the Figure 2.3 is hydrophobic i.e. it does not absorb water. By contrast, the fabric on the left has not been treated and is absorbing water [13].

Figure 2.3 Freshness of textile application by Ciba [13]

Another example is pilot production of non-aggregated ceramic powders as raw materials for textile refinement and EMPA’s [14] nanopowder pilot facility. The nano particles that are produced in the facility as “dwarfs with the strength of giants”: 30 grams of powder have the same surface area as a football pitch. Potential areas of application are the creation of materials with better flame-retardant properties and a reduced propensity for heat development, self-cleaning surfaces and more [13].

Research involving nanotechnology to improve performances or to create new functions is most advanced in nano structured composite fibers employing nano size fillers such as nano particles (clay, metal oxides, and carbon black), graphite nanofibers (GNF) and carbon nano tubes (CNT) [9].

The main function of nano size fillers is to increase mechanical strength and improve physical properties such as conductivity and antistatic behaviors. Being evenly distributed in polymer matrices, nano particles can carry load and increase the toughness and abrasion resistance; nanofibers can transfer stress away from polymer matrices and enhance tensile strength of composite fibers. Additional physical and chemical performances imparted to composite fibers vary with specific properties of the nano fillers used [9].

2.4. What is nanofiber?

With regard to fibers, “nano” refers to the diameter of the fiber. According to the National Science Foundation (NSF), nano materials are matters that have at least one dimension equal to or less than 100 nanometers [15]. However some scientists accept the nanofibers as less than 1 micron, while others describe them as less than 100 nanometers. To understand the dimension of nanofibers, some natural and artificial fiber diameters are given in Table 2.1.

Table 2.1 Diameters of selected natural and artificial fibers [16]

Material	**The Mean Diameter (nanometers)**	**Coefficient of Variation (%)**
Merino wool	25500	25.6
Nylon 6 filament	16200	3.1
Kevlar 29	13800	6.1
Polyester	13300	2.4
Spider silk	3570	14.8

Nanofibers are solid state linear nano materials which cannot be seen without visual amplification. Microscopic visuality of the nanofibres and a human hair is shown in the Figure 2.4.

Considering the potential opportunities, being produced with simple equipments and requiring low power provided by nanofibers are increasing interests in nanofiber technology.

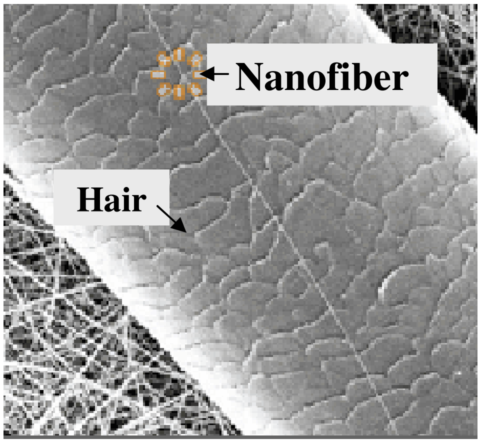


Figure 2.4 Human hair with nanofiber

2.5. Advantages of Nanofibers

Materials in fiber form are of great practical and fundamental importance. The combination of high specific surface area, flexibility and superior directional strength makes fiber a preferred material form for many applications ranging from clothing to reinforcements for aerospace structures. Fibrous materials in nanometer scale are the fundamental building blocks of living systems. From the 1.5 nm double helix strand of DNA molecules, including cytoskeleton filaments with diameters around 30 nm, to sensory cells such as hair cells and rod cells of the eyes, nano scale fibers form the extra-cellular matrices or the multifunctional structural backbone for tissues and organs. Specific junctions between these cells conduct electrical and chemical signals that result from various kinds of stimulation. The signals direct normal functions of the cells such as energy storage, information storage and retrieval, tissue regeneration, and sensing [17].

One of the main goals for nanofibers has been to produce the strength they should theoretically possess. In conventional fibers produced today, there are fairly defined limitations to the percentage of crystallinity that can be obtained in a fiber/yarn form. For example, the actual thickness of a carbon/carbon bond is approximately 1 nm. If a 5-nm-diameter fiber is produced, the molecular chains are effectively forced to align in a highly crystalline manner. Ideally, the resultant strength of the fiber produced will be determined by the strength of the carbon/carbon bond in the molecular chains of the polymer [1].

Another potential benefit of nanofiber technology is the tremendous increase in surface-area-to-weight or -volume ratios. The lure of nanotechnology stems from the possibility of redefining these limitations. If the fibers can be collected individually and aligned to specific orientations, it is possible to increase the maximum volume fraction of fibers in a matrix, thus increasing the material's strength. The increased surface-area-to-weight ratio also will allow for improved bonding with the matrix to help prevent failure due to pullout of the fibers [1].

For fibers having diameters from 5 to 1000 nanometers, as shown in Figure 2.5, the surface area per unit mass is around 10 to 1000 m^2 per kilogram. In nanofibers that are three nanometers in diameter, and which include approximately 40 molecules; about half of the molecules are on the surface.

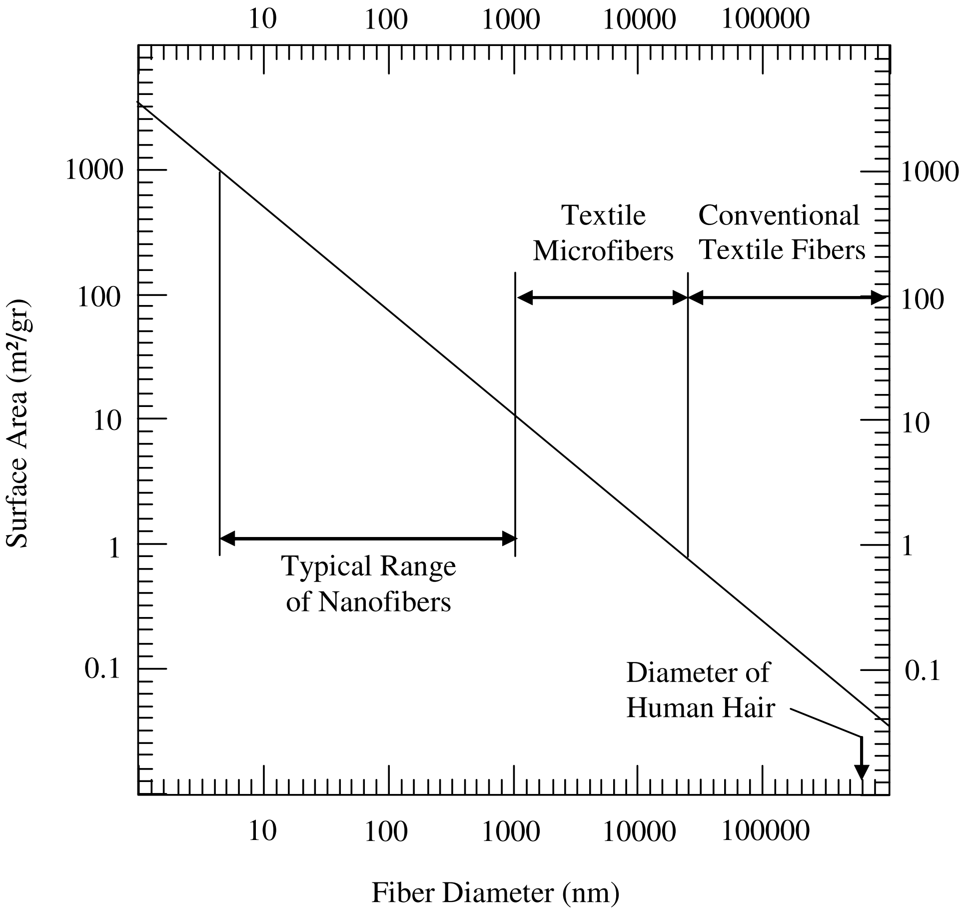


Figure 2.5 Effect of fiber diameter on surface area [17]

Other aspects of the nanofibres are given at below:

- High performance in the filtration.
- In the properties of fabric performance such as water proofing, stain resistance, wrinkle resistance increase to great extent.
- The ability to control pore size.
- Good and soft handling.
- Low basis weight.

2.6. Production Methods of Nanofibers

Polymeric nanofibers can be processed by a number of techniques such as Drawing, Template Synthesis, Phase Separation, Self-Assembly and Electrospinning, which are briefly reviewed in this section. A comparison of the various issues relating to these processing methods can be found in Tables 2.2 and 2.3 [18].

Table 2.2 Comparison of processing techniques for obtaining nanofibers [18]

Process	**Technological advances**	**Can the process be scaled?**	**Repeatability**	**Convenient to process?**	**Control on fiber dimensions**
Drawing	Laboratory	X	√	√	X
Template Synthesis	Laboratory	X	√	√	√
Phase Separation	Laboratory	X	√	√	X
Self-Assembly	Laboratory	X	√	X	X
Electrospinning	Laboratory (with potential for industrial processing)	√	√	√	√

Table 2.3 Advantages and disadvantages of various processing techniques [18]

Process	**Advantages**	**Disadvantages**
Drawing	Minimum equipment requirement.	Discontinuous process
Template Synthesis	Fibers of different diameters can be easily achieved by using different templates.	
Phase Separation	Minimum equipment requirement. Process can directly fabricate a nanofiber matrix. Batch-to-batch consistency is achieved easily. Mechanical properties of the matrix can be tailored by adjusting polymer concentration.	Limited to specific polymers
Self-Assembly	Good for obtaining smaller nanofibers.	Complex process
Electrospinning	Cost effective. Long, continuous nanofibers can be produced.	Jet instability

2.6.1. Drawing

Nanofibers have been fabricated with citrate molecules through the process of drawing. A micropipette with a diameter of a few micrometers was dipped into the droplet near the contact line using a micromanipulator. The micropipette was then withdrawn from the liquid and moved at a speed of approximately $1x10^{-4}ms^{-1}$, resulting in a nanofiber being pulled. The pulled fiber was deposited on the surface by touching it with the end of the micropipette (seen in Figure 2.6). The drawing of nanofibers was repeated several times on every droplet [18].

Drawing a fiber requires a viscoelastic material that can undergo strong deformations while being cohesive enough to support the stresses developed during pilling. The drawing process can be considered as dry spinning at a molecular level [18].

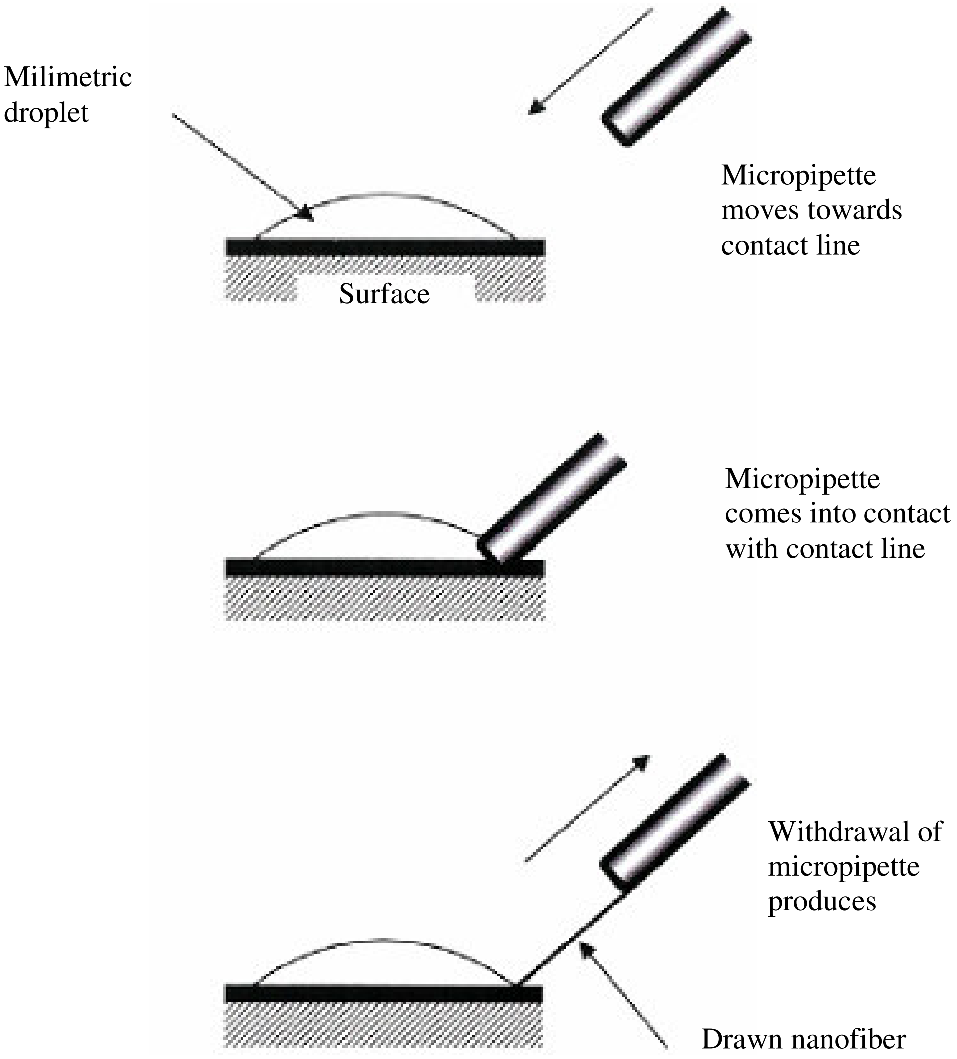


Figure 2.6 Obtaining nanofibers by drawing [18]

2.6.2. Template synthesis

Template synthesis implies the use of a template or mold to obtain a desired structure [16]. The template refers to a metal oxide membrane with through thickness pores of nano-scale diameter (seen in Figure 2.7). Under the application of water pressure on one side and restrain from the porous membrane causes extrusion of the polymer which, upon coming into contact with a solidifying solution, gives rise to nanofibers whose diameters are determined by the pores [18].

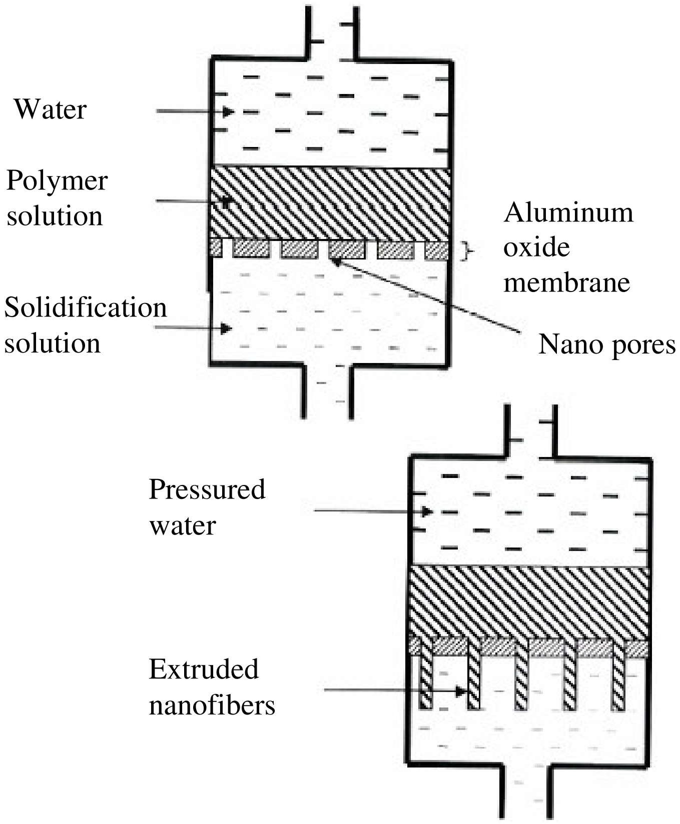


Figure 2.7 Obtaining nanofibers by template synthesis [18]

2.6.3. Phase separation

In phase separation, a polymer is firstly mixed with a solvent before undergoing gelation. The main mechanism in this process is the separation of phases due to physical incompatibility. One of the phases which are that of the solvent is then extracted, leaving behind the other remaining phase. A simplified generic representation of phase separation is shown in the Figure 2.8 [18].

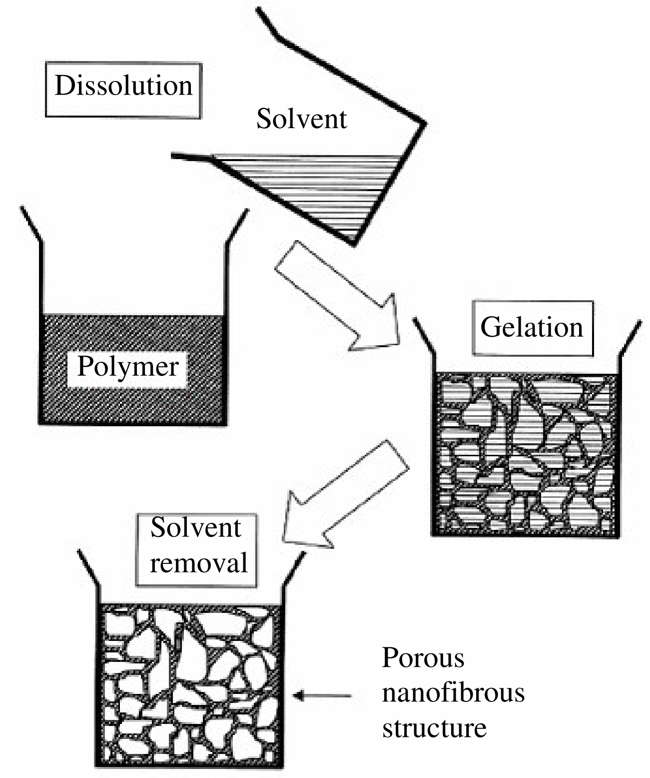


Figure 2.8 Generic schematics of phase separation for obtaining nanofibrous structure [18]

2.6.4. Self-assembly

In general, self-assembly of nanofibers refer to the build-up of nanofibers using smaller molecules as basic building blocks. Figure 2.9 shows a simple schematic of self assembly for obtaining nanofibers. Here, a small molecule (seen in Figure 2.9 top) is arranged in a concentric manner such that bonds can form among the concentrically arranged small molecules (seen in Figure 2.9 middle) which upon extension in the plane's normal gives the longitudinal axis of a nanofiber (seen in Figure 2.9 bottom). The main mechanism for a generic self-assembly is the intermolecular forces that bring the smaller units together and the shape of the smaller units of molecules which determine the over shape of the macromolecular nanofiber [18].

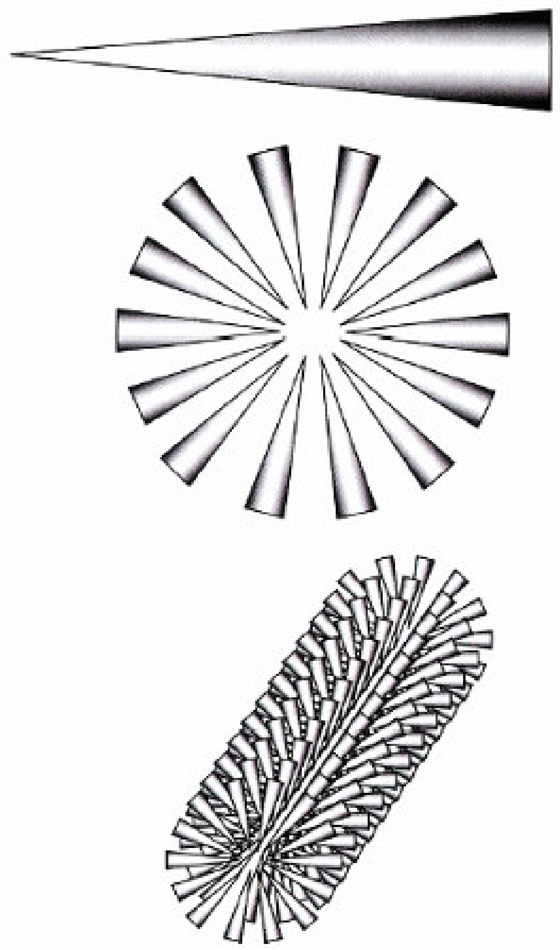


Figure 2.9 An example of self-assembly for obtaining nanofibers [18]

2.6.5. Electrospinning process

Electrospinning is the most advantageous and effective method for producing nanofibers. Long and continuous fibers can be produced with a wide range of polymer solutions and melts. By using this process to produce fibers is easy and cheap. This process will be discussed detailed in the Chapter 3.

2.7. Applications of Nanofibers

In the constructions made by nanofibers, the high volume to weight ratio, soft handling, and high strength and to form barrier to microorganisms and small particles etc. are the main reasons for using them in many applications. These advantages of nanofibers make them very appealing for a broad array of potential applications in many industry segments. Nanofiber applications are shown in Figure 2.10.

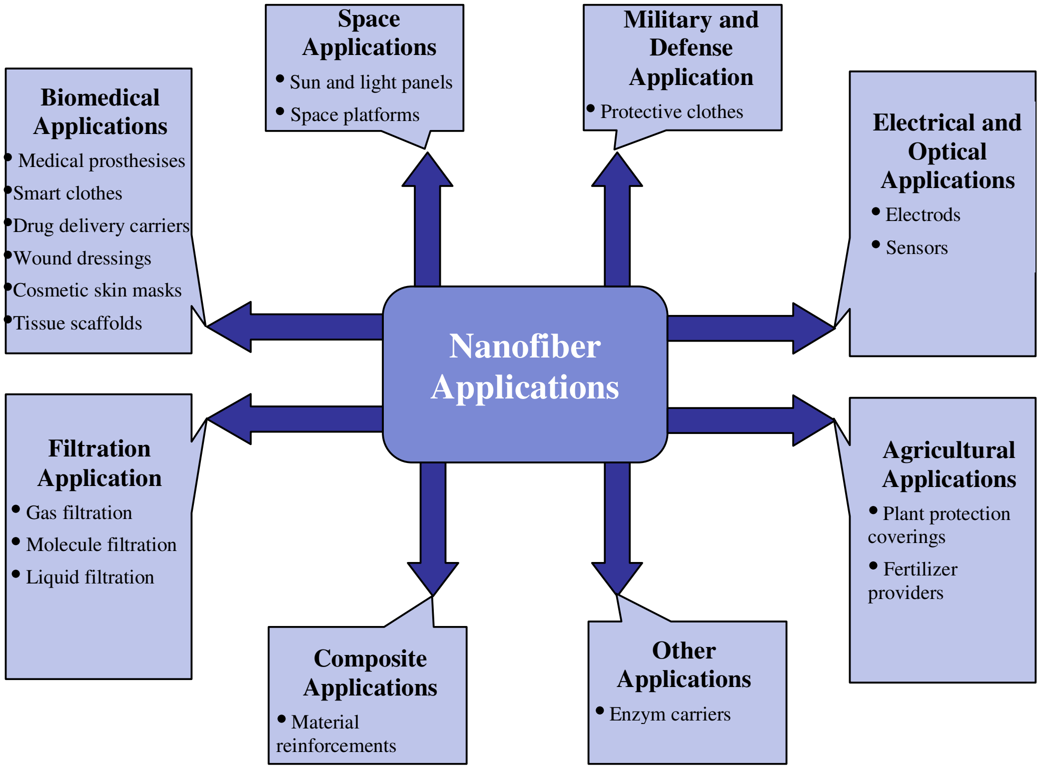


Figure 2.10 Application areas of nanofibers [19]

2.7.1. Filtration applications

Small fibers in the submicron range, in comparison with larger ones, are well known to provide better filter efficiency at the same pressure drop in the interception and inertial impaction regimes [20].

The filtration industry has begun utilizing nanofibers, and in some cases has generated commercially available products. With differing fiber diameters, the pore size of the mat can be controlled to a fairly high degree. As a result, nano fibrous mats can be designed to block out molecules of specific sizes [1].

