

ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE
ENGINEERING AND TECHNOLOGY

**PRODUCTION OF CELLULOSE NANOWHISKERS REINFORCED
ELASTOMERIC NANOFIBERS WITH ELECTROSPINNING TECHNIQUE**

M.Sc. THESIS

Onur AYAZ

Department of Nano Science And Nano Engineering

Nano Science And Nano Engineering Programme

JANUARY 2013

ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE
ENGINEERING AND TECHNOLOGY

**PRODUCTION OF CELLULOSE NANOWHISKERS REINFORCED
ELASTOMERIC NANOFIBERS WITH ELECTROSPINNING TECHNIQUE**

M.Sc. THESIS

**Onur AYAZ
(513101016)**

Department of Nano Science And Nano Engineering

Nano Science And Nano Engineering Programme

Thesis Advisor: Prof. Dr. Nuray UÇAR

JANUARY 2013

İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

**SELÜLOZ NANOWHİSKER İLE GÜÇLENDİRİLMİŞ ELASTOMERİK NANO
LİFLERİN ELEKTROEĞİRME YÖNTEMİ İLE ÜRETİLMESİ**

YÜKSEK LİSANS TEZİ

**Onur AYAZ
(513101016)**

Nano Bilim ve Nano Mühendislik

Nano Bilim ve Nano Mühendislik Programı

Tez Danışmanı: Prof. Dr. Nuray UÇAR

OCAK 2013

Onur Ayaz, a **M.Sc** student of ITU **Institute of / Graduate School of Nano Science and Nano Engineering** student ID **513101016**, successfully defended the **thesis** entitled “Production of Cellulose Nanowhiskers Reinforced Elastomeric Nanofibers With Electrospinning Technique”, which he prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

Thesis Advisor : **Prof. Dr. Nuray Uçar**
İstanbul Technical University

Jury Members : **Prof. Dr. Ali Demir**
İstanbul Technical University

Prof. Dr. Ayşen Önen
İstanbul Technical University

Date of Submission : 10 December 2012
Date of Defense : 21 January 2013

To my family and friends,

FOREWORD

First of all I would like to express my gratitude to my thesis advisor, Prof. Dr. Nuray UÇAR for her continuous patience, guidance and helpful critics in my studies.

I also appreciate the financial support provided by TUBITAK (The Scientific and Technological Research Council of Turkey) under Project Number 109M267.

I would like to thank Prof. Dr. H. Ayşen