Electrospun nanofibers, with fiber diameters of 0.25 microns have been used in industrial, consumer and defense filtration applications for more than twenty years. Electrospun nanofibers have fiber diameters that are 5-10 times smaller than the smallest meltblown fibers available. Recently, Ultra-Web® nanofiber filter media from Donaldson Company [21] has become available to the non-wovens and filtration industries for a broad range of filtration applications. Figure 2.11 is a photo micrograph of commercially-available nanofibers electrospun onto a cellulose substrate for air filtration applications. The nanofiber diameter is approximately 250 nanometers, as compared to the cellulosic fiber structure, with diameters exceeding 10 microns [20].

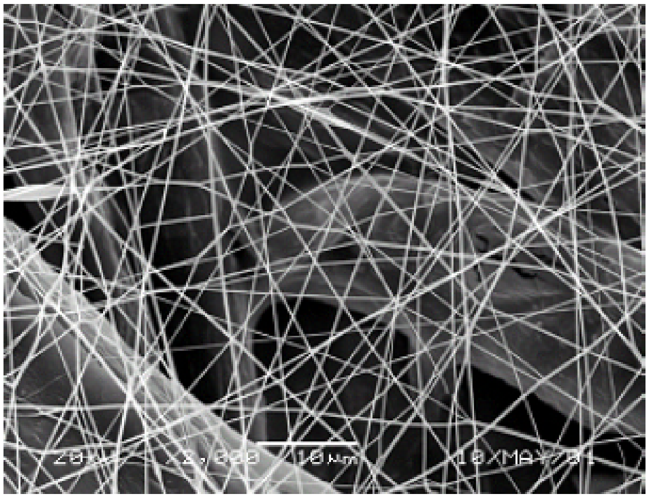


Figure 2.11 Ultra-Web® nanofiber filter media [20]

In the Figure 2.12, nanofiber composite manufactured by Donaldson [21] is observed that this specimen holds 2.5 times more dust than polyester filter spunbond fabric. The improvement in increase of the holding dust capacity depends on the decrease in fiber diameter and the increase in the specific volume to weight ratio.

Nanofibers provide dramatic increases in filtration efficiency at relatively small (and in some cases immeasurable) decreases in permeability. In many laboratory tests and actual operating environments, nanofiber filter media also demonstrate improved filter life and more contaminant holding capacity [20].

Nanofiber filter media have enabled new levels of filtration performance in several diverse applications with a broad range of environments and contaminants [20].

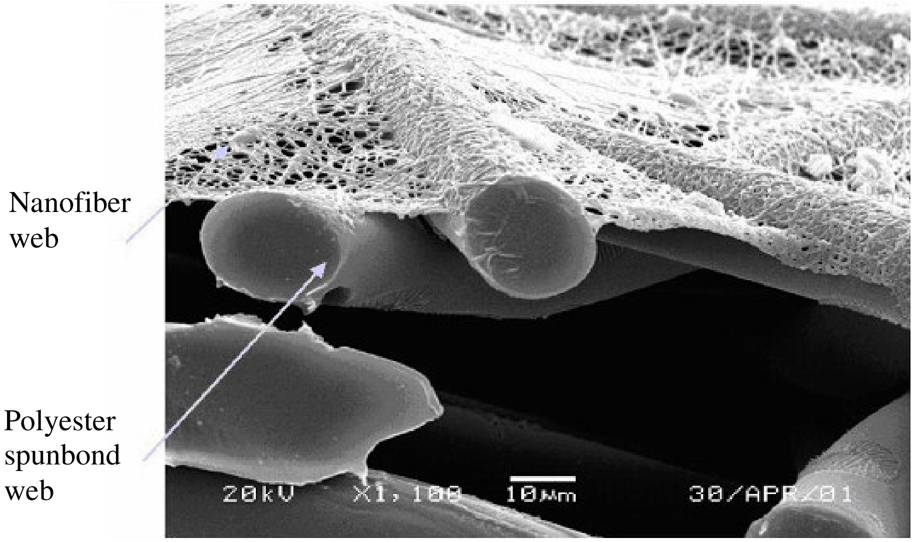


Figure 2.12 Filter system that formed by electrospun nanofibers on the polyester spunbond nonwoven [22]

2.7.2. Composite applications

The composites industry is especially interested in nanofiber technology because it potentially allows the creation of products that are much smaller and lighter in weight, yet capable of performing at the same or enhanced mechanical standards compared to traditional composites [1].

Especially in the fields of engineering, fibers such as carbon, kevlar, and glass are used in reinforcement of composites. The reinforcement composites get important properties such as high modulus and strength to weight ratio.

2.7.3. Biomedical applications

From biological viewpoint, almost all of the human tissues and organs are deposited in nano fibrous forms or structures. Examples include: bone, dentin, collagen, cartilage, and skin. All of them are characterized by well organized hierarchical fibrous structures realigning in nanometer scale. As such, current research in electrospun polymer nanofibers has focused one of their major applications on bioengineering. We can easily find their promising potential in various biomedical areas [23]. Biomedical applications of nanofibers are medical prostheses, smart clothes, drug delivery carriers, wound dressings, cosmetic skin masks, and tissue scaffolds.

One of the sub-sections of the biomedical application of nanofibers is to cure for wound and burnings in human skin. It can be designed for especially haemostatic tools. Electrospun biodegradable polymers can be spun onto the wound skin. They form a thin web onto the skin. This web protects skin from microbe. Moreover, it helps to heal the wound quickly. Finally, it minimizes the possibility of scar. Electrospun nanofiber equipment used in wound healing is shown in Figure 2.13.

Figure 2.13 Application of electrospun nanofibers used in wound covering and healing [23]

Similarly, nano fibrous mats are being explored as biomedical grafts and wound dressings. It has been found that cells can adhere to and proliferate into the mats with a great deal of success. Also, because of the extremely small size of the nano-fibers, the potential exists for layering of different polymers with specific functionalities [1].

2.7.4. Military and defense applications

In military applications, protecting clothes are expected especially to hold the possibility of survival, enable long term protection, stand heavy weather conditions, endure nuclear, chemical, and biological effects and increase efficiency. Protecting clothes now being used have made of heavy fabrics. The light and high porous fabrics which absorb the air and air vapor can easily react with chemical gases that cause fabric to decompose. Because of the higher surface area and low pore size of the nanofibers, fabrics, produced by them, are suitable for protecting clothes. Additionally, neutralization can be provided with these fabrics. Also, it allows the clothes to breath. Nanofibers which have high numbers of pores with small pore sizes provide high resistance to penetration of the chemicals into the fabrics. In military applications, it is benefited from nano sensors for work of finding trace, from nano electronics for various controls, from nano composites for platforms that need to lightness.

2.7.5. Agricultural applications

Plants are covered with a web that produced by electrospun nanofibers. One of the functions of this web is protection against harmful insects and chemicals. It can be used as a greenhouse covering. Furthermore, fertilizers, which were injected to the web before, can be given by the help of nanofiber web. The study about nanofiber web for plant done in our department is shown in Figure 2.14.

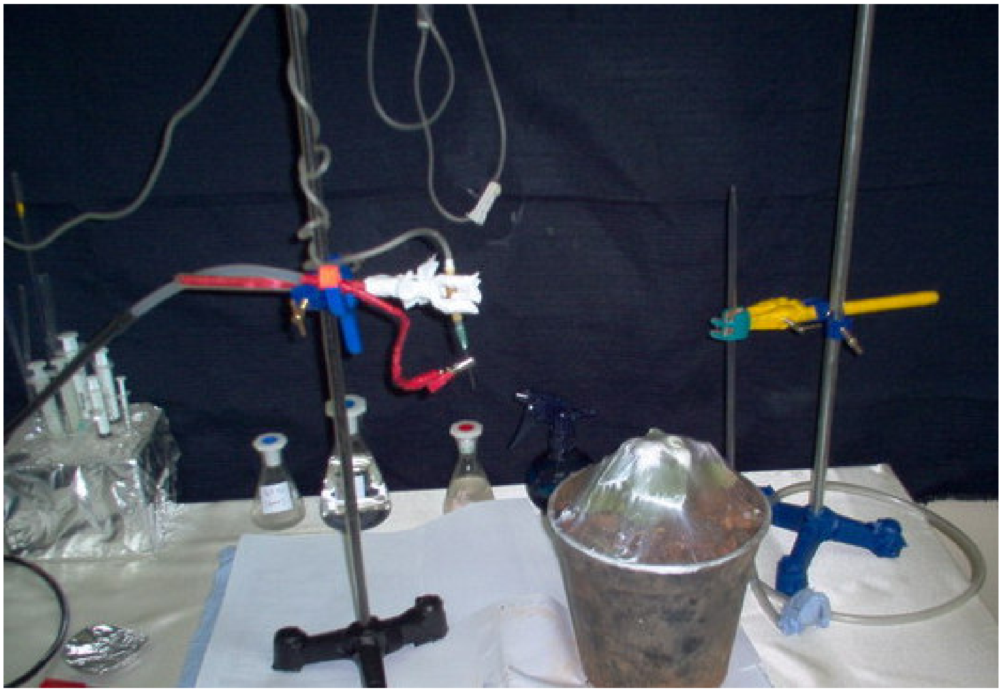


Figure 2.14 A plant covered with nanofiber web [24]

2.7.6. Space applications

Especially, carbon based nanofibers which have light weight and high strength, like being hundred times stronger than steel, are utilized in many applications of space vehicles and devices such as space shuttle. Moreover, nanofibers can be used in sun and light platforms in the space.

2.7.7. Electrical and optical applications

Production of nanofibers which have the ability to transmit electricity creates many advantages. These nanofibers are used in the production of the small electronic devices and in the fabrication of some machines. Because surface area of the electrodes is proportional to the chemical reaction speed, electrospun nanofiber membranes are used appropriately in the production of improved high performance batteries.

2.7.8. Other applications

The other potential applications of nanofibers are wires, capacitors, transistors and diodes for information technology and enzyme carriers.

The application of nanofibers in textiles is not aimed only at specialized industries involved in technical textiles. The introduction of micro fibers into traditional textile markets has created a wave of new garments claiming stain resistance and extremely soft hand. The introduction of nanofibers and nano coatings can take apparel innovations further. For example, man-made cashmere has been developed with a softer hand than that of worsted wool, offering the feel of cashmere at a fraction of the cost [1].

CHAPTER 3
ELECTROSPINNING PROCESS

3.1. Introduction

Electrospinning is the most effective process that produces nanofibers as mentioned in Chapter 2. It is a process that uses electrostatic forces instead of mechanical forces such as drawing in melt spinning. Simply stated, applied potential voltage difference between a charged polymer and a grounded or oppositely charged collector causes to begin the process. The applied voltage leads to formation of the electrical force at the surface of a polymer solution or polymer melt, which overcomes the surface tension. Then a charged jet is ejected from polymer drop. The jet extends in a straight line for a short distance (stability region), and then bends and follows a spiraling path (instability region). When the electrical forces elongate the jet thousands or even millions of times and the jet becomes very thin, the solvent evaporates, or the melt solidifies. Finally, very long nanofiber collects on an electrically grounded collector (seen in Figure 3.1). Extremely fine fibers ranging in diameter from less than 10 nanometers (nm) to several micrometers can be produced by this way.

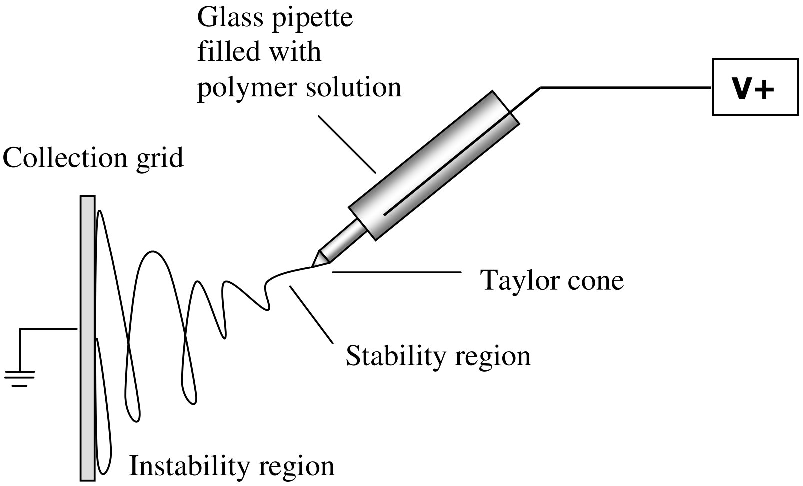


Figure 3.1 Electrospinning station

3.2. Historical Background

Electrospinning process is not a new technology. The phenomeon that a spherical drop of water on a dry surface was drawn into a cone when a piece of electrically charged amber is held at a suitable distance above it, was pointed out about 370 years ago by William Gilbert. This is the beginning of the story electrospinning and electrostatic spraying [25].

In late 1800's Lord Rayleigh investited the hydrodynamic stability of a liquid jet, with and without an applied electric field. In 1882, he studied the condition of instability occuring in electrically charged liquid droplets. He showed that when the electrostatic force overcomes the surface tension force, which acts in the opposite direction of the electrostatic force, liquid is thrown out in fine jets [25].

Although the term "Electrospinning", derived from "electrostatic spinning", was used relatively recently (in around 1994), its fundamental idea dates backmore than 60 years earlier. From 1934 to 1944, Formhals published a series of patents [26–30], describing an experimental setup for the production of polymer filaments using an electrostatic force. A polymer solution, such as cellulose acetate, was introduced into the electric field. The polymer filaments were formed, from the solution, between two electrodes bearing electrical charges of opposite polarity. One of the electrodes was placed into the solution and the other onto a collector. Once ejected out of a metal spinnerette with a small hole, the charged solution jets evaporated to become fibers which were collected on the collector. The potential difference depended on the properties of the spinning solution, such as polymer molecular weight and viscosity. When the distance between the spinnerette and the collecting device was short, spun fibers tended to stick to the collecting device as well as to each other, due to incomplete solvent evaporation [23].

In 1952, Vonnegut and Neubauer [31] were able to produce streams of highly electrified uniform droplets of about 0,1 mm in diameter. They invented a simple apparatus for the electrical atomization. A glass tube was drawn down to a capillary having a diameter in the order of a few tenths of millimeter. The tube was filled with water or some other liquid and an electric wire connected with a source of variable high voltage (5–10 kV) was introduced into the liquid [23].

In 1955, Drozin [32] investigated the dispersion of a series of liquids into aerosols under high electric potentials. He used a glass tube ending in a fine capillary similar to the one employed by Vonnegut and Neubauer [31]. He found that for certain liquids and under proper conditions, the liquid was issued from the capillary as a highly dispersed aerosol consisting of droplets with a relatively uniform size. He also captured different stages of the dispersion [23].

In 1966, Simons [33] patented an apparatus for the production of nonwoven fabrics of ultra thin and very light in weight with different patterns using electrical spinning. The positive electrode was immersed into the polymer solution and the negative one was connected to a belt where the nonwoven fabric was collected. He found that the fibers from low viscosity solutions tended to be shorter and finer whereas those from more viscous solutions were relatively continuous [23].

In 1971, Baumgarten [34] made an apparatus to electrospin acrylic fibers with diameters in the range of 0,05–1,1 microns. The spinning drop was suspended from a stainless steel capillary tube and maintained constant in size by adjusting the feed rate of an infusion pump. A high-voltage DC current was connected to the capillary tube whereas the fibers were collected on a grounded metal screen [23].

Since 1980s and especially in recent years, the electrospinning process essentially similar to that described has regained more attention probably due in part to a surging interest in nanotechnology. As ultrafine fibers or fibrous structures of various polymers with diameters down to submicrons or nanometers can be easily fabricated with this process [23].

To the mid-1990s, after Reneker and his group [35-37] began to study about electrospinning process, many researchers intensified on this subject as well. After then, published article and thesis gradually increased and the graphic about this topic that gave the number and years of publications which were published on Sci-Finder search system to the 2004 July was prepared by Kataphinan [25] and this is shown in Figure 3.2.

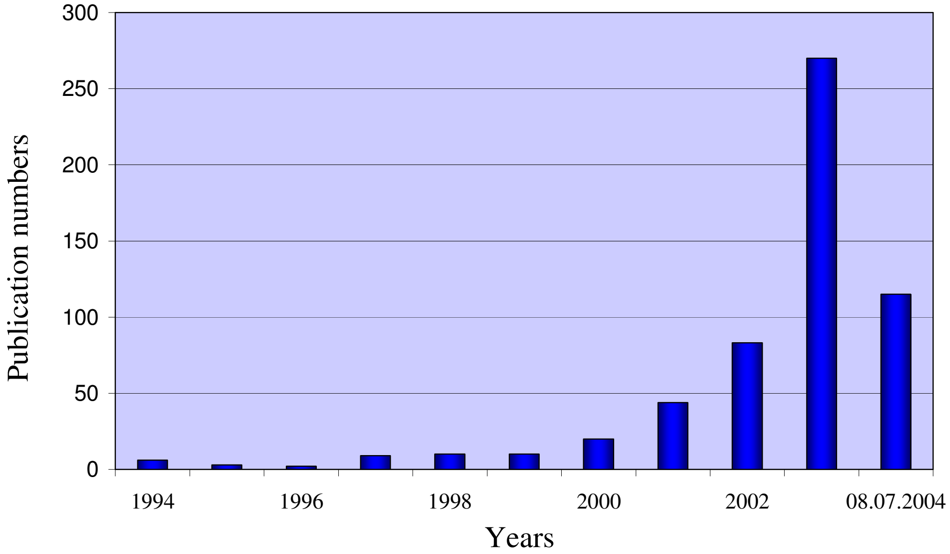


Figure 3.2 Numbers and years of the publications about electrospinning process [25]

3.3. Theory and Process

In the prosess of electrospinning, a wide range of polymers can be used. These polymers are either dissolved in an appropriate solvent or melted by heat. Some of them are given in Table 3.1 and Table 3.2.

Table 3.1 Polymers electrospun in solution form

Polymer	**Solvent**	**Concentration**
Cellulose Acetate (CA)	Acetone, acetic acid, dimethylacetamide	12.5–20%
Polyethylene Terephtalate (PET)	Dichloromethane:trifluoroacetic acid (1:1)	4–18 wt.%
Nylon 6.6 (PA 6.6)	Formic acid	10 wt.%
Polyurethanes (PU)	Dimethylformamide	2.5-21.2 wt.%
Polyacrylonitrile (PAN)	Dimethylformamide	15 wt.%
Polyvinil Alcohol (PVA)	Distilled water	1–16 wt.%
Polyvinylchloride (PVC)	Tetrahydrofuran/dimethylformamide= 100/0, 80/20, 60/40, 50/50, 40/60, 20/80, 0/100 (vol.%)	10–15 wt.%
Silk/PEO blend	Silkaqueous solutions	4.8–8.8 wt.%
Nylon6 (PA-6) /Montmorillonnite (Mt)	Hexa-fluoro-isopropanol (HFIP), HFIP/dimethylformamide: 95/5 (wt%)	10 wt.%

Table 3.2 Polymers electrospun in melt form

Polymer	**Processing temperature (ºC)**
Polypropylene (PP)	220–240
Nylon 12 (PA-12)	220
Polyethylene (PE)	200–220
Polyethylene terephthalate (PET)	270
Polyethylene naphthalate (PEN)	290
PET/PEN blends	290

Whereas solution of polymer is inserted into the syringe or a pipet which have small hole, polymer melt is electrospun from an extruder with the help of spinneret that has a small diameter. Then, a high voltage in the range of 0 to 100 kV is applied between the one end of the polymer in the syringe or spinneret, called feeding unit, and a collector which is placed next to the feeding unit.

Polymer drop hanging on the tip of the neddle in the feding unit takes up a conicle shape, due to the forces that surface tension applies, until a critical voltage applied potential difference reaches threshold voltage (V_c), electrostatic forces equalize to the surface tension forces. At this point, polimer drop changes its shape from conical shape named as "Taylor Cone". Figure 3.3 shows (a) passing polymer drop from semi-conical shape to the Taylor Cone, (b) the shape in Taylor Cone, and (c) leaving from Taylor Cone like jet. At the value of critical voltage, semi-cone angle that Taylor found in his study is 49.3º degrees.

After polymer drop became Taylor drop, with very small increasing in voltage, a jet spurt out from the tip of cone. Jet follows different ways while it goes between the collector and metal needle tip. Charged jet moves in a determined way at a certain distance after it leaves from Taylor Cone. Then, an instability in jet is observed.

Three changable instability happens, depending on the property of polymer solution or melt and system parameters. These instability circumstances are explained and modelled mathematically by Shin et al. [38-39] as clasic Rayleigh instability, axial symetric electric field, and whipping instability.

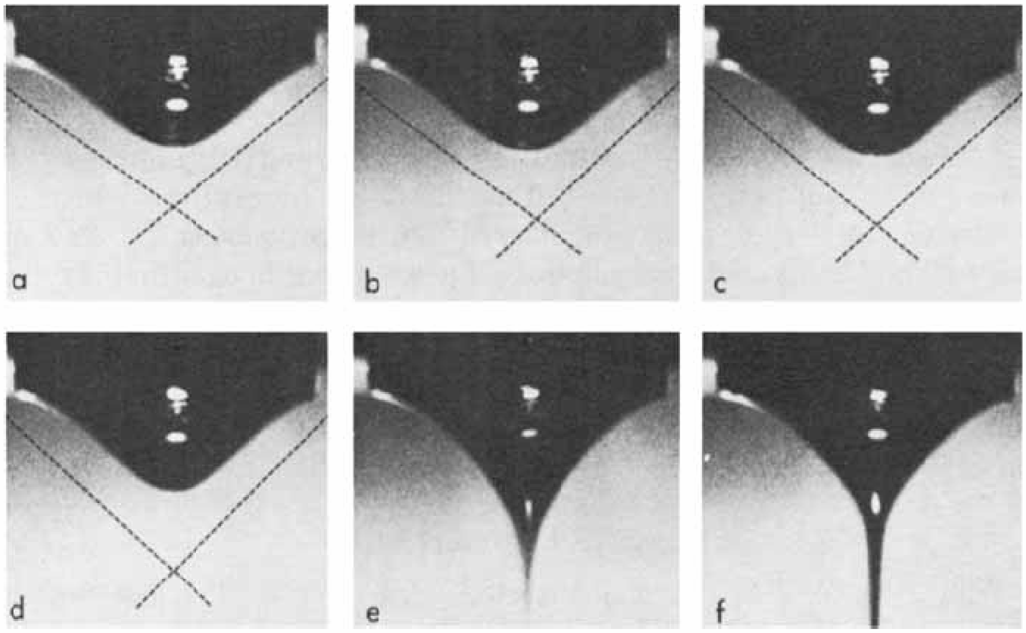


Figure 3.3 Formation of the Taylor Cone and polymer jet by the means of increasing voltage on the end of the needle or capillary tube (a) 110º, (b) 107º, (c) 104º, (d) 100º, (e) jet initiation, (f) jet extention [40-42]

The most common instability observed in electrospinning process is the whipping instability. The reason of whipping occurence may be explained as follows; electrostic charges exists on the surface of the jet where they repel each other and hence creates a torque that forms a spiral movement rather than a linear movement. When jet approaches to the collector, small jets which leaves from basic jet occur. The reason of the occurence of these small jets is to seperate from basic jet in result of pushing radial loads eachother. When jet thins and viscoelastic forces are damped enough, new whipping instabilities occur. This instability is called second whipping instability. The jet path, reference axes, relative arrangement of parts of the apparatus, stability region and instability regions where the whipping instability grew rapidly are shown in Figure 3.4.

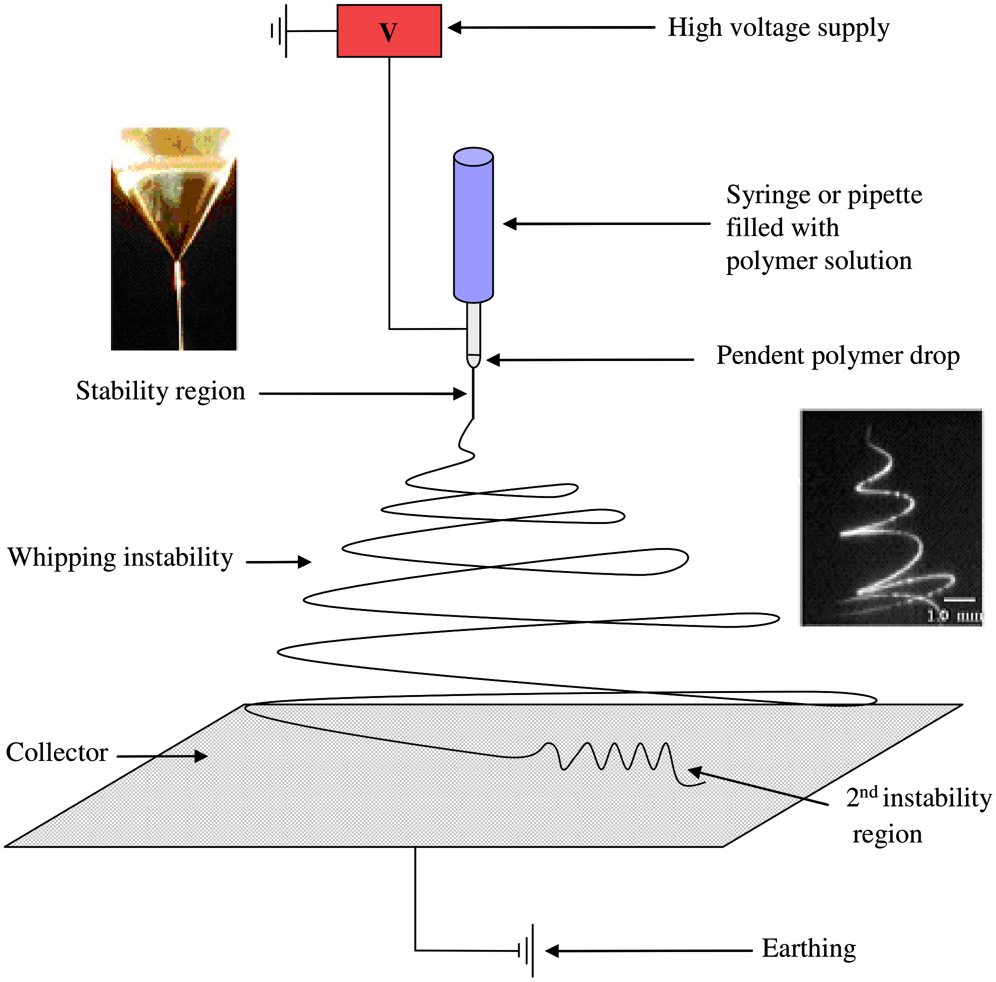


Figure 3.4 Schematic drawing of the electrospinning process

The resulting product is usually a nonwoven fiber mat that is composed of tiny fibers with diameters between less than 10 nanometers to several microns. Also, some different collection devices can be used to collect fibers in different forms. If the target is allowed to move with respect to the feeding position, specific fiber orientations (random or paralell alignment) can be achieved.

3.4. Literature and Patent Reviews

Martin, Cockshott, and Fildes [43] invented fibrillar mat, with two and three dimensional articles for prosthetic device comprising a plurality of fibers of organic material, wherein the fibers were produced by electrostatic spinning. Materials involved included suspension of PTFE, polyurethanes and aqueous solutions of polyvinyl alcohol, polyvinyl pyrrolidone and polyethylene oxide. The spinning material is fed into an electrostatic field from a syringe reservoir to the tip of an earthed syringe needle (seen in Figure 3.5). An electrostatically charged surface was placed at an appropriate distance. Fiber is formed between the tip of the syringe needle and the charged surface. Potential maintained was around 20 kV at a distance of 5–35 cm between syringe needle and collecting surface. Mats collected on a rotating nonconducting belt had a few microns to a few centimeters thick, highly porous, low diameter, and high surface area. These fiber mats were supposedly made for medical purposes, especially wound dressing [3].

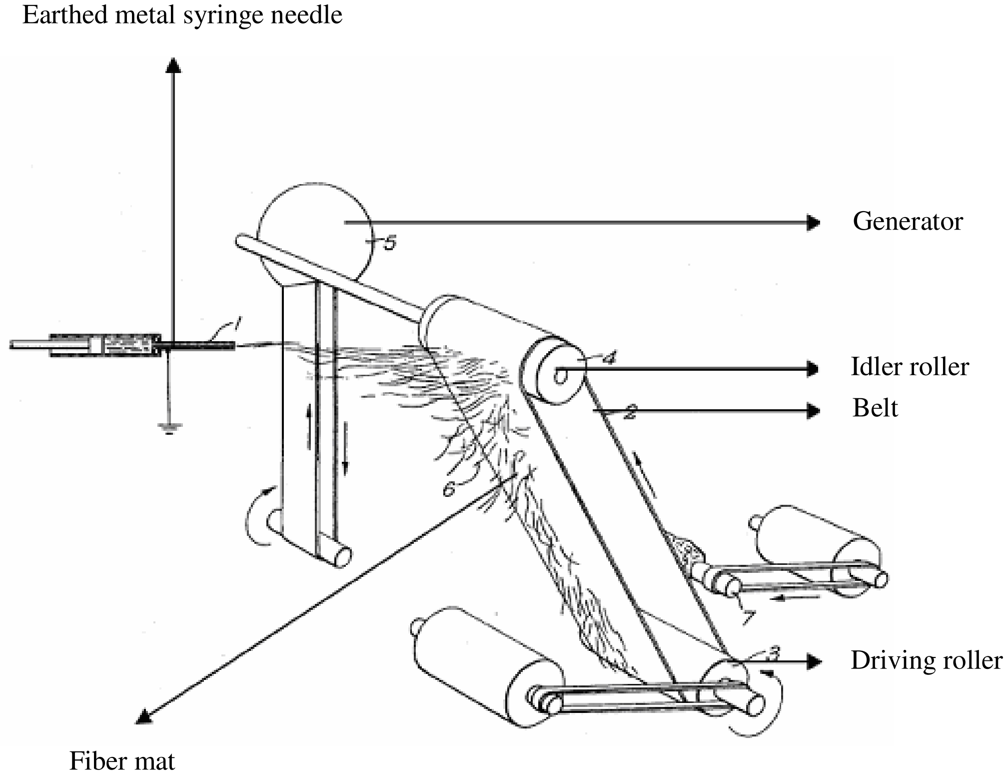


Figure 3.5 Diagrammatic side view of the apparatus for continuous production of fibers used by Martin et al. [43]

Fine and Tora [44] considered a liquid solution of a thermoplastic elastomeric polyurethane in a volatile solvent (like tetrahydrofuran) contained in a cup supplied to a surface rotating about an axis to form a film which is whirled by centrifugal force. By charging the cup to a high electric potential, an electric field is created on the surface of the solution. The electrostatic potential is maintained between this film and the collecting surface, an aluminum foil in the form of a belt and the fibers are attracted and collected in this surface. So, the filaments are formed by the combined action of centrifugal force and the electrostatic force [3]. Mechanism that Fine and Tora took patent in 1980 is shown in Figure 3.6.

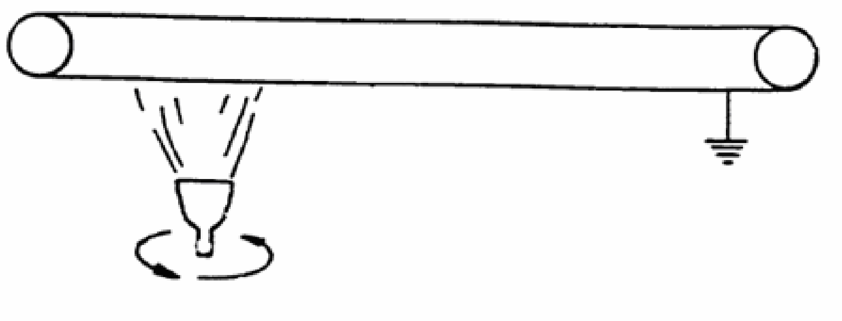


Figure 3.6 Mechanism of electrospinning system patented by Fine and Tora [45]

Bornat [46] in 1982 described the electrostatic spinning process for the production of tubular products, used in medical field. In this process biologically acceptable polymeric substances were used such as PTFE, polyurethanes, dispersions of polytetrafluoroethylene, thermoplastics such as polyamides, polyacrylonitrile, water-soluble polymers such as polyvinyl alcohol, polyvinyl pyrrolidone and polyethylene oxide. The spinning solution is fed to an electrostatic field from a syringe reservoir to the tip of an earthed syringe needle (seen in Figure 3.7). An electrostatically charged surface is kept at a distance and the fibers were formed between the needle tip and the charged surface. This system also involved several capillaries for higher production rate and spinning solution was filled in these capillaries. The potential was maintained between these capillaries and the collecting surface. The collecting device is a rotating mandrel or a rod so as to impart a core-sheath structure to the collected fibers so as to obtain a tubular product. The core may be conductive or non-conductive whereas the sheath is a non-electrically conducting material made of sheet metal or metal foil and is collapsible. The collected composite fibers in tubular form have low diameter and thickness, and are porous [3].

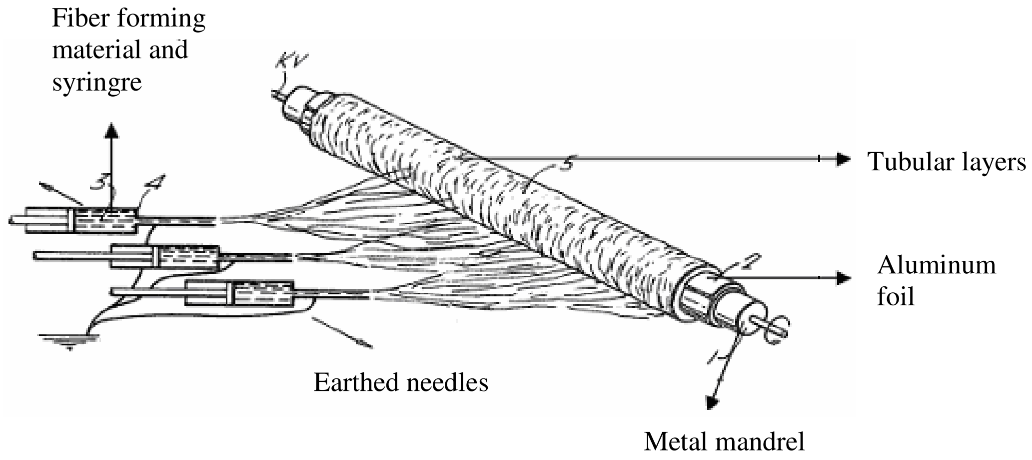


Figure 3.7 Apparatus for preparing tubular products used by Bornat [46-47]

How [48] described a process for the production of synthetic vascular grafts from polyurethane. The polymer solution was ejected through a stainless steel nozzle from a syringe, wherein the nozzle is earthed (seen in Figure 3.8). Flow of the polymer solution through nozzle is maintained by the syringe piston, which is subjected to a constant hydraulic force. Fluid from the nozzle is fed to an electrostatic field surrounding a charged mandrel which is charged to around –12 kV. Because of the high electric potential, filaments are drawn and collected here. This invention essentially relies on the controlling the speed of rotation of the mandrel (between 2000 to 20000 rpm) such that a desired degree of anisotropy is present in the graft. This is because, the purpose for which these grafts are produced, the natural arteries are generally anisotropic [3].

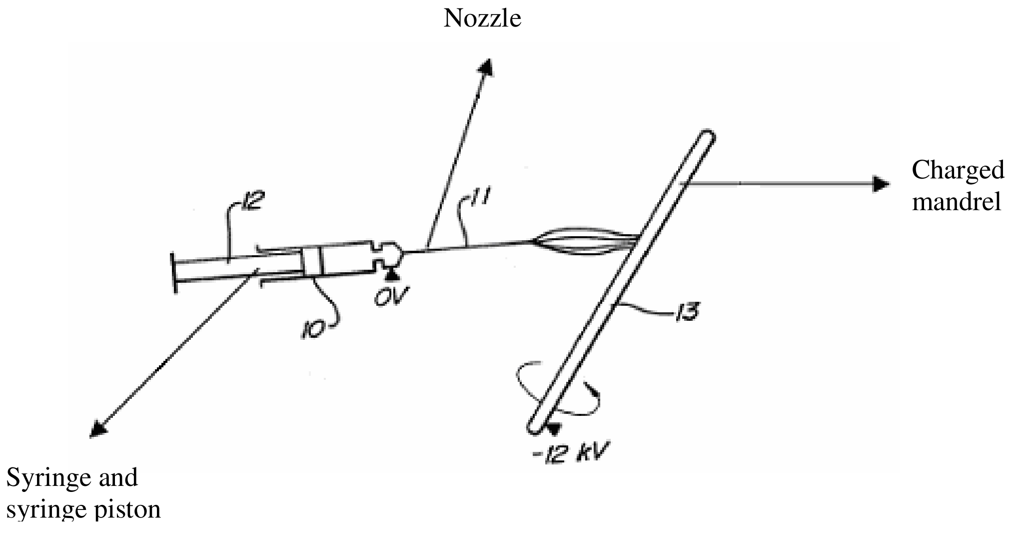


Figure 3.8 Diagrammatic illustration of electrospinning system used by How [48]

Berry [49] invented a method for producing electrostatically tubular fibrous spun products using polyurethanes. The spinning solution is fed into the electrostatic field through capillary needles. The emerging droplets were attracted towards electrostatically charged mandrel kept at a distance. The mandrel consisted of two charged grids and a potential of 6 to 12 kV is maintained. Because of the two charged grids the tubular fibrous structure produced had fibers of different diameters and varying fiber orientations along their length, as the needles traversed. These low diameter fibers were oriented circumferentially around the tube, offered little resistance to bending and assumed a very tight loop without kinking. Also, it had greater axial compliance and when compressed along its axis, it shortened with a minimal tendency to buckle [3].

In 2001 Demir et al. [50] studied on electrospinning behaviour of elastomeric polyurethaneurea copolymer in solution. Original polymer solution was diluted with dimethylformamide (DMF). Concentrations ranging from wt. 2.5 to 21.2 % were used for electrospinning experiments. Electron micrograph of electrospun fibers that were spun from wt. 21.2 % solution in DMF with the help of temperature and an electrical field of 4.6 kV cm^{-1} is given in Figure 3.9.

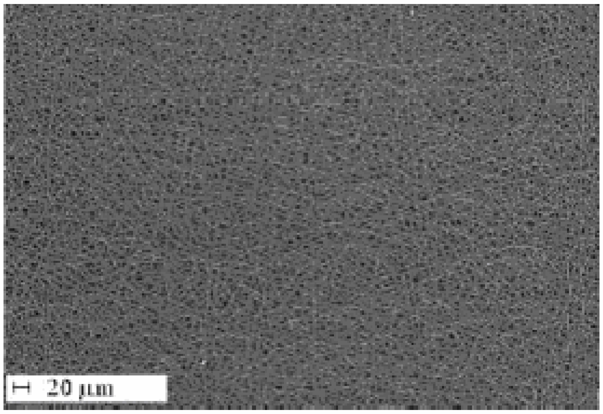


Figure 3.9 Electron micrograph of electrospun polyurethaneurea fibers [50]

The effects of electrical field, temperature, conductivity and viscosity of the solution on the electrospinning process and morphology and property of the fibers obtained were investigated. Results of observations made by optical microscope, atomic force microscope and scanning electron microscope were interpreted [50].

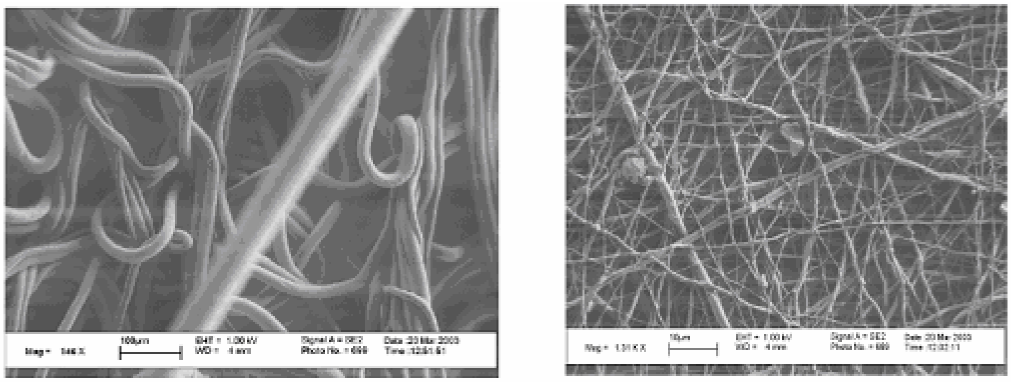
In their study, ultra fine elastic fibers with submicron diameters had been succesfully produced by electrospinning of polyurethaneurea solutions. Fiber diameters in the range 7 nm to 1.5 µm were obtained by varying the solution concentration. Fiber diameters increase as the third power of solution concentration. Viscosity, i.e. the concentration of the solution and temperature, is the dominant factor among the other solution properties. Concentration effects on the electrospinning process and final product were investigated. A trimodal distribution of fibers in diameter has been found in electrospinning of highest concentration. The morphology of electrospun fibers is strongly correlated with viscosity, equivalently concentration and temperature. Low concentration solutions drive towards the formation of fibers with beads, whereas increased concentration fovors the formation of curly fibers. Both morphological imperfections result in decreasing the surface area to volume ratio of electrospun fibers. They found that it is possible to improve the fiber morphology by increasing the solution temperature. Fibers spun at high temperature are uniform unlike those obtained at room temperature. Moreover, high temperature makes the electrospinning process quick, so it is an important advantage from the aspect of industrial applications [50].

Roth et al. [51] reported datas on the distribution function of electrospun fiber diameters measured from digitized SEM images of electrospun Nylon, polyurethane (PU), polyacrylonitrile (PAN), polycaprolactam (PCL), and polycarbonate (PC) fabrics. They also reported the effects of one atmosphere uniform glow discharge plasma (OAUGDP) exposure on two surface characteristics of electrospun Nylon and PU nanofiber fabrics:

a) The strength and the surface energy of the fabric as functions of the plasma exposure time.
b) The surface energy/wettability as a function of time after exposure (ageing effect) [51].

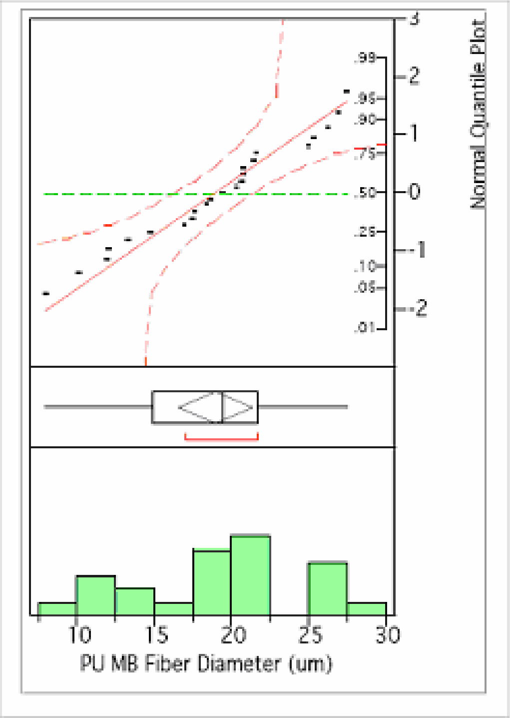
They also described their recent progress in electrospinning and plasma treatment technology, including a rotating cylindrical drum collector, and the treatment of nanofiber fabrics using recent improvements in OAUGDP™ reactor technology [51].

They took the SEM images and analyzed the fiber diameter statistics of polymeric fabrics made from five materials: Nylon, polyurethane (PU), polyacrylonitrile (PAN) polycaprolactam (PCL), and polycarbonate (PC) [51]. PU were represented by both meltblown and electrospun fabrics as shown in Figure 3.10. Diameter statistics of PU meltblown and PU electrospun, and diameter distribution function of micro- and nanofiber fabrics are given respectively in Figure 3.11, Figure 3.12, and Table 3.3.



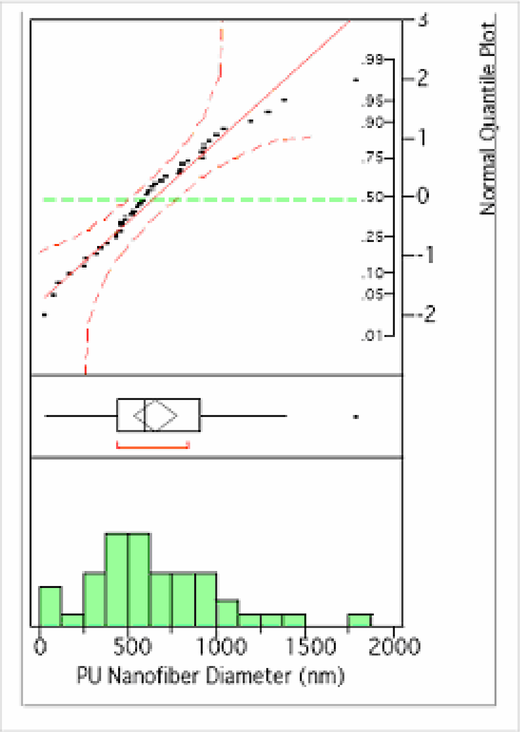
(a) (b)

Figure 3.10 Scanning Electron Micrographs (SEM) of two polyurethane (PU) fabrics, a) meltblown polyurethane (PU) with human hair diagonally in the foreground – note 100 micron fiduciary marker b) Electrospun polyurethane (PU) – note 10 micron fiduciary marker [51]



Quantiles		
100.0%	maximum	28
99.5%		28
97.5%		28
90.0%		27
75.0%	quartile	22
50.0%	**median**	**20**
25.0%	quartile	15
10.0%		11
2.5%		8.0
0.5%		8.0
0.0%	minimum	8.0
Moments		
Mean		19.0
Std Dev		5.4
Std Err Mean		1.1
upper 95% Mean		21
lower 95% Mean		17
N		**23**

Figure 3.11 Polyurethane (PU) meltblown (MB) diameter statistics [51]



Quantiles		
100.0%	maximum	1800
99.5%		1800
97.5%		1800
90.0%		1200
75.0%	quartile	900
50.0%	**median**	**600**
25.0%	quartile	440
10.0%		180
2.5%		41
0.5%		40
0.0%	minimum	40
Moments		
Mean		660
Std Dev		370
Std Err Mean		58
upper 95% Mean		770
lower 95% Mean		540
N		**40**

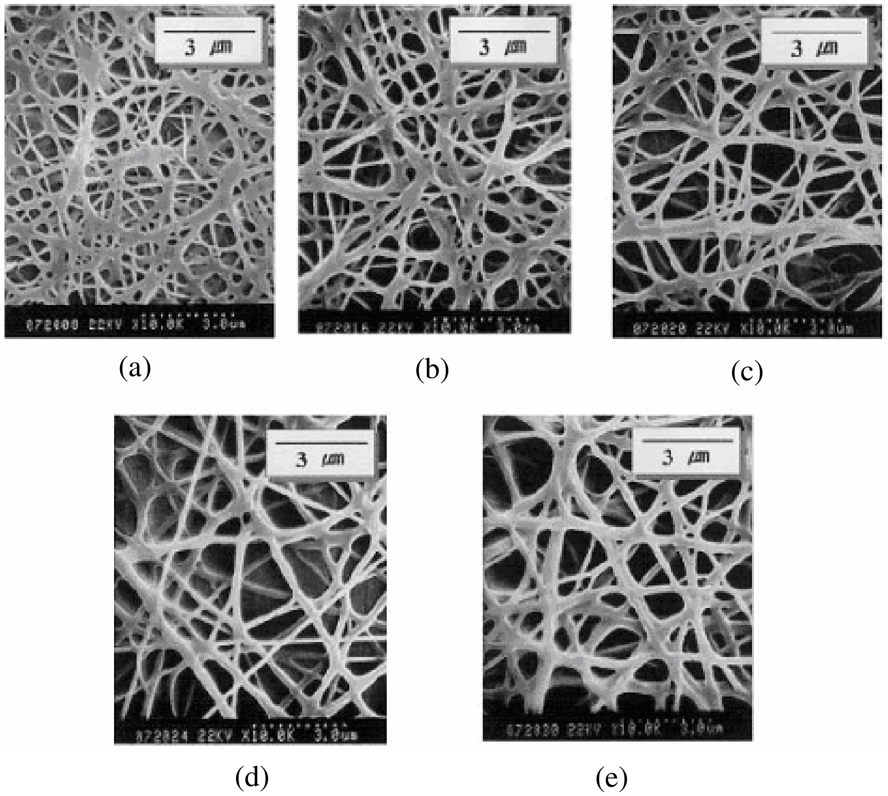
Figure 3.12 Polyurethane (PU) electrospun (ES) diameter statistics [51]

Table 3.3 Diameter distribution function of micro- and nanofiber fabrics [51]

Fabric Type	# points	Median	Mean	Standard Deviation	Coefficient of Variation (%)
PU MB	23	20	19	5.4	28 %
PU Nano	40	600	660	370	62 %

They also tested the breaking strength and the wettability/surface energy of meltblown and electrospun Nylon and PU fabrics. They showed that electrospun PU nanofiber fabrics have about twice the areal mass-normalized strength as PU meltblown microfiber fabrics. They found that OAUGDP™ exposure greatly increases the surface energy and contact angle of meltblown PU and Nylon microfiber fabrics. The surface energy of PU and Nylon nanofiber fabrics is increased to values above 70 dynes/cm by 5 seconds of OAUGDP™ exposure [51].

Khil et al. [52] pointed that produced via electrospinning, polyurethane membrane, which has a unique property, has been of interest in medical fields. A nanofibrous PU membrane was prepared by electrospinning, and its performance as a wound dressing was evaluated. This wound dressing showed controlled evaporative water loss, excellent oxygen permeability, and promoted fluid drainage ability due to the nanofibers with porosity and inherent property of PU. Neither toxicity nor permeability to exogenous microorganism was observed with the nanofibrous membrane. Histological examination confirmed that epithelialization rate was increased, and the exudate in the dermis was well controlled by covering the wound with the electrospun membrane. Thus, nanofibrous PU membrane prepared by electrospinning could be properly employed as wound dressings [52]. SEM images of PU membrane are shown in Figure 3.13. The solution concentration, voltage, and tip to collector distance were wt. 25 %, 12 kV, and 12 cm respectively.



(a) (b) (c)

(d) (e)

Figure 3.13 SEM images of electrospun PU fibers as a function of the solvent (DMF/THF, v/v); (a) 100/0, (b) 70/30, (c) 50/50, (d) 30/70, and (e) 0/100 [52]

In the study of Pedicini and Farris, a thermoplastic polyurethane was electrospun from solution to produce an isotropic fiber mat. The mechanical behavior of the mat was characterized by uniaxial tensile tests. The electrospun polyurethane produces a stress–strain response characteristically different to that of the material from which the mat is spun. Scanning electron microscopy and infrared spectroscopy were also used to characterize the electrospun material and determine the source of the differing mechanical responses [53].

The stress–strain behavior of an electrospun thermoplastic polyurethane has been observed and compared to the bulk material from which it is spun (seen in Figure 3.14). The two forms of the PU have characteristically different stres-strain responses resulting from two phenomena; molecular orientation within the fibers as a result of electrospinning, and a strain-induced orientation of the electrospun fiber mat. Electron microscopy and vibrational spectroscopy were used to illustrate this morphological change upon stretching and molecular orientation in the electrospun fibers, respectively (seen in Figure 3.15). The apparent molecular orientation in the electrospun fibers also leads to the pronounced reduction in elongation to failure of the electrospun mat, relative to the bulk [53].

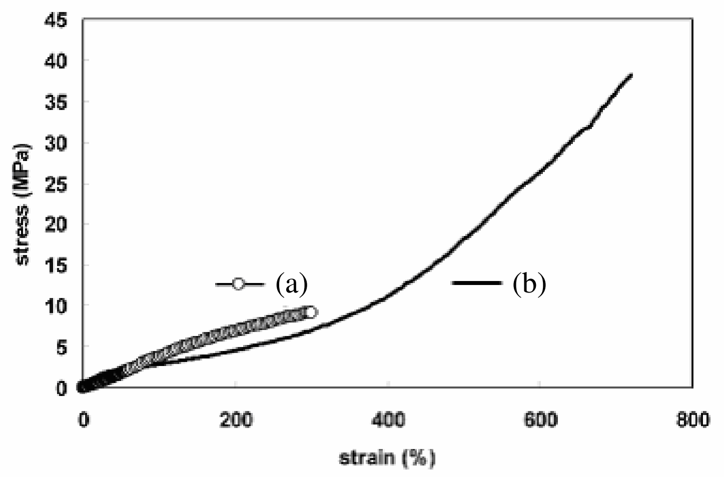


Figure 3.14 Engineering stres-strain curves for Pellethane® 2103-80AE tested in unaxial tension; (a) bulk and (b) electrospun [53]

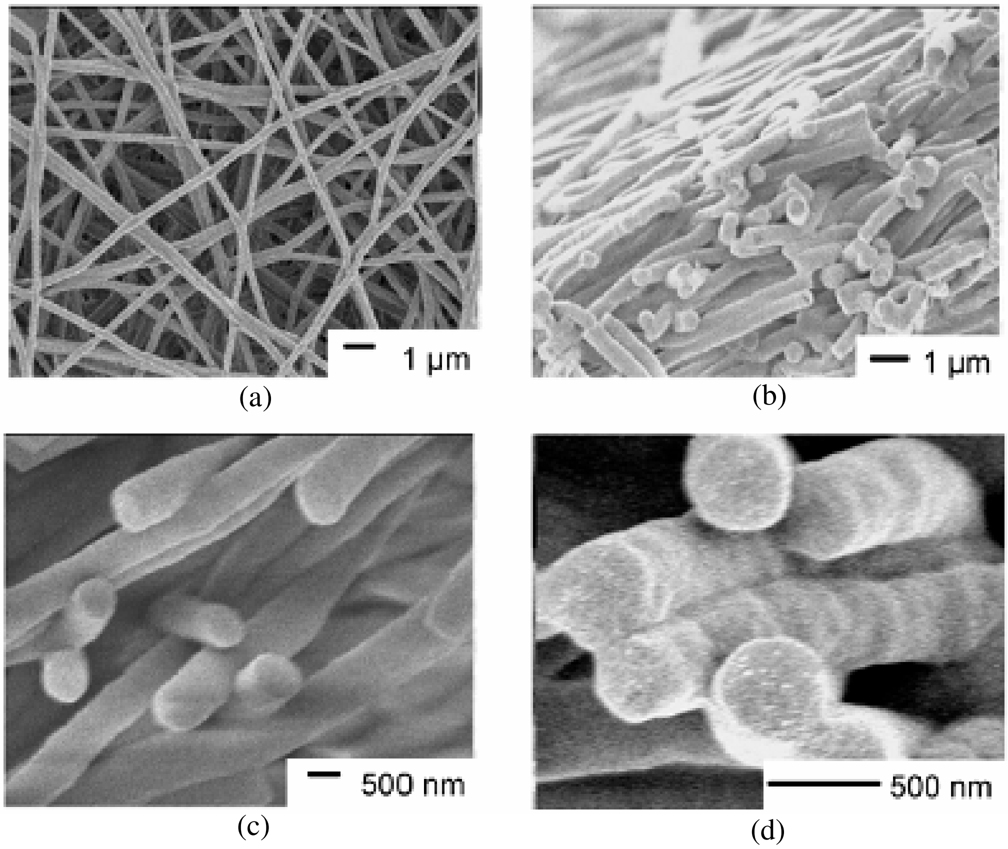


Figure 3.15 SEM images of electrospun Pellethane® 2103-80AE; spun from wt. 7 % solution in DMF; (a) View orthogonal to the plane of the electrospun mat; (b)-(d) cross-sectional views taken from a cryo-fractured electrospun mat [53]

In the study of Gibson and Schreuder [54], by using the process of electrospinning with elastomeric polyurethanes, highly deformable membrane structures were made that exhibit strain capacity of over 200 % with full elastic recovery. Measurements indicated that changes in elastomeric membrane structure under different states of biaxial strain were reflected in measurements of air flow through the membrane. Changes in membrane structure were also evident in environmental scanning electron microscope images of the pore/fiber rearrangement as the membrane was stretched. Two elastomeric electrospun membranes and one knit spandex fabric (chosen for comparison purposes) were tested under biaxial strain conditions for the transport properties of water vapor diffusion and air flow resistance. Air flow resistance of all three materials decreased as the pores were stretched open under increasing strain levels (seen in Figure 3.16). The water vapor diffusion resistance was unaffected within the measurement capability of the test system; boundary layer effects dominated the diffusion results. SEM images of the deformed elastomeric nanofiber membranes confirmed that the elastic fibers were under an increasing state of tension while interfiber pore space increased [54].

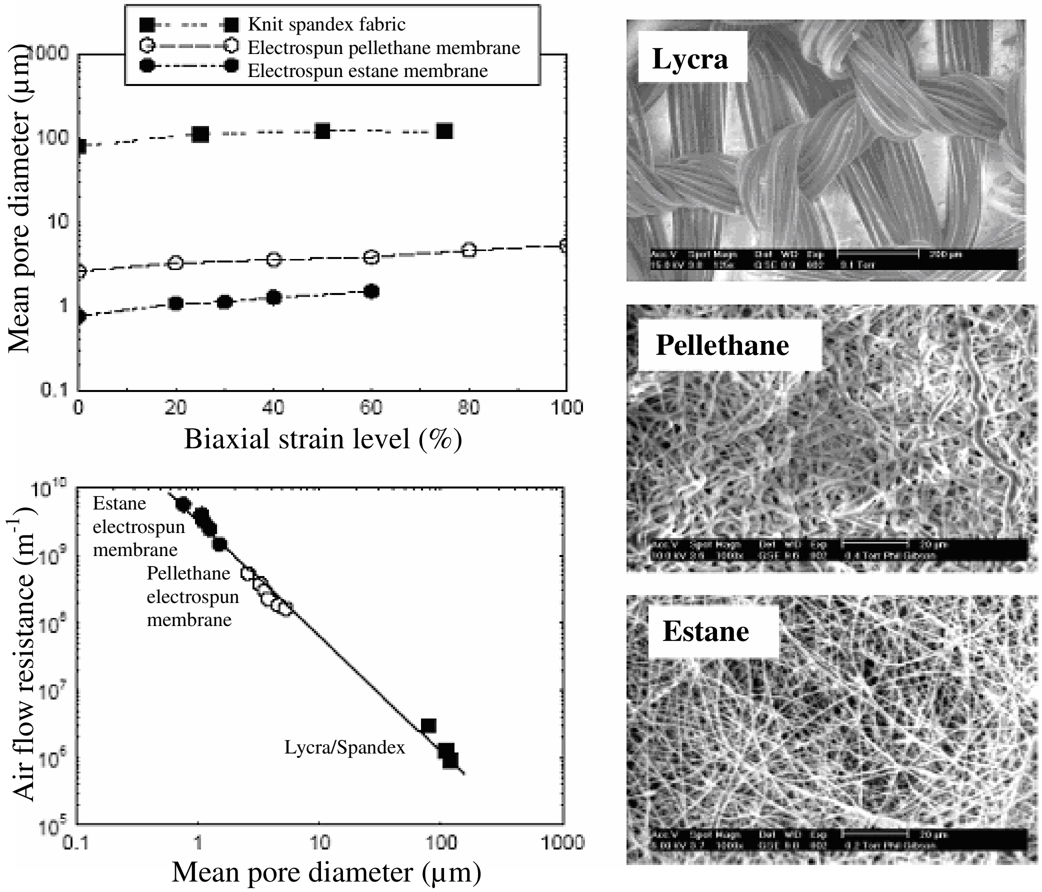
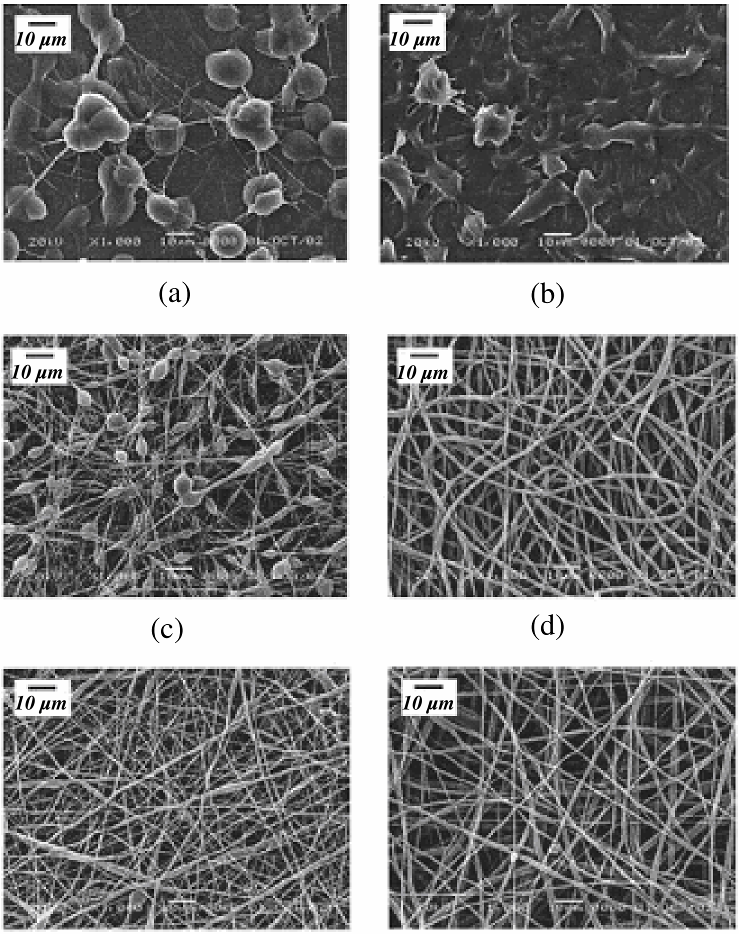


Figure 3.16 Measurements of changes in mean pore sizes under different levels of biaxial strain for three porous elastic materials and correlation between mean pore size and air flow properties of three porous elastic materials with SEM images of Lycra, Pellethane, and Estane [54]

Cha Et. Al. [55] found that electrospun nonwovens of shape-memory PU block copolymers with hard-segment concentrations of wt. 40 and 50 % were successfully prepared by electrospinning processing. The PU nonwovens spun at a lower solution viscosity had an average fiber diameter of 800 nm and a beaded-on-fiber structure. In contrast, the samples spun at a high solution viscosity showed a smooth fiber surface with an average diameter of 1300 nm. Using SEM, they observed that the electrospun PU nonwovens were composed of a broad distribution of fiber diameters (seen in Figure 3.17). With a universal testing machine, they observed that for a similar degree of viscosity, the electrospun PU nonwovens with a hard-segment concentration of wt. 50 % had higher stress than those with a hard-segment concentration of wt. 40 %. The mechanical properties of the electrospun PU nonwovens were also affected by the hard-segment concentration. More than 80 %

shape recovery was obtained in the electrospun PU nonwovens with hard-segment concentrations of wt. 40 and 50 %. Consequently, they clearly established that controlling the hard-segment concentration in PU constitutes a significant parameter in the preparation of electrospun shape-memory nonwovens [55].



(a) (b) (c) (d) (e) (f)

Figure 3.17 SEM images of electrospun PU fibers: (a) hard-segment concentration = wt. 30 % and solution concentration = wt. 36 %, (b) hard-segment concentration = wt. 30 % and solution concentration = wt. 40 %, (c) hard-segment concentration = wt. 40 % and solution concentration = wt. 26 %, (d) hard-segment concentration = wt. 40 % and solution concentration = wt. 30 %, (e) hard-segment concentration = wt. 50 % and solution concentration = wt. 30 %, (f) hard-segment concentration = wt. 50 % and solution concentration = wt. 38 % [55]

CHAPTER 4
MATERIALS AND METHODS

4.1. Introduction

A detailed literature survey has been caried out prior to the establishment of an electrospinning set up. In the course of this literature survey, the electrospinning set up at University of Sabanci was also observed. Finally, the apparatus and the devices necessary for the electrospinning set up were purchased with support of TUBITAK (Project no: 104M414).

An experiemental set up as seen in Figure 4.1 was established at the Textile Engineering Department of the Textile Technologies and Design Faculty, in Istanbul Technical University (ITU). The initial trials were realized at there. Then, this laboratory set up (seen in Figure 4.2) was temporarily moved to the Textile Engineering Department of the Engineering Faculty in Gaziantep University. Experiments reported in this thesis have all been done using this set up at Gazianep University.

Figure 4.1 Electrospinning set up in Istanbul Technical University

Figure 4.2 Electrospinning set up in Gaziantep University

In this chapter firstly the materials and their properties used in the experiments are given. Secondly, the apparatus used in electrospinning laboratory are explained. Then, two different electrospinning set-ups and experimental parameters applied on these systems are given. Finally, experimental devices for the characterization of the material are explained.

4.2. Materials

The thermoplastic polyurethane was used as the main polymer for this study. Dimethylformamide was also used to solve it. In addition to these, two major chemicals, some other polymers and fibers were also used.

4.2.1. Thermoplastic polyurethane (TPU)

Thermoplastic polyurethane (TPU) with the trademark name of Elastollan® in granule form was obtained from Renko Tekstil Sanayi ve Ticaret Ltd. Sti [Istanbul-Turkey].

Elastollan® TPU is produced by Elastogran GmbH [56] a subsidiary of BASF AG [57], a world leader in polyurethane technology, and is an exceptionally versatile polymer. It is elastic with good dimensional stability and is stable at temperatures from – 40° to +125° C. Together with good resilience, it has resistant to oils, fuels, UV radiation and hydrolysis, thereby giving it an optimum fit in a very broad span of applications and industries [58].

Elastollan® TPU, which can be coloured or painted and is recyclable, has already achieved significant success in applications ranging from automotive parts to medical equipment, wire and cable sheathing to components for the offshore industry and domestic appliances, as well as in leisurewear and sports goods [58]. Elastollan® TPU products have the following advantages;

- Excellent abrasion resistance
- High tensile, compressive, and tear strength
- Good flexibility over a wide range of temperatures
- Good hydrolytic stability
- Resistance to solvents and fungus attack
- Selection of a wide range of hardness
- Flame-retardant / halogen - free
- Suitable for matt surfaces [59].

Elastollan® has low specific gravity and high elongation at break. Some of the typical Elastollan® properties are given in Table 4.1.

Table 4.1 Typical Elastollan® properties [60]

Properties	**Hardness**	**Specific Gravity**	**Tensile Strength (ultimate)**	**Tear Strength**	**Elongation at Break**
Standard	ASTM D-2240	ASTM D-792	ASTM D-412	ASTM D-624	ASTM D-142
Units	Shore	g/cm^3	MPa	N/mm	%
Elastollan®	76 A	1.14	30	80	740

Chemical Structure of TPU Elastollan® is essentially formed from the reaction of three components: polyols (long-chain diols), diisocyanates, and short-chain diols [61].

The polyols and the short-chain diols react with the diisocyanates through polyaddition to form linear polyurethane molecules. The polyols form the flexible component of the elastomer (flexible or soft segment). The combination of diisocyanate with short-chain diol produces the rigid component (rigid or hard segment). Figure 4.3 shows the molecular structure in diagrammatic form. The properties of the product depend on the nature of the raw materials, the reaction conditions, and the ratio of the starting raw materials. The polyols used have a significant influence on certain properties of the thermoplastic polyurethane. Polyether and polyester polyols are used to produce Elastollan® [61].

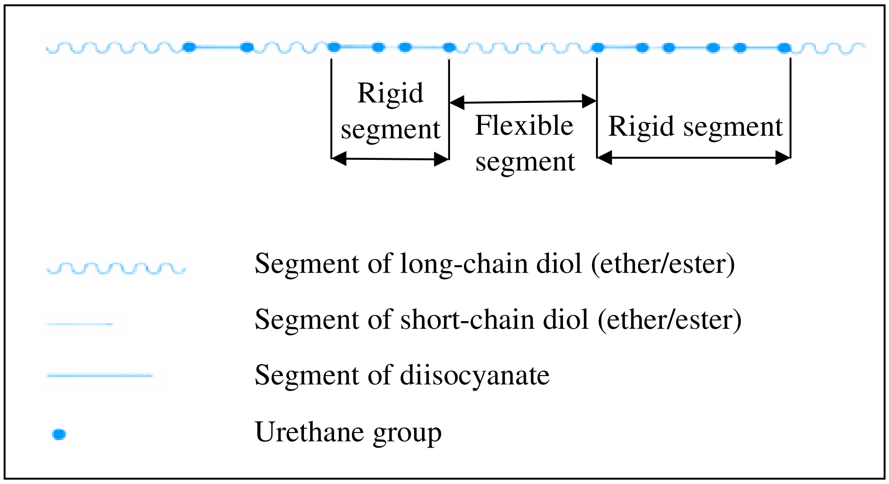


Figure 4.3 TPU chemistry hard and soft segments [61]

Three different solutions from TPU were prepared. Dimethylformamide was used as a solvent. The concentrations of solutions were wt. 5 %, wt. 7.5 %, and wt. 10 %. For example, wt. 5 % solution have 5 gr TPU granules and 95 gr dimethylformamide.

During the preparation of the solutions, firstly solvent was heated in closed beakers, the TPU granules were added on them. After that, the preparation is boiled about 1 hour when all granules had been dissolved completely. Then, the solutions were waited for 6 hours before electrospinning.

The solutions (seen in Figure 4.4) were prepared the same days of electrospinning at room temperature and stirred gently. Special care was taken to avoid any contact with humidity since TPU solution coagulates easily in aqueous media.

Figure 4.4 TPU solutions

4.2.2. Dimethylformamide

N,N-Dimethylformamide ($HCON(CH_3)_2$) was used as a solvent for TPU as mentioned before. It is the product of MERCK [62]. Its purification is higher than 99.8 %. Its density ranges from 0.949 to 0.952. Its boiling point ranges from 152 °C to 154 °C.

4.2.3. Other materials

Although TPU was the main polymer as discussed in Chapter 5, some other polymers and fibers were also tested in electrospinnning system. While polymers used in trials were polypropylene and polyvinylalcohol, the fibers were cotton and viscose.

Polypropylene (PP) was in the form of granule and had the melt flow index (MFI) of 35. In order to prepare its solution, it was dissolved in 1,2-Dichlorobenzene at boiling temperature. After it was dissolved completely, it was left stand stil untill it is cold. However this solution has transformed into a jelly like structure. Hence, it could not be used in the solution electrospinning. On the other hand, PP granules could be used in melt electrospinning system trials.

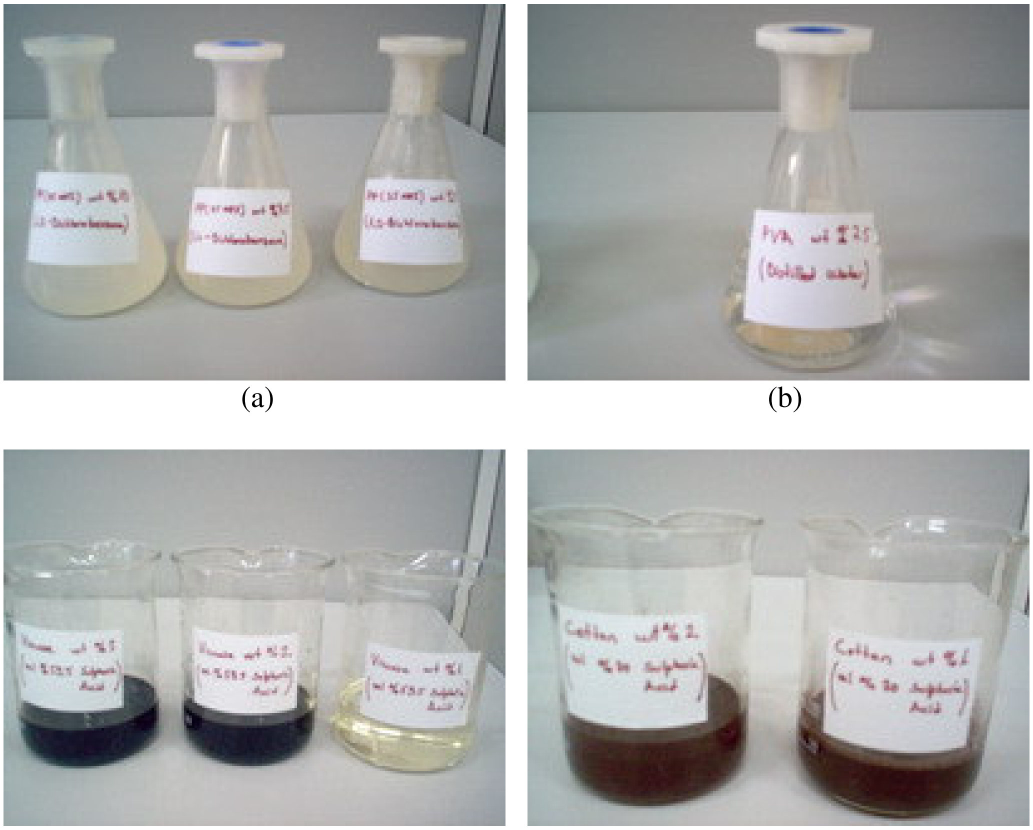
Polyvinylalcohol (PVA) was obtained in the form of powder. For the electrospinning trials, aquous solution of PVA was prepared. The solution concentration was wt. 7.5 %. Distilled water was used as solvent.

Viscose and cotton were used in the form of ordinary fiber. These fibers were dissolved in sulphuric acid. But, the trials from these solutions were unsuccessful.

Detailed informations about prepared solutions with either polymers or fibers are given in Table 4.2. Moreover, solutions are shown in Figure 4.5.

Table 4.2 The properties of the solutions used in electrospinning trials

Material	**Solvent**	**Concentration**	**Temperature**	**Time**
PP (35 MFI)	1,2-Dichlorobenzene	**wt. 5 %**	Boiling	5 min.
PP (35 MFI)	1,2-Dichlorobenzene	**wt. 7.5 %**	Boiling	5 min.
PP (35 MFI)	1,2-Dichlorobenzene	**wt. 10 %**	Boiling	5 min.
PVA	Distilled water	**wt. 7.5 %**	80 ºC	30 min.
Viscose	59.5 % Sulphuric acid	**wt. 1 %**	20 ºC	20 min.
Viscose	59.5 % Sulphuric acid	**wt. 2 %**	20 ºC	20 min.
Viscose	59.5 % Sulphuric acid	**wt. 3 %**	20 ºC	20 min.
Cotton	70 % Sulphuric acid	**wt. 1 %**	38 ºC	20 min.
Cotton	70 % Sulphuric acid	**wt. 2 %**	38 ºC	20 min.


(a) (b)

(c) (d)

Figure 4.5 Solutions used in electrospinning trials (a) PP, (b) PVA, (c) Viscose, and (d) Cotton solutions

4.3. Apparatus for Electrospinning

Electrospinning system needs three main parts to realize the process. They are feeding unit, collector, and high voltage power supply. In addition, some other auxiliary apparatus and devices were used to make the process easy.

4.3.1. Feeding units

Two different polymer feeding systems were used in experimental set-ups. While, a medical serum set was utilized as a feeding unit in the process of solution electrospinning, the melt flow index tester was employed in the melt electrospinning system.

4.3.1.1. The medical serum set

In the solution electrospinning system, irregular and discontinuous polymer flow has been a big problem for the researchers. Some of them used micro pumps to regulate the polymer flow. But, they are very expensive. In the current work, this problem is solved in a simple manner by using a medical serum set. A medical serum set not only provides a continuous flow but also enables to adjust flow rate.

The medical serum set (seen in Figure 4.6) used in experiments had a capacity of taking 100 ml liquid and ability of adjusting liquid flow. One drop of liquid which drips from the serum set is 0.05 ml. The serum set was firstly cleaned with distilled water and then dried. After that, polymer solution was filled in it by the help of syringes. The flow was adjusted manually with flow adjuster. Finally, desired flow could be provided.

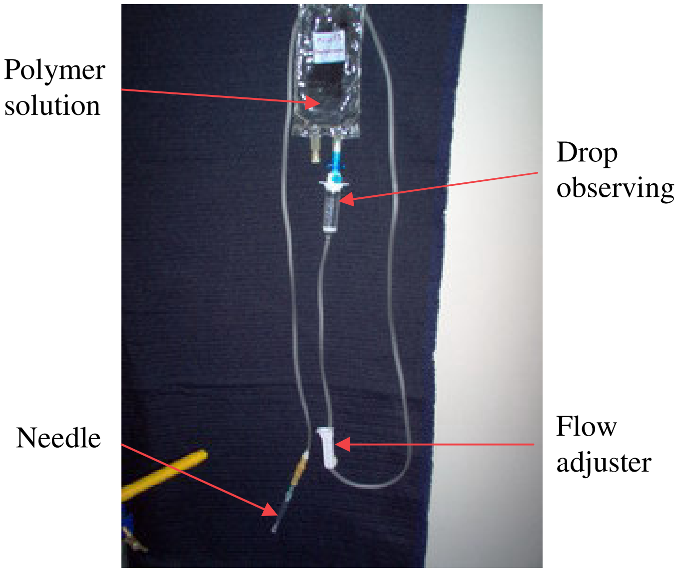


Figure 4.6 The medical serum set

4.3.1.2. Melt flow index tester

Melt flow index tester is a product of ATSfaar [63]. It is an apparatus for determining melt flow rate of plastic materials especially thermoplastic polymers. It has two resistance set and one PID digital thermoregulator for thermal control. Its working temperature is between 50 °C to 400 °C with a sensitivity of 0.2 °C. It was used as an feeding unit because of its ability to melt thermoplastic polymers at desired temperature.

Desired temperature was set on the screen of thermoregulator. When it was reached at this temperature, polymer granules were fed into the heating zone by means of a funnel. Then, these polymers were melted in the heating zone. Finally, they left the system passing into a spinneret. Schematic drawing of the melt index apparatus used as a feeding unit in melt electrospinning is shown in Figure 4.7.

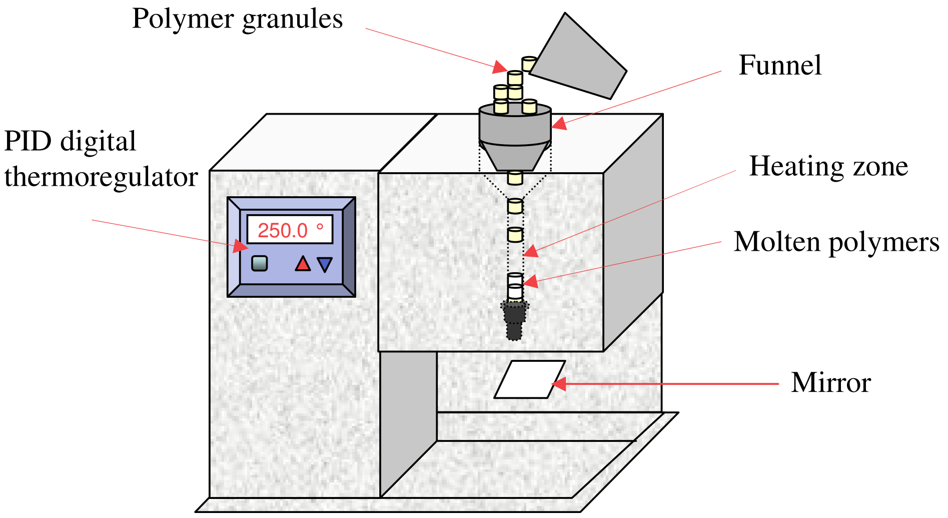


Figure 4.7 Schematic drawing of the melt flow index apparatus (ATSfaar)

4.3.1.2.1. Spinnerets

Melt flow index tester has an original spinneret which is shown in Figure 4.8. Because of its shortness (8 mm) and having a large hole diameter (2 mm) of this spinneret, the electrospinning process by using that spinneret in melt index could have not been realized. So, a new spinneret which was longer (25 mm) than the other one was designed (seen in Figure 4.9). Additionally, a specific inner part design of the spinneret was done. The first inner part of the spinneret was designed largely (5 mm) for the purpose of facilitating the molten polymer flow. On the other hand, the end of the inner part of the spinneret was smaller than the original one for the purpose of making the electrospinning system more effective.

Figure 4.8 Spinnerets of melt index

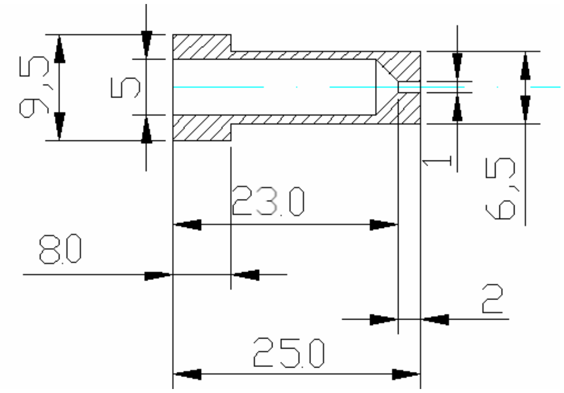


Figure 4.9 Technical drawing of the new spinneret [19]

Having designed the new spinneret, it was manufactured. Then, it was tested on the melt flow index tester. Lastly, the temperature of the end point of the spinneret hole was measured by a multimeter (seen in Figure 4.10) for observing temperature differences.

Figure 4.10 Temperature measurement on the end point of designed spinneret hole

4.3.1.2.2. Protector cabin

A closed cabin (seen in Figure 4.11 a) that is suitable for the melt flow index tester was designed for the purpose of realizing the electrospinning process in it. This cabin helps to avoid any electrical discharge. Furthermore, the cabin was used as protector against the unwanted exterior effects, while electrospinning process was taking place.

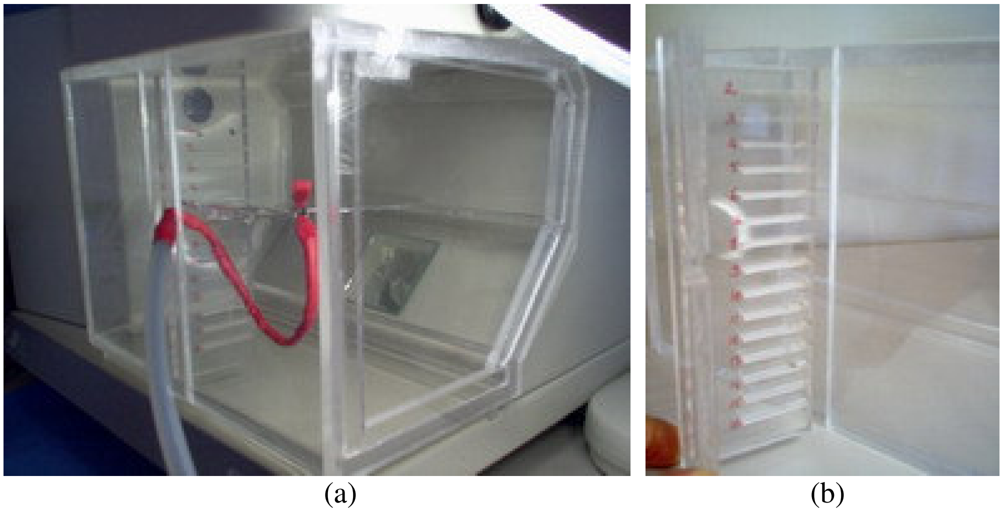

(a) (b)

Figure 4.11 Protector cabin; (a) placed into melt index and (b) collector holder

When the cabin was designed, a hole was placed on upper side of the cabin. The aim of the hole on the cabin was to position the spinneret through the inside of the cabin. Moreover, a collector holder (seen in Figure 4.11 b) that could be mounted on closed cabin was designed to place the collector at a fixed distance between collector and spinneret which was adjusted by the means of spaces on the part in the range of 2 cm to 16 cm with 1 cm apiece.

4.3.2. Collector

There are several collector types used in the electrospinning process. Their main functions are to provide grounding and to collect fibers. In this study, a circular shaped galvenized thin metal plate coated with aliminium foil was used as collector. Its diameter and thickness of the plate were 150 mm and 1.5 mm respectively.

4.3.3. High voltage power supply

Gamma ES 100 as seen in Figure 4.12 that is able to apply voltage between 0 to 100 kV, was used in all experiments. It is a DC power supply. Voltage can be gradually regulated. It has a high voltage output wire for connecting to electrode with a mini alligator jaw clipped to collector or feding unit. Then the voltage can be adjusted. The output voltage can both be adjusted before or during the electrospinning process.

Figure 4.12 High voltage power supply (Gamma ES100)

4.4. Solution Electrospinning System

Prepared solutions were injected into the serum set with the help of suitable syringes. The polymer solution flow rate was manually adjusted. The thin plate collector was coated with aluminium foil and weighed together. So, the collector was made ready. It was then placed on to tripod. After that, the needle which is a part of the serum set was fixed at a desired distance from collector. The mini alligator clip of the high voltage power supply was mounted on to the needle. This was anode (+). The other electrode, cathode (-), which was connected with grounding electric cable was clipped on to collector. Then the desired voltage was adjusted on high voltage power supply. Finally, power supply was switched on and system started to run as seen in the Figure 4.13.

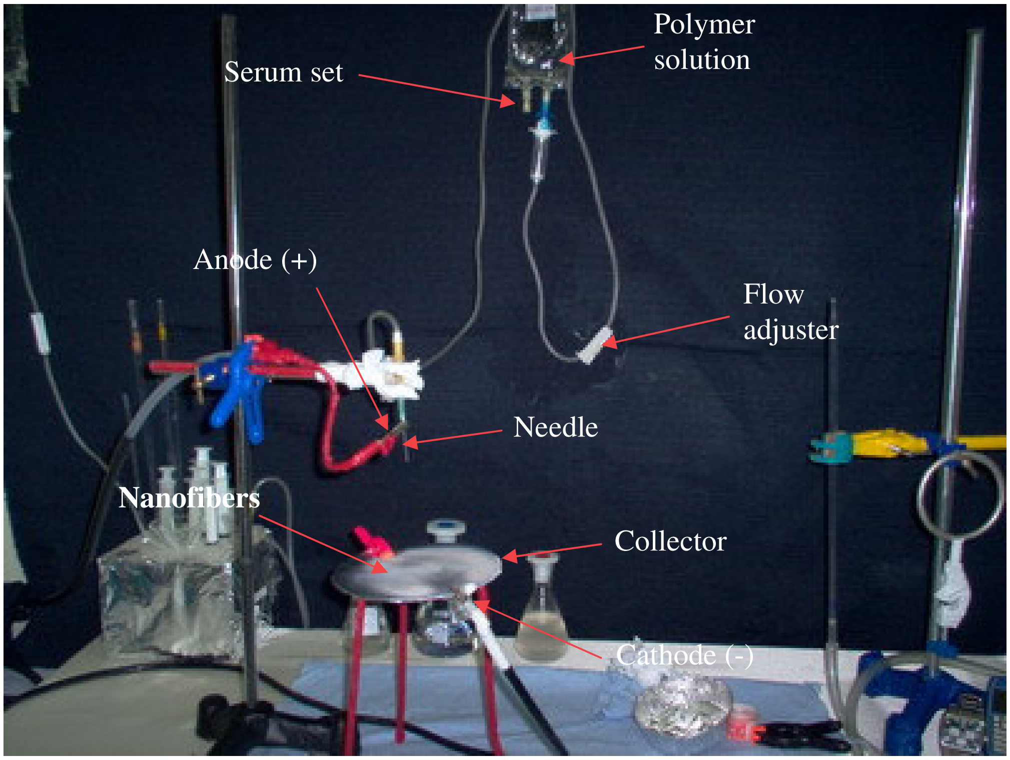


Figure 4.13 Solution electrospinnig set up

4.4.1. Experimental parameters

In the solution electrospinning process, the solutions of TPU with dimethylformamide were used. Table 4.3 summarizes the experimental parameters used in obtaining nanofibers from TPU polymer solutions.

Table 4.3 List of experimental variables in solution electrospinning

Material	Solution of TPU with dimethylformamide
Solution Concentrations	wt. 5 %, wt. 7.5 %, wt. 10 %
Applied Voltages	2 kV/cm, 3 kV/cm, 4 kV/cm
Distances	6 cm, 8 cm, 10 cm
Time	2 min, 4 min, 8 min
Flow Rate	0.05 ml/min

4.5. Melt Electrospinning System

In melt electrospinning system as seen in the Figure 4.14, firstly processing temparature was set on the PID thermoregulator of the melt flow index tester. Then polymer granules were placed into the heating zone of the melt flow index apparatus by the help of a funnel. The thermoplastic polymer is then started to melt at there. At the same time, the collector was placed into collector holder. The mini alligator clip which came from high voltage power supply was mounted on to the collector. This was anode (+). The other electrode, cathode (-), which was connected with grounding electric cable was clipped on to a cable that was mounted on to the spinneret. The lid of the protector cabin was made sure to be closed. The voltage was then adjusted to the desired value. Finally, the power supply was switched on. The system is then started to run.

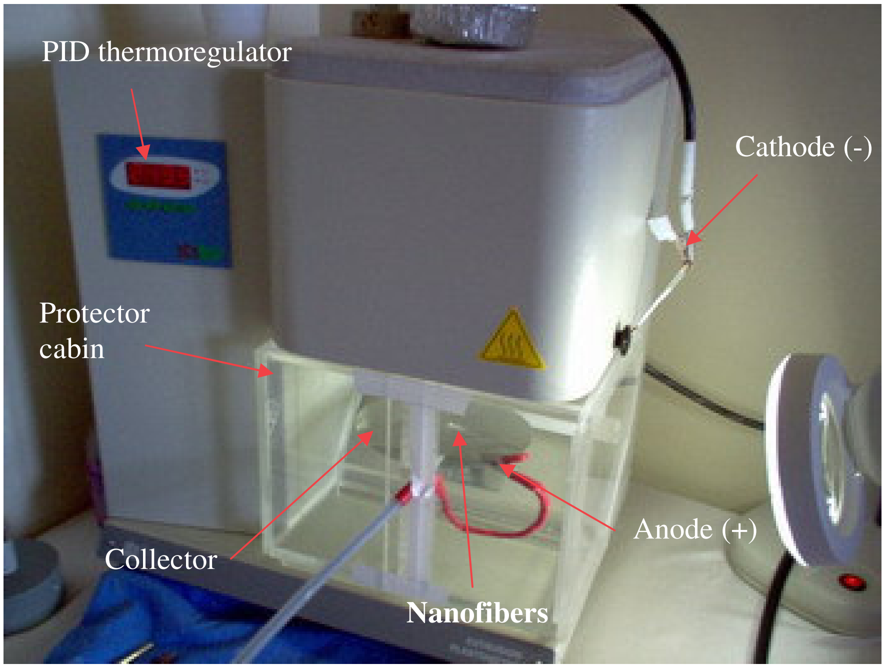


Figure 4.14 Melt electrospinning set up

4.5.1. Experimental parameters

In melt electrospinning process, TPU granules were used. Table 4.4 summarizes the experimental parameters used in obtaining nanofibers from TPU granules.

Table 4.4 List of processing variables altered for TPU during melt electrospinning experiments

Material	TPU granules
Processing Temperatures	200 °C, 210 °C, 220 °C, 230 °C, 240 °C, 250 °C, 255 °C, 257.2 °C, 260 °C, 265 °C, 270 °C, 280 °C
Applied Voltages	4 kV/cm, 5 kV/cm, 6 kV/cm
Distances	6 cm, 8cm, 10 cm
Time	2 min, 4 min, 8 min

4.6. Characterization Techniques

TPU granules and electrospun TPU nanofibers were tested. In this section, digital melting point apparatus, thermogravimetric analysis (TGA) apparatus, differential scanning calorimeter (DSC), and field emmission scanning electron microscope (FESEM) are described briefly.

4.6.1. Digital melting point apparatus

Electrothermal IA9200 (seen in Figure 4.15) was used to measure melting point of thermoplastic polymers. Polymer samples ground into tiny particles submitted for the analysis were firstly enclosed in glass capillary tubes and brought to a melting condition under strictly controlled parameters of time and temperature. By using this instrument, the melting temperatures of TPU and PP were measured. Firstly, the approximate melting temperatures of the polymers were adjusted. Then, three cappillary tubes were inserted in when temperature had reached at set point. The samples were waited about 2 or 3 minutes for the purpose of balancing the possible temperature differences. After that temperature ramp rate was set as 1 °C/min. Finally, the capillary tubes were observed.

Figure 4.15 Digital melting point apparatus

4.6.2. Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) is a thermal analysis technique used to measure changes in the weight (mass) of a sample as a function of temperature and/or time. TGA is commonly used to determine polymer degradation temperatures, residual solvent levels, absorbed moisture content, and the amount of inorganic (noncombustible) filler in polymer or composite material compositions. A simplified explanation of a TGA sample evaluation may be described as follows. A sample is placed into a tared TGA sample pan which is attached to a sensitive microbalance assembly. The sample holder portion of the TGA balance assembly is subsequently placed into a high temperature furnace. The balance assembly measures the initial sample weight at room temperature and then continuously monitors changes in sample weight (losses or gains) as heat is applied to the sample. TGA tests may be run in a heating mode at some controlled heating rate, or isothermally. Typical weight loss profiles are analyzed for the amount or percent of weight loss at any given temperature, the amount or percent of noncombusted residue at some final temperature, and the temperatures of various sample degradation processes [64].

TPU granules were tested with thermogravimetric analyses were done in Polmag Laboratory [65] in the Chemistry Department of the Faculty of Science and Letters at Istanbul Technical University. The apparatus used in TGA experiments is shown in Figure 4.16.

Figure 4.16 Thermogravimetric analysis (TGA) apparatus

4.6.3. Differential scanning calorimetry (DSC)

Differential scanning calorimetry can be used to measure a number of characteristic parameters of a sample. Using this technique it is possible to observe fusion and crystallization events as well as glass transition temperatures (Tg). In addition to these applications DSC can be used to study oxidation as well as other chemical reactions. Glass transitions occur as the temperature of an amorphous solid is increased. A glass transition is characterized by a decrease in viscosity (seen in Figure 4.17). These transitions appear as a step in the baseline of the recorded DSC signal. This is due to the sample undergoing a change in heat capacity, but no formal phase change occurs. As the temperature increases, an amorphous solid will become less viscous. At some point the molecules will obtain enough freedom of motion to spontaneously arrange themselves into a crystalline form. This is known as the crystallization temperature (Tc). This transition from amorphous solid to crystalline solid is an exothermic process, and results in a peak in the DSC signal. As the temperature increases the sample eventually reaches its melting temperature (Tm). The melting process results in an endothermic peak in the DSC curve. The ability to ascertain transition temperatures and enthalpies makes DSC an invaluable tool in producing phase diagrams for various chemical systems. DSC may also be used in the study of liquid crystals. As matter transitions between solid and liquid, it often goes through a third state, which displays properties of both phases. This anisotropic liquid is known as a liquid crystalline or mesomorphous state. Using DSC, it is possible to observe the small energy changes that occur as matter transitions from a solid to a liquid crystal and from a liquid crystal to an isotropic liquid [66].

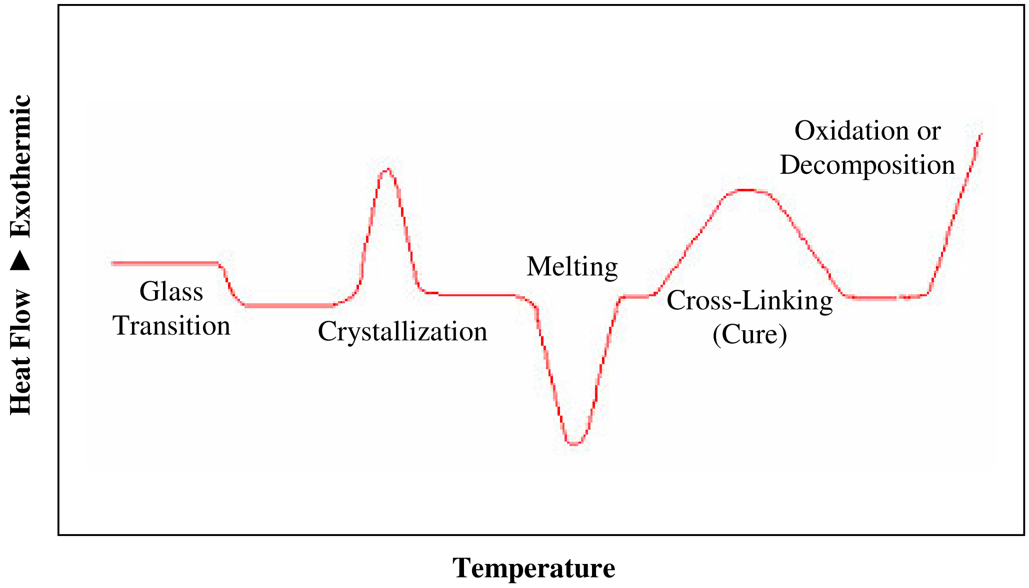


Figure 4.17 Effect of temperature changing on heat flow of material

Electrospun materials were tested by using DSC. These measurements were done in Polmag Laboratory [65] in Istanbul Technical University, Faculty of Science and Letters, Chemistry Department. Differential scanning calorimeter Q10 used in experiments is shown in Figure 4.18.

Figure 4.18 Differential scanning calorimeter Q10

4.6.4. Coating equipment

Electrospun nanofiber samples were coated in order to observe them in field emmision scanning electron microscope. Samples were inserted sample holder. Then it was installed into coating machine (seen in Figure 4.19). Afterwards, samples were coated with gold about six times.

Figure 4.19 Coating equipment

4.6.5. Field emmision scanning electron microscope (FESEM)

The JEOL JSM-6335F (seen in Figure 4.20) which is a cold cathode field emission scanning electron microscope (FESEM) was used to characterize nanofibers. It has a resolution of 1.5 nm at 15kV and 5 nm at 1kV. The sample stage is fully automated, with computer control of X, Y, Z tilt and eucentric rotation [67]. Also it has a magnification between 10 and 500000 [68].

FESEM allows us to investigate specimens at very high resolution both in secondary and back-scattered modes. In addition, the FESEM has excellent depth resolution enabling 3D-like images from the scanned surfaces. It is also possible to take stereo pair images from the specimens. The measurements and annotates can be depicted to the digital images [68].

Scanning electron microscope labaratory (seen in Figure 4.20) in TUBITAK Marmara Research Center [Kocaeli-Turkey] was used for taking scanning electron micrographs of samples.

Figure 4.20 Field emmision scanning electron microscope (FESEM)

CHAPTER 5
RESULTS AND DISCUSSIONS

5.1. Introduction

In this chapter, the results obtained from the evaluation of the samples formed by two different electrospinning set-ups are visually discussed and statistically analysed. Firstly, the results of TPU polymer characterisation are given and discussed. Secondly, the re-evaluation of electrospinning processes is given. Hence, the effects of process parameters on fiber collections are illustrated. Deposited nanofibre weight measurement values are related to the process parameters. After weight measurement, diameter measurements of samples taken on electron scanning micrographs (FESEM images) and their statistical analysis are given. With the help of these measurements, between diameter values of electrospun fibers which were produced with process variables and their statistics are related. Moreover, comparisons are made by using electron micrographs of electrospun fibers.

5.2. Characterization of Thermoplastic Polyurethane (TPU)

Melting point and melting interval of the TPU granules were determined by using melt index instrument. After that, the temperature that TPU can begin to decompose was measured by thermogravimetric analysis (TGA). Lastly, the glass transition temperature (Tg), temperature of crystallinity (Tc) with percentage of crystallinity and melting temperature (Tm) were also measured by the means of differential scanning calorimetry (DSC).

5.2.1. Melting point of TPU

Prior to the beginning of melt electrospinning experiments, in order to determine the processing temperature, the results of observations done with using melt index instrument were found that melting point and melting interval of TPU granules were 207 °C and 195 °C – 207 °C respectively.

5.2.2. Thermogravimetric analysis (TGA)

Thermogravimetric analysis of TPU polymer is shown in Figure 5.1. In this graph, horizontal axis indicates temperature (°C) changes while vertical axis indicates weight percentage of the sample. The analysis was done with 20 °C/min temperature increase. When the result which observed from the graph is analysed, it is clearly seen that TPU polymer began to decompose after 260 °C. Since the sample weight was reducing sharply, the percentage of the sample began to decrease after this temperature. The weight loss percentages of TPU sample were 49.97 % at 390 °C and 94.76 % at 500 °C.

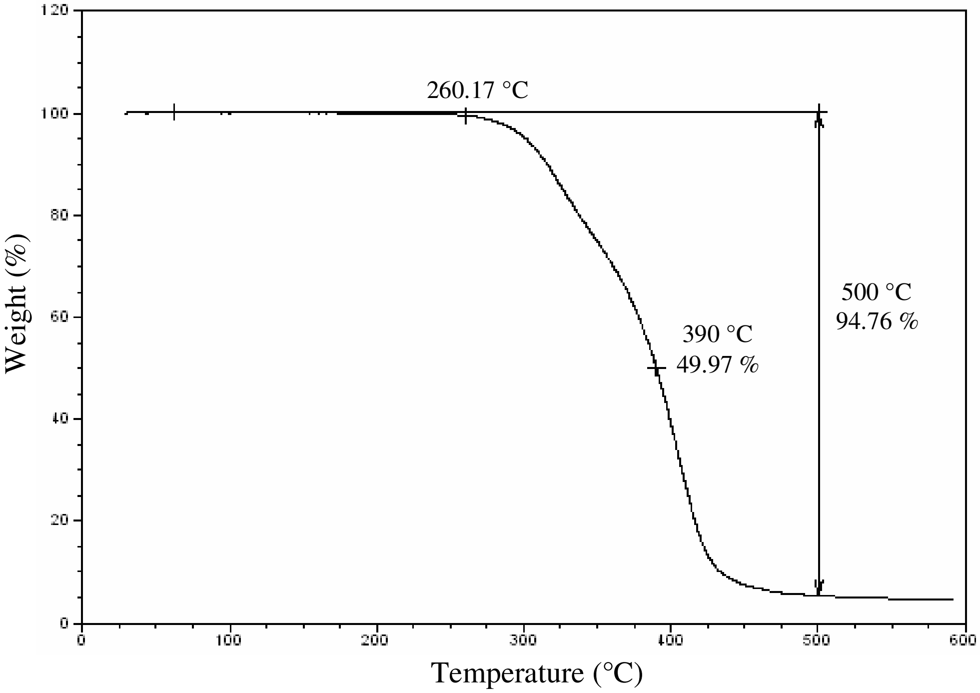


Figure 5.1 Thermogravimetric analysis (TGA) of TPU polymer

5.2.3. Differential scanning calorimeter (DSC) measurement

Differential scanning calorimeter measurement of TPU polymer is shown in Figure 5.2. The horizontal axis of this graph indicates temperature (°C) changes while vertical axis indicates the changes in heat flow (W/g). The measurement was done with 10 °C/min temperature gradient. When the results observed from this graph was examined, temperature interval of glass transition was found out to be between -34.14 °C and -28.58 °C. In the meantime, the temperature of glass transition (Tg) was found -28.60 °C. Also, it was found that crystallinity (Tc) temperature of TPU polymer is 83.52 °C and the percentage of crystallinity is 31.89 %. Finally, melting temperature (Tm) of TPU polymer has been observed as 207.75 °C.

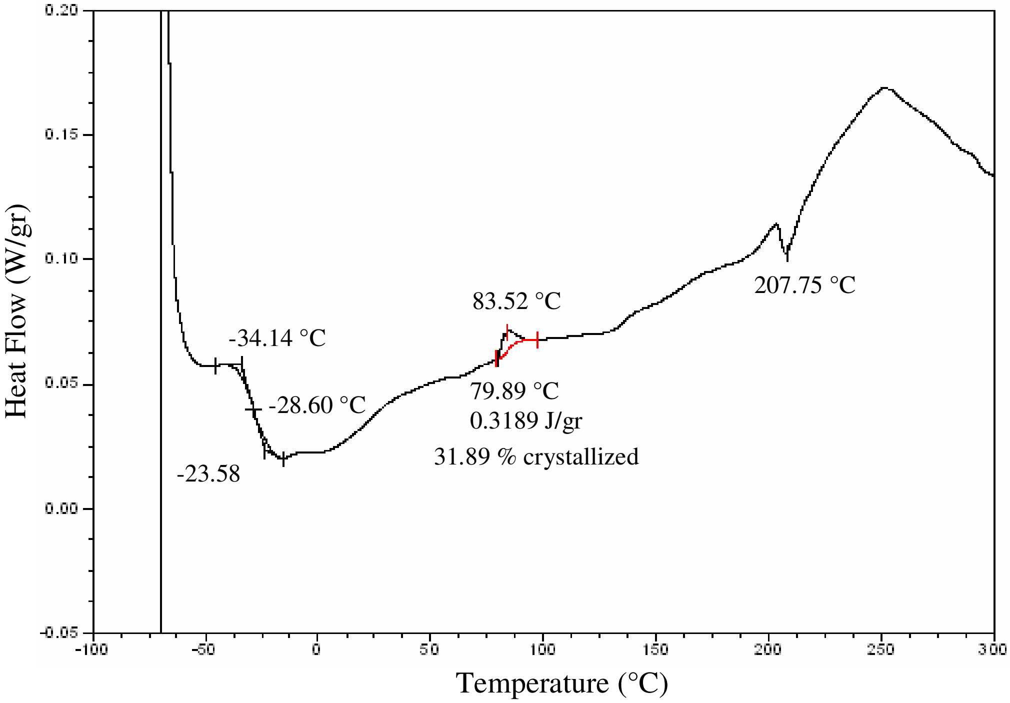


Figure 5.2 Differential scanning calorimeter (DSC) measurement of TPU

5.3. Solution Electrospinning of TPU

Electrospun fibers were produced by using solution electrospinning system in an average temperature of 33 °C and relative humidity of 30 %. While electrospinning process was taking place, it has been observed carefully. Fiber collection onto the aluminum foil was examined and photos taken. Then, electrospun fibers were weighed. Electrospun fiber samples taken from collectors were analysed on the FESEM. And scanning electron micrographs were taken. Fiber diameters have been measured from these micrographs.

5.3.1. Process observations

The electrospinning process was initialized with an early adjusted voltage value. However, voltage value was gradually increased in order to determine critic voltage value (Vc) while the process was taking place. Thus, Vc was found as 5 kV at wt. 5 % TPU concentration and 6 cm distance from tip of the needle to collector. The first polymer jet formed at this voltage value. Because of higher voltage values used in experiments, it was observed that more than one jet could be formed from the handled drop that stayed at the tip of needle during the electrospinning process.

When the process firstly started, some little polymer drops which came from handled drop might fall onto the collector. One or over one stable jet took over these little polymer drops in a short time. Then, these jets were observed to move fastly from handle drop to collector. While jets were moving between them, dimethylformamide which had a function of solvent on the TPU solution evaporated. As a result of this evaporation, only TPU remained and electrospun TPU fibers were formed (seen in Figure 5.3).

Figure 5.3 Formation of electrospun TPU fibers onto collector

5.3.2. Electrospun fiber collection

A fixed collector was obtained by covering a thin galvenized metal plate with an aluminium foil and placed on a tripod. Then, this collector was grounded. Electrospun fibers that were carried by jets were collected homogeneously onto the collector. After a while, electrospun fibers which collected onto a certain part of the collector moved to another part of the collector (seen in Figure 5.4). The reason of this is that the first collection part of the electrospun fibers is isolated in the course of time. Also, it was observed that at the beginning of the process and during the exchanging of jet or jets, very little solution drops drippled onto collector.

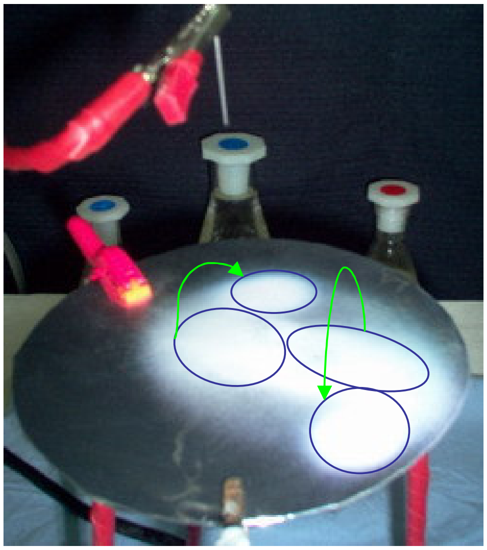
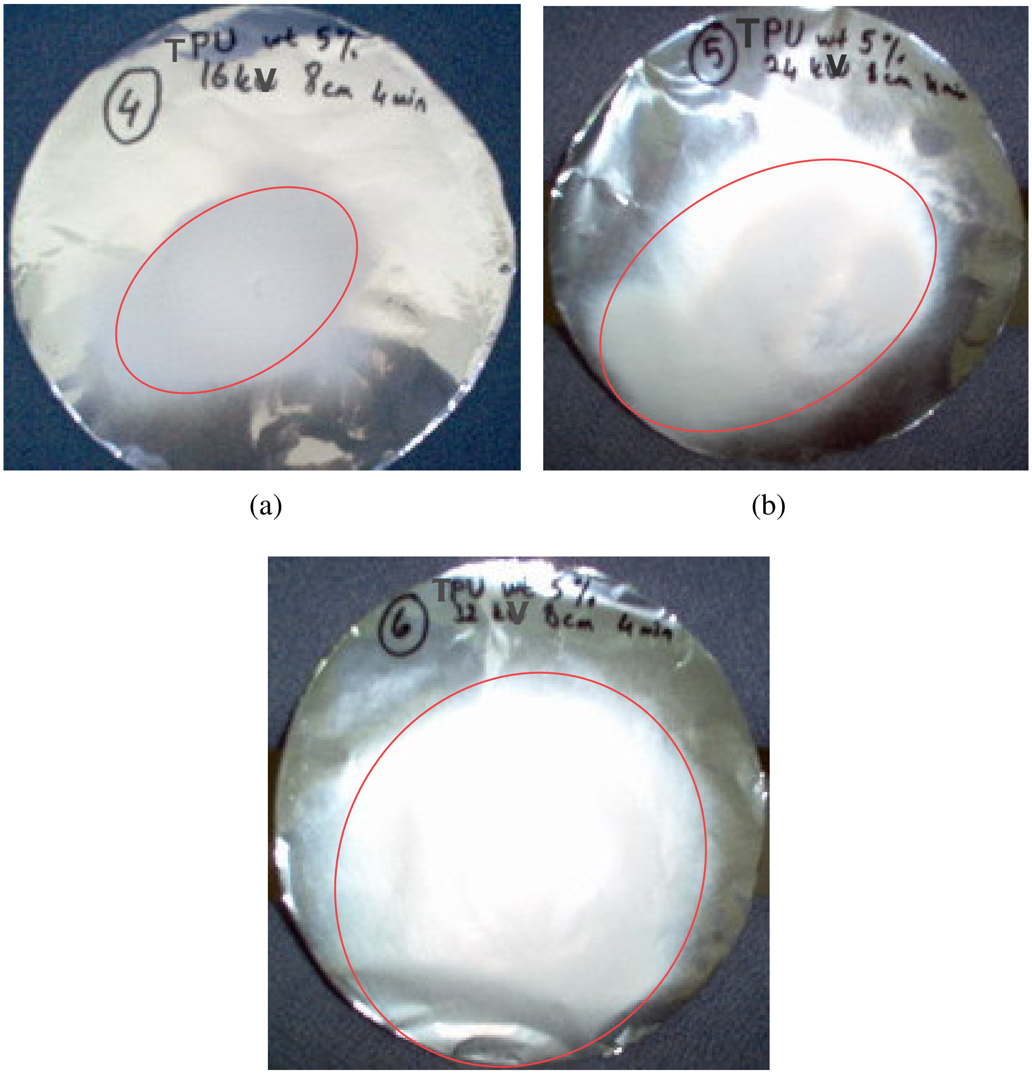


Figure 5.4 Electrospun TPU fibers collection as a result of jet movement

Another observed result is that when applied voltage is increased, electrospun fibers are positioned as covering more surface area onto the collector. Three samples which was produced at wt. 5 % TPU concentration and 8 cm distance from tip of the needle to collector are given in Figure 5.5. These samples were produced at different voltage values as 2 kV/cm, 3 kV/cm, and 4 kV/cm. The effect of voltage increase on fiber collection surface area is clearly observed from these samples.



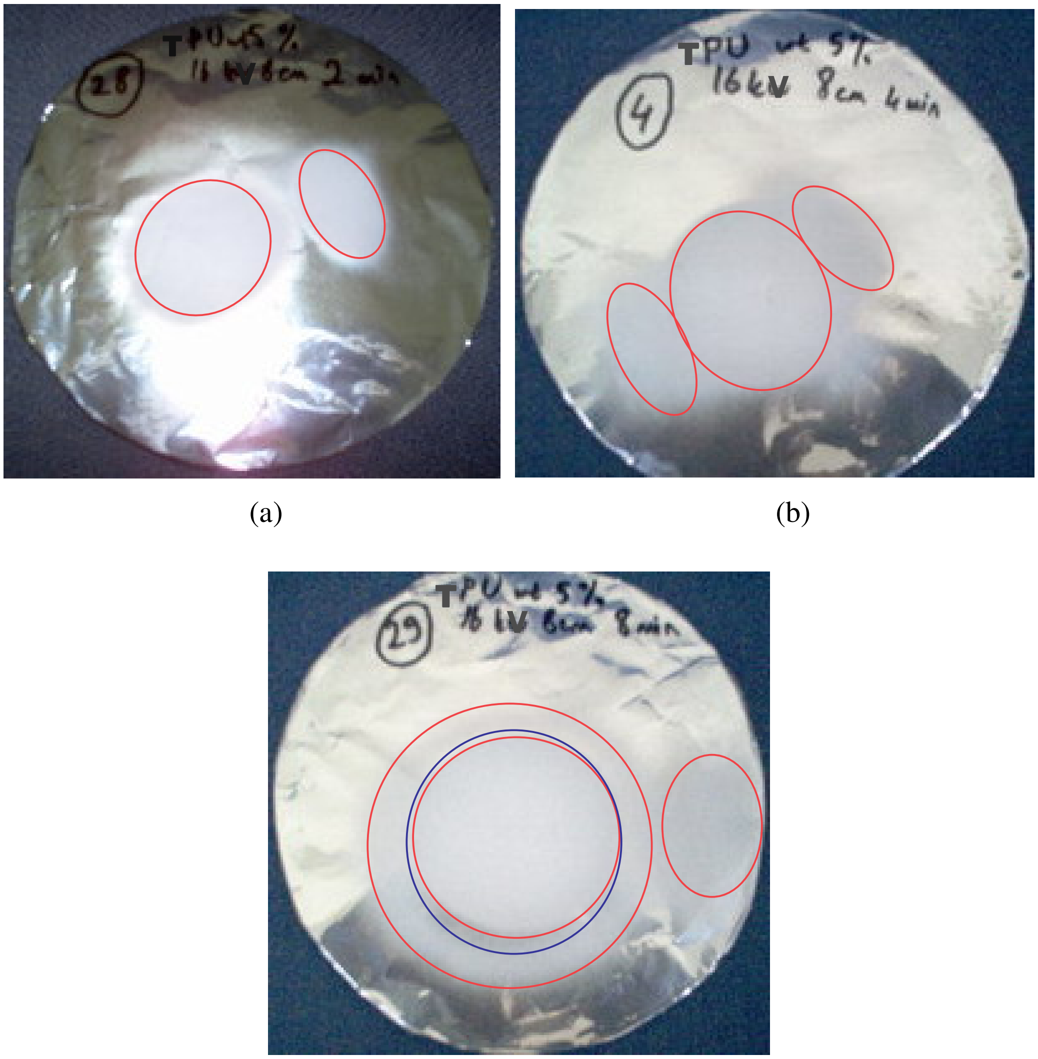
(a)

(b)

(c)

Figure 5.5 Effect of applied voltage on fiber collection (a) 2 kV/cm, (b) 3 kV/cm, (c) 4 kV/cm

Figure 5.6 shows the effect of time on fiber collection. Samples shown in Figure 5.6 were produced at wt. 5 % TPU concentration and 8 cm distance from tip of the needle to collector. Production times of these samples were 2 min, 4 min, and 8 min respectively. The aim of this experiment was not only to examine fiber collection but also to observe the continuity of the process. In the end of this experiment, process was observed to continue without any interruption. Also, when the process time was increased, electrospun fibers were collected not only at fixed position onto the collector but also other places of the collector regularly.



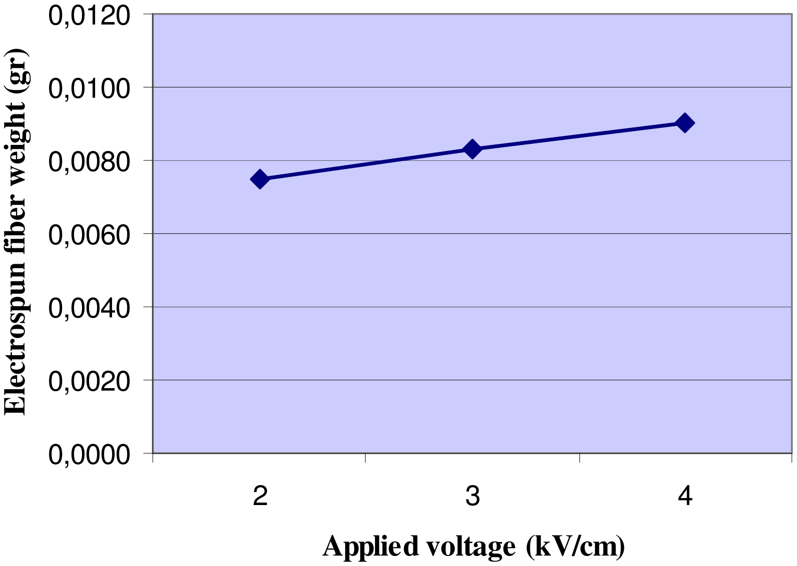
(a) (b)

(c)

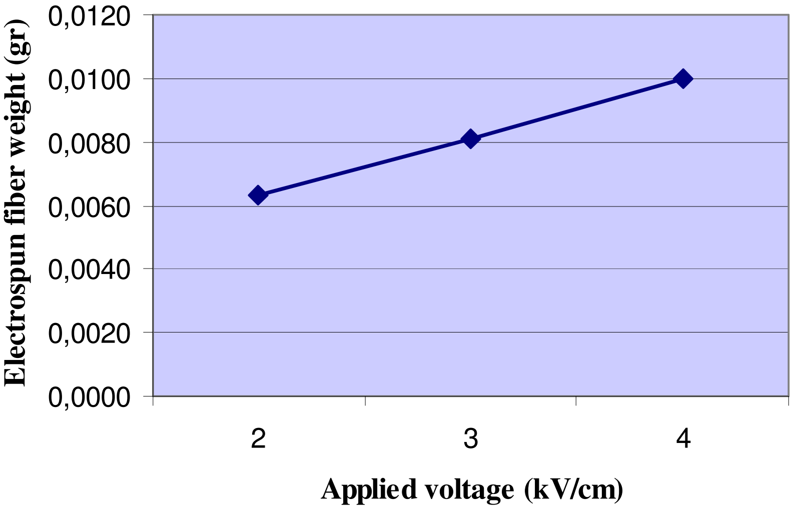
Figure 5.6 Effect of time on fiber collection (a) 2 min, (b) 4 min, (c) 8 min

5.3.3. Electrospun fiber weight

The weights of the electrospun fibers were measured with subtracting the weight of the collector weighed before the process from weight of the collector weighed after the process by using a sensitive weigh balance. The graphs given in Figure 5.7 show that, an increase on the applied voltage causes an increase on fiber weight. Furthermore, according to the comparison of graphs, increase of weight ratio of the electrospun fibers which were produced at 10 cm distance from tip of the needle to collector (seen in Figure 5.7 b) is higher than that of 6 cm (seen in Figure 5.7 a).



(a)



(b)

Figure 5.7 Effect of applied voltage on electrospun fiber production weight at 4 min with distances of (a) 6 cm, (b) 10 cm

5.3.4 Electrospun fiber diameter

Electrospun fiber diameter measurements were done by using FESEM images of electrospun fibers. Electrospun fiber diameters were measured to proportionate between electrospun fiber diameter and ratio scale which is stated on the bottom right of the FESEM images. Totally 60 diameter measurements were done for each FESEM images. These measurements were performed by determining 20 fibers chosen from each FESEM images and 3 diameter measurement for each of these fibers. The results are given in Table 5.1.

Table 5.1 Diameter measurements of solution electrospun TPU fibers

TPU Concentration (wt. %)	Applied Voltage (kV/cm)	Distance (cm)	Processing Time (min)	Minimum Fiber Diameter (nm)	Maximum Fiber Diameter (nm)	Mean Fiber Diameter (nm)	Standart Deviation (%)
5	2	8	8	212	336	279	9
5	2	8	4	212	372	281	15
5	3	8	4	177	336	249	15
5	4	6	4	153	324	218	20
5	4	8	4	159	354	240	19
5	4	10	4	165	271	221	13

5.3.5. Effect of solution concentration on final product

Of the solutions containing TPU at percentages of wt. 5 %, wt. 7.5 %, and wt. 10 %, fibers could only be produced from the solution of wt. 5 %. Nanofibers made from this concentration have great morphological surface structures (shown in Figure 5.8). However, after analyzing FESEM images shown in Figure 5.9 and Figure 5.10, it was observed that the products of other solutions, wt. 7.5 % and wt. 10 %, are in the shape of small particules that resemble polymer drop rather than fibers on the collector.

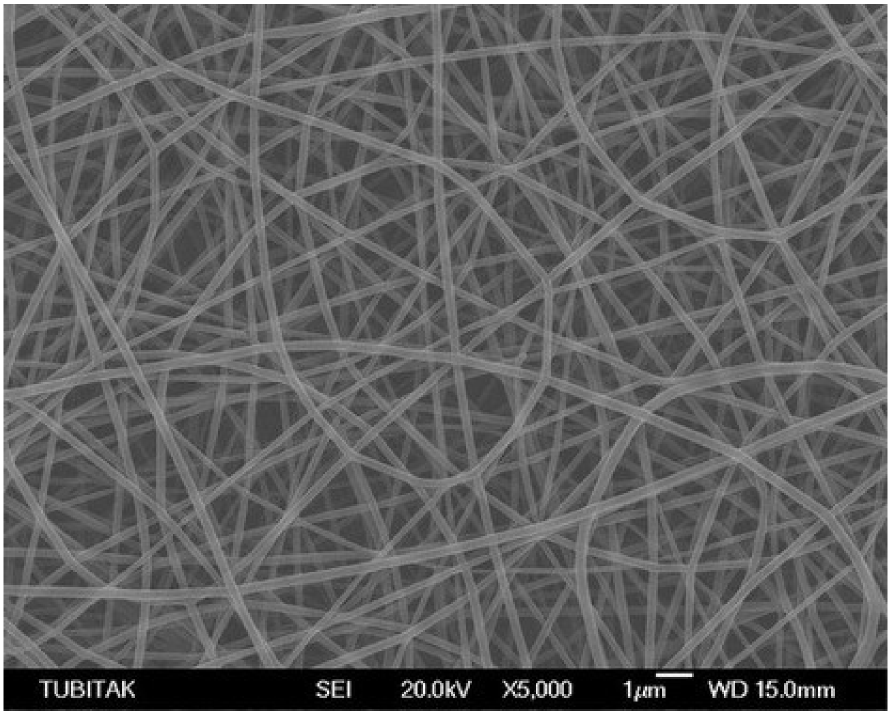


Figure 5.8 Scanning electron micrograph of solution electrospun TPU nanofibers produced at wt 5 % TPU concentration, 4 kV/cm applied voltage, and 10 cm distance

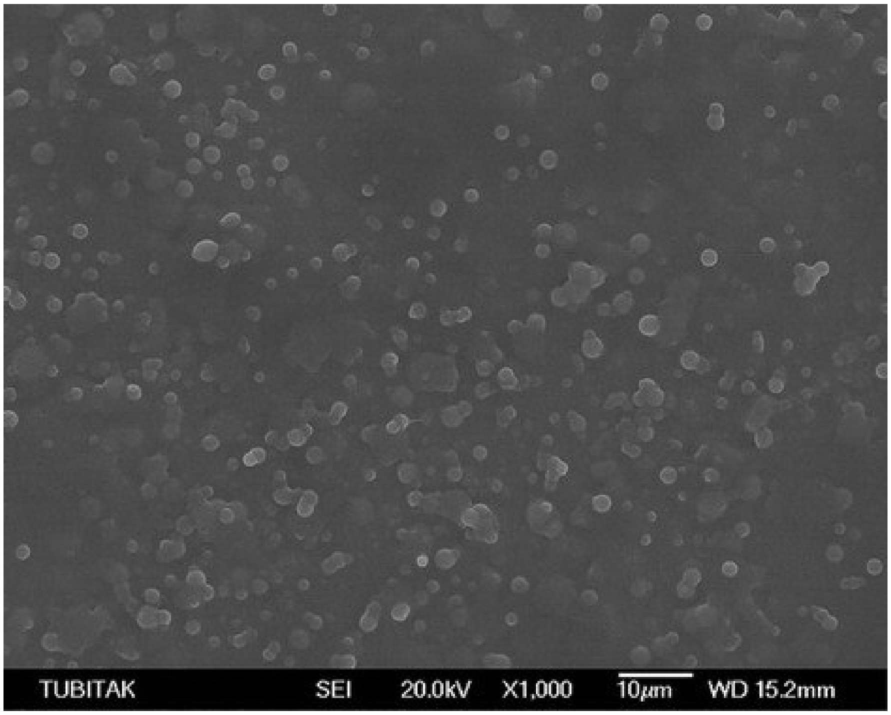


Figure 5.9 Scanning electron micrograph of solution electrospun TPU polymer drops produced at wt. 7.5 % TPU concentration, 4 kV/cm applied voltage, and 10 cm distance

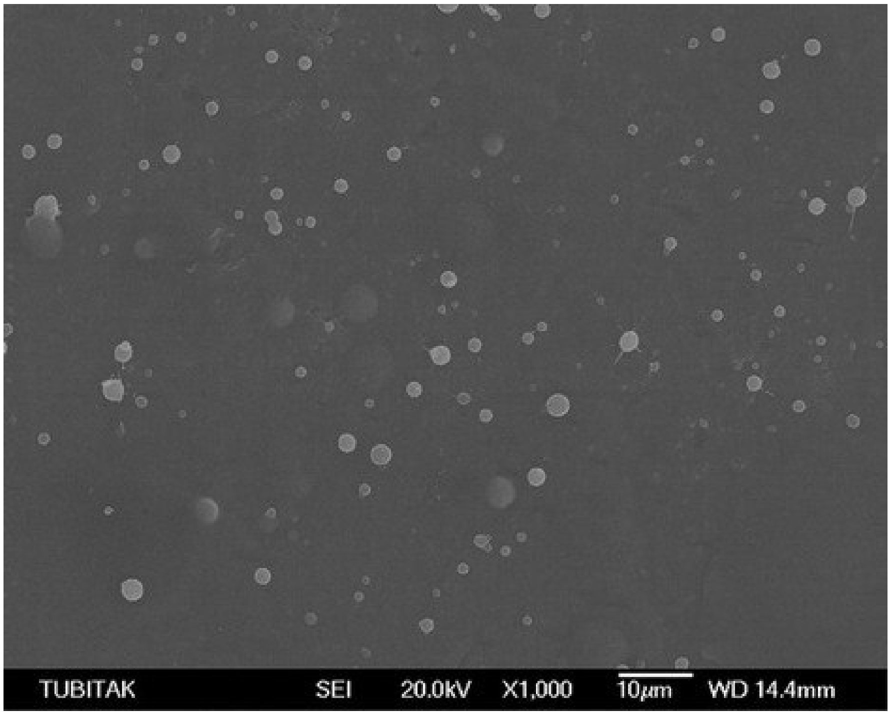


Figure 5.10 Scanning electron micrograph of solution electrospun TPU polymer drops produced at wt. 10 % TPU concentration, 4 kV/cm applied voltage, and 10 cm distance

5.3.6. Effect of applied voltage on fiber diameter

As soon as the effect of voltage values on average fiber diameter is determined, the factors of distance and concentration are fixed. Afterwards, it was observed that when applied voltage value on each cm increased, average fiber diameter decreased (seen in Figure 5.11).

5.3.7. Effect of distance from needle to collector on fiber formation

When the effect of distance from tip of the needle to collector is examined, the factors of concentration and applied voltage value on each cm are fixed. In conclusion, when the distance value is increased, it was observed that the formed web was smoother. After FESEM images were examined, with increase of distance value, fibers tended to stick to together (seen in Figure 5.12-14). It was observed that the most correct fiber forms were obtained at distance of 10 cm.

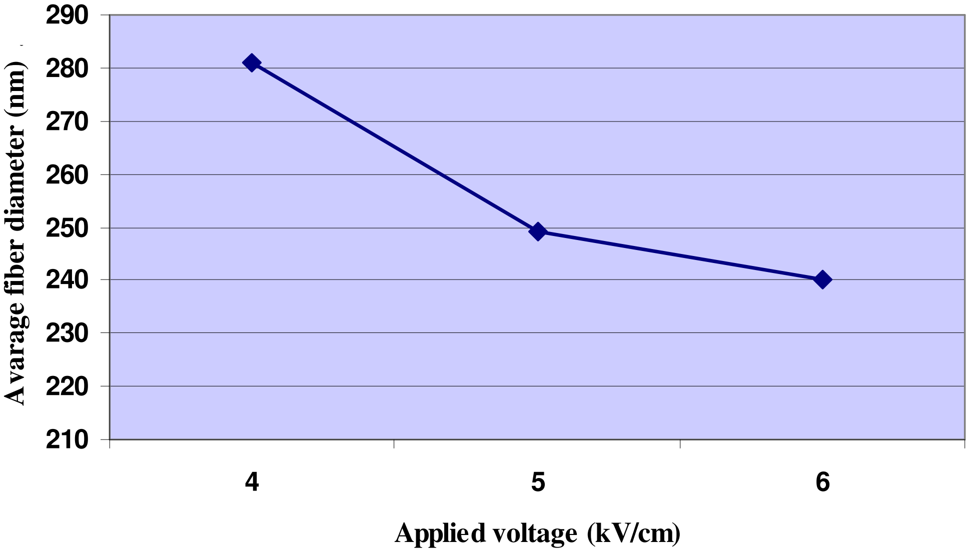


Figure 5.11 Effect of applied voltage on fiber diameter

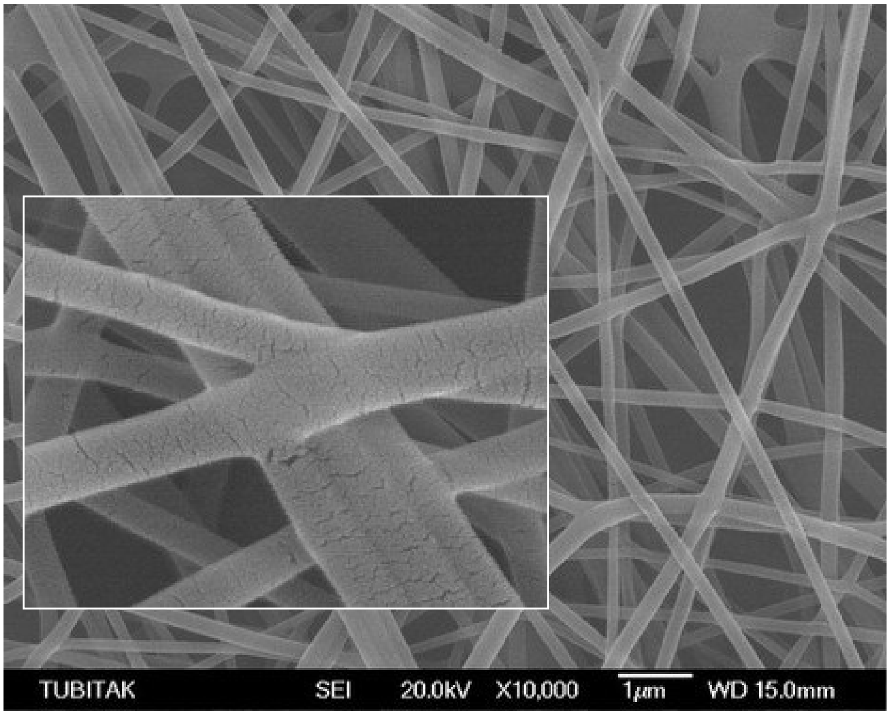


Figure 5.12 Scanning electron micrograph of solution electrospun TPU nanofibers produced at wt. 5 % TPU concentration, 4 kV/cm applied voltage, and 6 cm distance

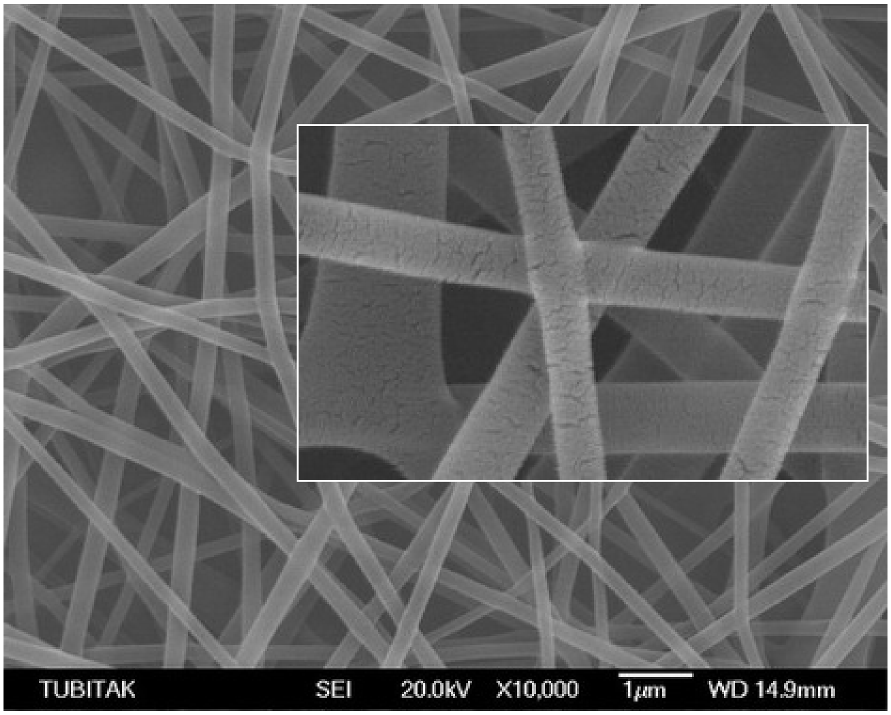


Figure 5.13 Scanning electron micrograph of solution electrospun TPU nanofibers produced at wt. 5 % TPU concentration, 4 kV/cm applied voltage, and 8 cm distance

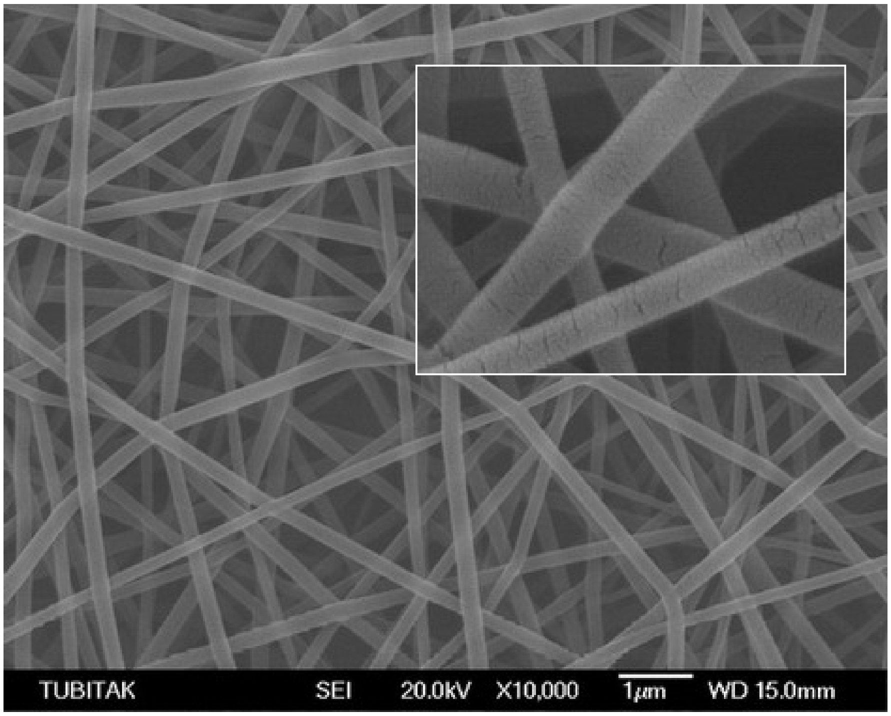


Figure 5.14 Scanning electron micrograph of solution electrospun TPU nanofibers produced at wt. 5 % TPU concentration, 4 kV/cm applied voltage, and 10 cm distance

5.3.8. Effect of processing time on fiber diameter

With the aim of observing the effect of processing time on fiber diameter, two samples that were produced at factors of 2 kV/cm applied voltage and 8 cm distance from tip of the needle to collector from wt. 5 % TPU were evaluated. While the first sample was obtained by the electrospinning process done in 4 min, second sample was obtained in 8 min. According to the statistical analysis taken from diameter measurement values, average diameter value of the first and second experiments are 281 nm and 279 nm respectively. These values are very close to eachother and it is concluded that process can be repeated in a reliable way. Another important conclusion of these samples is standart deviation on the diameter value of electrospun nanofibers produced in that two different time intervals. When the upper layer of electrospun webs were closely examined, nanofibers formed after the process time of 8 min showed a standart deviation value of 9 %. Nevertheless, nanofibers which were formed after the process in 4 min had a standart deviation value of 15 %. After this, it is proven that variation on the average diameter is less with the increase of process time.

5.4. Melt Electrospinning of Thermoplastic Polyurethane

Before the melt electrospinning process was carried out, measurements were done for new spinneret that was mounted on the melt flow index instrument. Thus, processing temperatures could be estimated for TPU experiments. Then, the melt electrospinning process of TPU granulles was observed carefully. Fiber collection onto aluminum foil was examined with photographs taken. After that, electrospun fibers were weighed. Electrospun fiber samples that were taken from collectors were analysed on the FESEM. And scanning electron micrographs were taken. Fiber diameters were measured from these micrographs.

5.4.1. Process observation

In order to prevent TPU granulles exposing long heating time, low amount of feeding was done in each experiment. Also, before each experiment, the inside of spinneret was carefully cleaned. After the system had been made ready, previously adjusted voltage has been applied to the system. First unstable jet releasing from drop that was hanged on the tip of the spinneret carried a thick polymer melt on the collector. Then, jet stabilized and it carried molten polymer to the collector systematically. Molten TPU polymer that was carried by jet cooled between collector and tip of the spinneret and electrospun fibers collected on a part of the collector (seen in Figure 5.15).

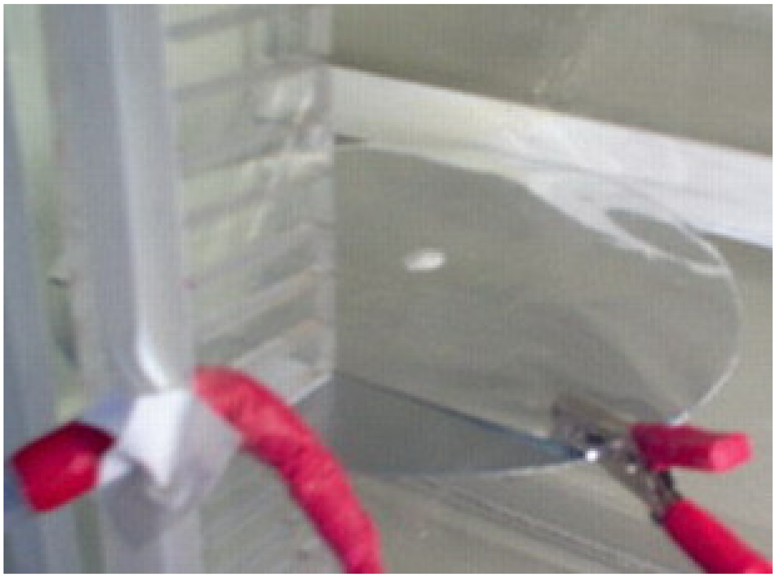


Figure 5.15 Formation of electrospun TPU fibers onto collector

5.4.2. Electrospun fiber collection

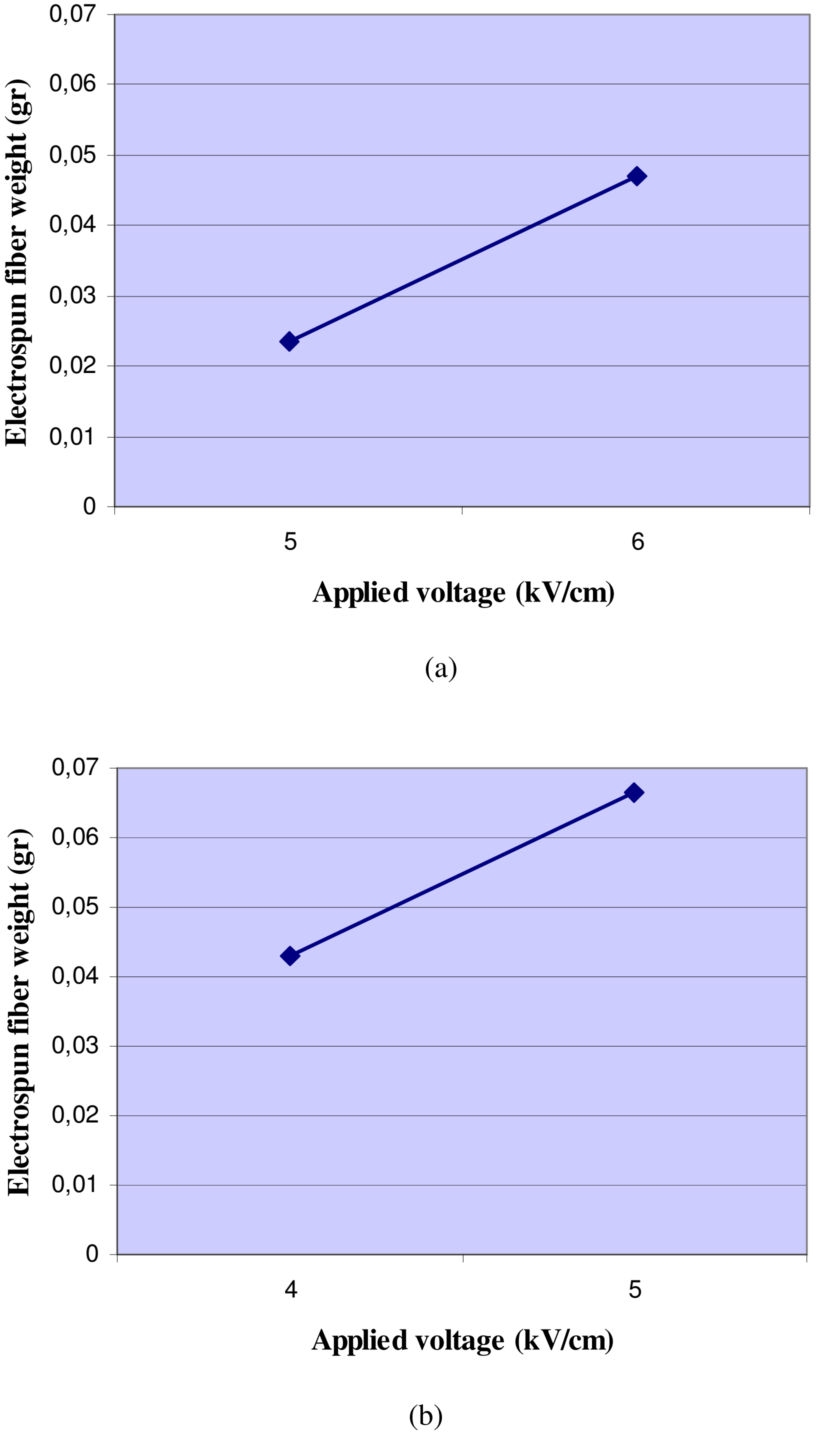
On the contrary of solution electrospinning process, electrospun fibers were collected by accumulating one on the top of the other in a way to form a hill like structure. The shape of hill like collected fibers are shown in Figure 5.16. Also, how the fibers were collected after the process is shown in Figure 5. 17.

Figure 5.16 Electrospun TPU fibers collection

Figure 5.17 Electrospun TPU fiber collection samples

5.4.3. Electrospun fiber weight

Weight measurements of the melt electrospun fibers have been done in the same way as weight measurement of the solution electrospun nanofibers. Weights that drops of polymer solution drippled onto the collector surface were not reflected in the results. The proportions of melt electrospun fibers weight to applied voltage were shown on graphs in Figure 5.18. After these graphs were examined, it was clearly seen that as the value of applied voltage is increased, so was the weight of melt electrospun fibers. Also, when these two graphs are compared, with increasing of distance value, melt electrospun fibers weight increases.



(a)

(b)

Figure 5.18 Effect of applied voltage on melt electrospun fiber production weight at 4 min with distances of (a) 6 cm and (b) 10 cm

5.4.4. Electrospun fiber diameter

Diameter measurements of melt electrospun TPU fibers were done in the same way as solution electrospun fiber diameter measurement by using FESEM images. Similarly, diameter measurements of melt electrospun fibers were done by examining 60 diameter measurements from 20 fibers on each scanning electron micrograph. The results are given in Table 5.2.

Table 5.2 Diameter measurements of melt electrospun TPU fibers

Processing (Set) Temperature (°C)	**Applied Voltage (kV/cm)**	**Distance (cm)**	**Processing Time (min)**	**Minimum Fiber Diameter (µm)**	**Maximum Fiber Diameter (µm)**	**Mean Fiber Diameter (µm)**	**Standart Deviation (%)**
250	4	10	4	2.50	7.26	4.90	26
257.2	4	10	2	10.6	17.1	14.4	12
257.2	5	10	4	2.62	9.40	5.01	34
257.2	6	8	4	3.10	9.17	5.85	28
260	4	10	4	1.32	5.60	8.21	28
260	5	8	4	1.31	7.26	4.32	36
260	5	10	4	4.52	16.43	8.98	33
260	6	6	4	1.79	5.71	4.01	28

5.4.5. Effect of processing temperature

In order to determine the suitable processing temperatures, the melt temperature of TPU polymer was firstly determined as 207 °C. Therefore, the exit surface temperatures of the new spinneret were measured for the purpose of determining the set temperatures on melt flow index instrument. The temperature of the exit surface of the spinneret was measured delicately with a multimeter. This spinneret temperature which can be observed from graph (Figure 5.19) is intersected from set temperature that was entered melt flow index device.

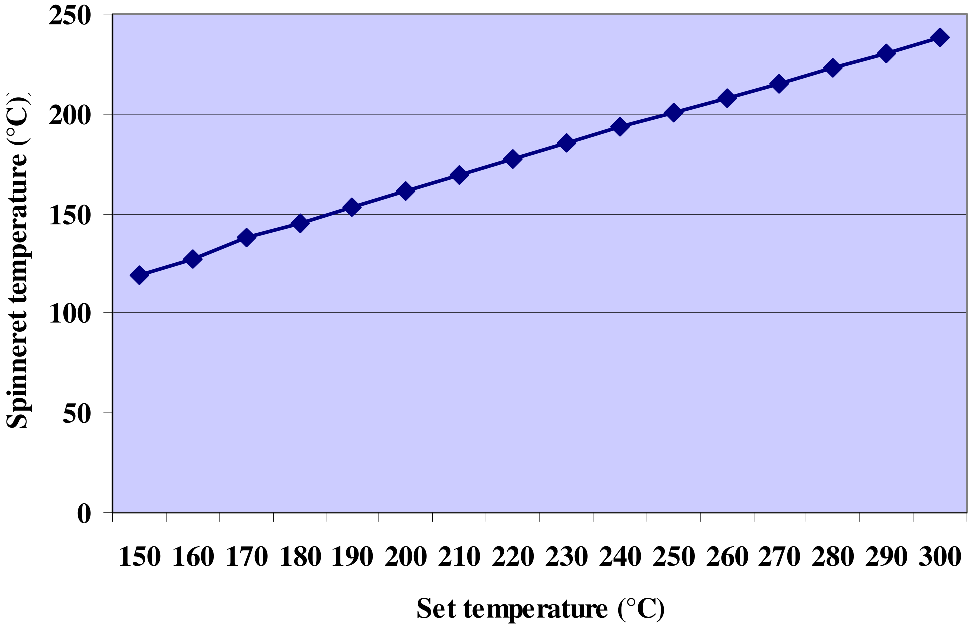


Figure 5.19 Spinneret temperature measurements

The melting temperature (Tm) was determined to be about 207 °C for TPU polymer which needs to be molten on the exit of the spinneret. Then, approximately 260°C set value has been determined as the temperature giving the nearest spinneret exit temperature as 207 °C. With this value and process temperatures near to this value are used frequently as set value. In the system, trials were also done with these processing temperatures which were higher or lower of this value.

In the experiments which set values were 240°C and lower, TPU polymer that was molten on heating chamber was resulting in a solidified polymer at the exit surface of the spinneret. The temperature at the exit surface of the spinneret was almost 194 °C.

As the set value (240 °C) was increased, TPU polymer on the exit of spinneret has reached its melting temperature and hence the process has taken place.

The temperature values on spinneret exit that caused the process taken place are equal to melting temperature of TPU polymer (207 °C). These temperature values could be reached by setting melt flow index chamber temperature between 255°C and 260°C. These set values have given the best results for the melt electrospinning experiments.

Scanning electron micrograph (seen in Figure 5.20), taken from a sample which was produced with a 257.2 °C set value of melt electrospinning process confirms this result. However, at temperatures above 260 °C, especially at 270 °C, the polymer has become a drop on the exit surface of the spinneret. Therefore, the polymer melt was carried to the collector without forming any fibre. So, the produced samples have not obtained the desired structures.

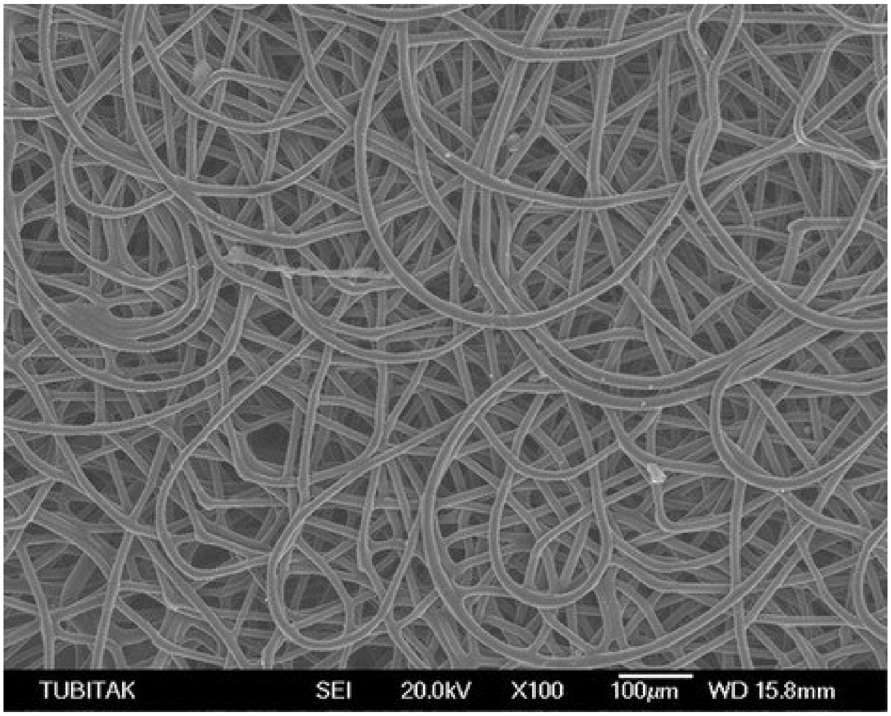


Figure 5.20 Scanning electron micrograph of melt electrospun TPU fibers produced at 257.2 °C set temperature, 4 kV/cm applied voltage, and 10 cm distance

5.4.6. Effect of applied voltage on process

In the melt electrospinning process, the total applied voltage is more effective than the voltage value applied on each cm. For example, in the experiment that 4 kV/cm voltage value was applied at 260 °C set temperature with 6 cm distance from exit of spinneret to collector, any fiber formation has not been realised. However, fiber formation could be observed at higher total voltage values which raised directly by means of increases in distance. On the other hand, higher applied voltage values may easily cause to discharge of the system. So, the experiments that 6 kV/cm applied voltage value which had early determined and 10 cm distance value were not succeded.

5.4.7. Effect of distance on fiber diameter

Samples produced at 260 °C set value at 6 cm, 8 cm, and 10 cm distances from spinneret exit to collector, after 4 min have resulted in an average diameters of 4012 nm, 4315 nm, and 8208 nm respectively. Graph which shows the effect of these distances on average fiber diameter is given in Figure 5.21. When graph is examined, it is observed that distance increase results in an increase of melt electrospun average fiber diameter.

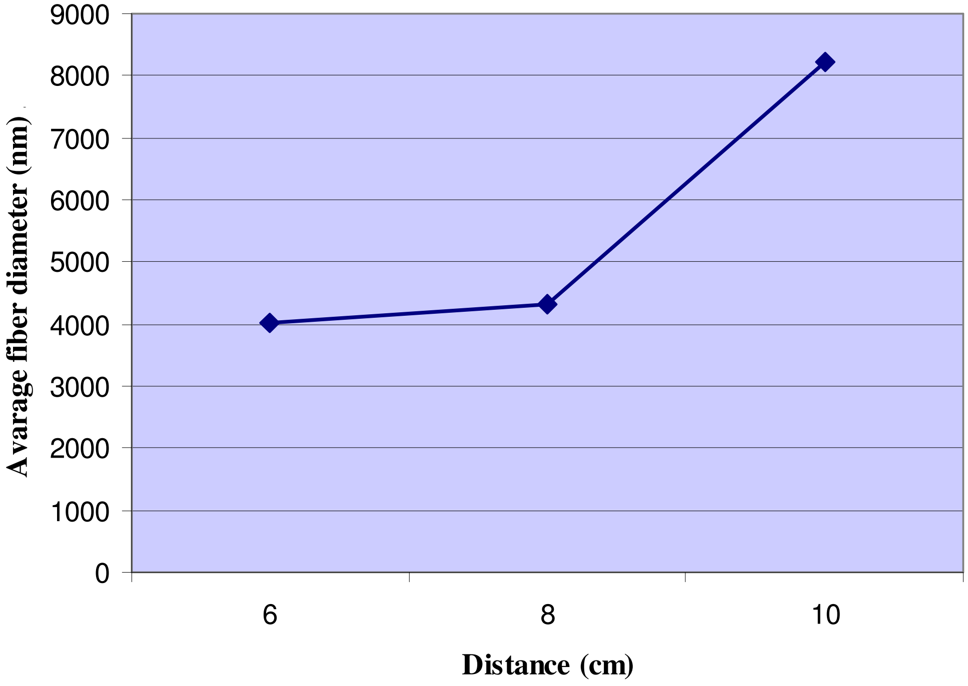


Figure 5.21 Effect of distance on electrospun fiber diameter

5.4.8. Effect of distance on fiber morphology

Effect of distance value on electrospun fiber was studied by using scanning electron micrographs of the samples. Firstly a visual comparison of the scanning electron micrographs has been done. As a result of this comparison, it was observed that with increase of distance value, tendency of sticking electrospun fibers into eachother decreases (Figure 5.22-24). Electrospun fibers having the best fiber morphology were acquired by samples produced at 10 cm distance in the experiments.

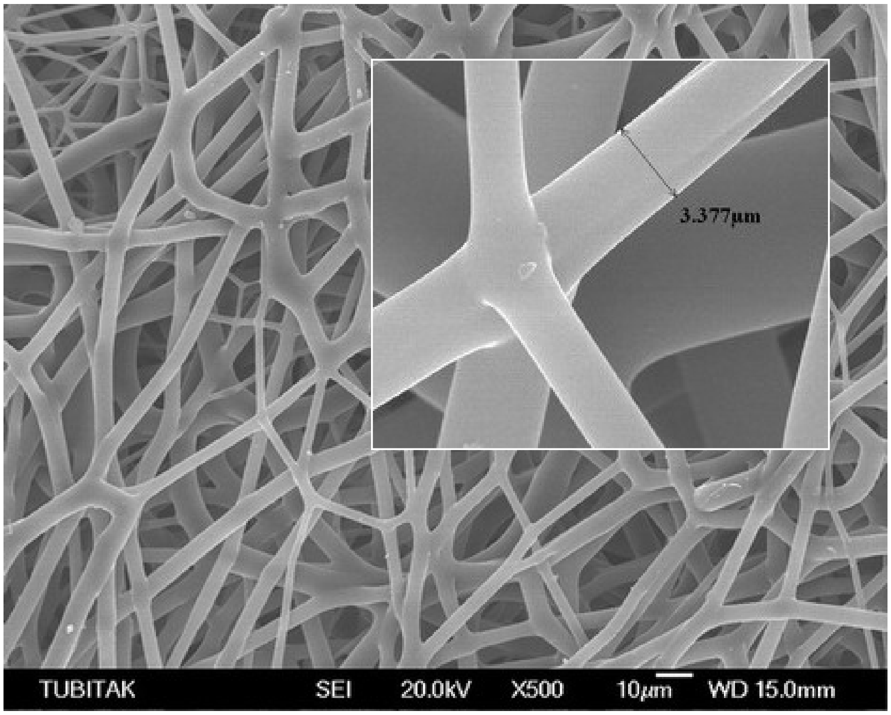


Figure 5.22 Scanning electron micrograph of melt electrospun TPU fibers produced at 260°C set temperature, and 6 cm distance

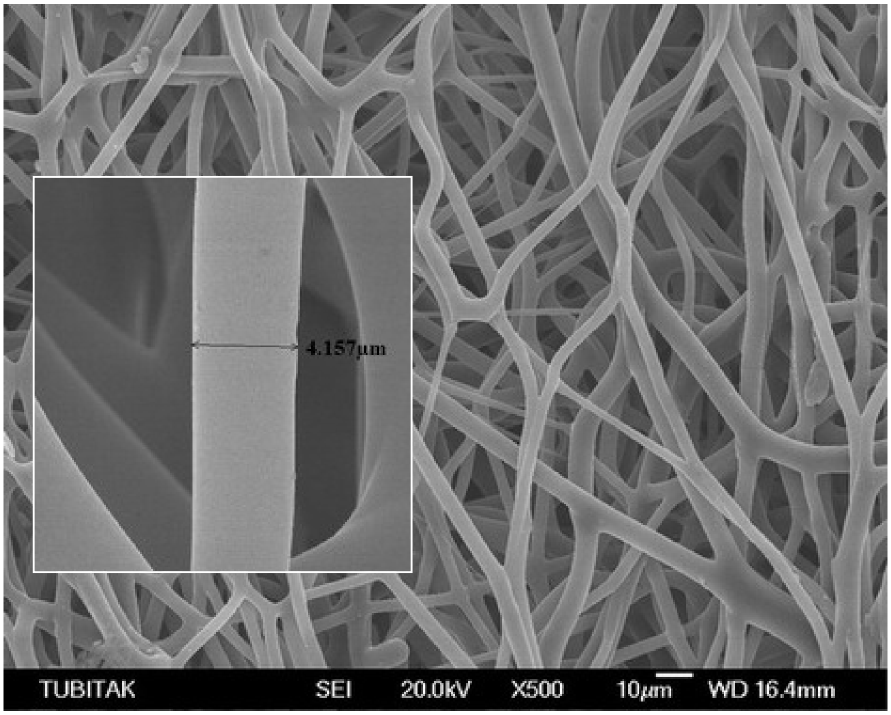


Figure 5.23 Scanning electron micrograph of melt electrospun TPU fibers produced at 260°C set temperature, and 8 cm distance

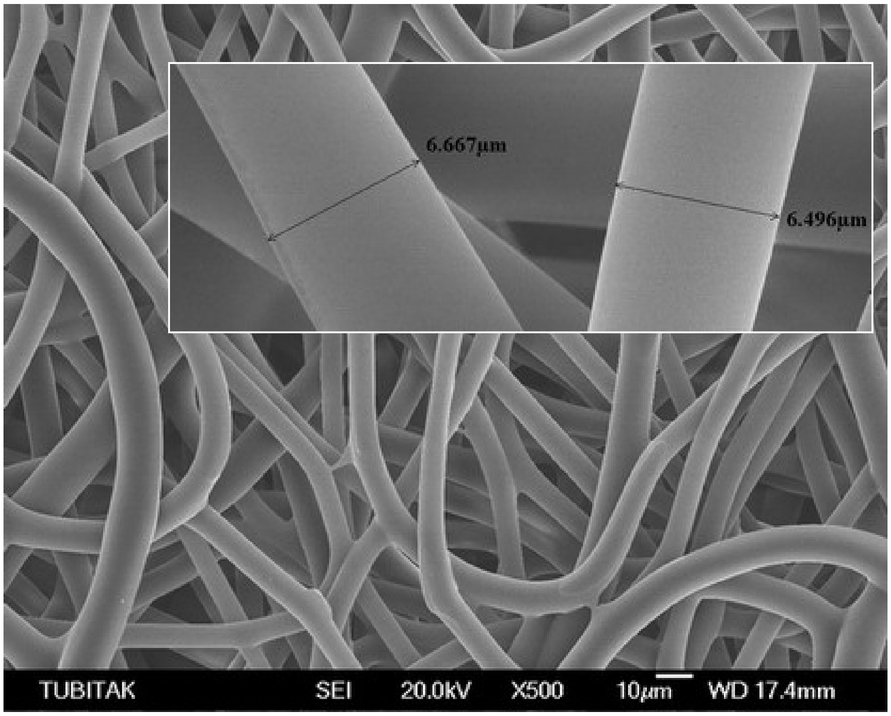


Figure 5.24 Scanning electron micrograph of melt electrospun TPU fibers produced at 260°C set temperature, and 10 cm distance

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS FOR FURTHER WORK

Solution electrospinning and melt electrospinning set-ups were established in order to produce nanofibers from thermoplastic polyurethane (TPU). Experiments for this work have been made on these systems. With the knowledge obtained from the results, conclusions and recommendations are included in this chapter.

In solution electrospinning, the reason why nanofibers can not be formed from solution of wt. 7.5 % and wt. 10 % that contain high amount of TPU is to have these solutions more viscosity than the solution of wt. 5 % TPU concentration. The more concentration of the solution increases, the more its viscosity value increases. Thus, voltage needed to create a jet also increases.

As the voltage value increases, so does the quantity of fibers collected on collector surface. At the same time, the quantity of area surrounding on collector surface increases, too. Therefore, more fiber could be produced at high voltage values. Another crucial result is that the mean electrospun fiber diameter decreases with the increasing voltage in solution electrospinning of TPU.

It was observed that, the electrospun nanofibers were collected more homogenously by spreading on a wide area in solution electrospinning of TPU than by spreading on the top of the other on a limited area in melt electrospinning of TPU. Also, it was observed that while process continued, with increasing fiber quantity that was collected on certain areas on the collector surface, jets, by changing their paths, turned towards empty surfaces on collector in the course of time. In the end of this observation, an active carrier band can be used as a collector in future experiments.

Electrospun nanofibers that were formed with the increase of distance from tip of the needle to the collector in solution electrospinning system were observed to be smoother, although in low distance values electrospun nanofibers tended to stick together.

The results obtained from the average fiber diameter statistics showed that the standard deviation decreases with an increase in process time. Besides, it was observed that there was only a difference of less than 1 % in average fiber diameter value. The fact is that the process is reliable and the repeatability is ensured.

Since the electrospinning process could not take place with the original spinneret of the melt flow index device, a new spinneret was designed. Having integrated this designed spinneret onto the system, the melt electrospinning process was then possible. However, that newly designed spinneret was longer than the old one caused the temperature on exit area of spinneret to be lower than the set value. Because of this, the melt electrospinning needed high set values. This led polymer to show sometimes tendency to decomposition by exposing higher heat. For the future experimental work, a heating element mounted to the tip of spinneret can give better results.

It was a disadvantage to process TPU granules above 260 °C as they have decomposed easily. Therefore, the experiment work had to be repeated usually. Another problem was melt polymer that made impossible to happen electrospinning process due to solidification on the spinneret exit, because of the low temperature on it. Besides, that melt of TPU granules stay long time in heating zone can lead to decomposition of polymer. Therefore, after each experiment, the heating zone had to be emptied and cleaned.

Also, it was observed that electrospun fibers were collected by accumulated one on the top of the other. After examining FESEM images, fibers that collected on a motionless collector were observed to stick together. In the respect of preventing this sticking and evaluating formed fibers on a potential usage area, it needs to be used an active collector in the future studies. This collector can be designed as a revolving roller.

In the melt electrospinning process, as the applied voltage increases, so does the tendency to discharge. In the experiments done with 6 kV/cm applied voltage and 10 cm distance, it was clear that being total voltage 60 kV was the cause of discharging of the system. So, it was not possible to work very high voltage values. On the other, the result of low voltage and low distance, 4 kV/cm applied voltage and 6 cm distance where total voltage applied less, the process could not be realized. This voltage value was not enough to move molten TPU polymer. Moreover, it was deduced that when voltage quantity is increased, the weight of melt electrospun fibers increases highly.

One disadvantage observed in the melt electrospinning system was that drippling of molten TPU polymer from spinneret during experiments made process hard by effecting adversely to the product which was collected on the collector surface.

It was proven that in the melt electrospinning process, the collector distance was a crucial process parameter. Increasing of distance enabled molten polymer, carried by jet, to contact with air in a longer period. The morphology of the electrospun fibers obtained as a result is smoother. Furthermore, with increase of distance electrospun fiber production increases, but mean diameter of melt electrospun fibers decreases.

When the results obtained this study are compared with former studies, there is direct relation at effect of applied voltage in solution spinning. Also, in this study some improvements achieved such as low standard deviation in solution electrospinning. On the other hand, melt electrospinning of TPU polymer has not been investigated. So, this study would be a guide for further studies in this field.

In conclusion, TPU fibers at nano scale were only produced by solution electrospinning process. Besides, fibers having diameters at micron level were produced by melt electrospinning process. The TPU polymer, prepared as solution, was fed with serum set gave extremely good results such as low standard deviation values. Despite the fact that at the end of the preparatory work on melt electrospinning experiments has resulted no melt electrospun fibers, modifying the set up with new spinneret and protector cabin made electrospun fiber production possible. However, the system needs to be improved. During melt electrospinning, some problems have been faced due to temperature difference on spinneret to set value. These problems are to solidify melt polymer on the spinneret exit and decompose polymer by exposing too much heat. On the other hand, when electrospun fiber production quantity on melt electrospinning process was compared to solution electrospinning, it was realized that melt electrospun fiber production quantity was more than solution electrospun fiber production.

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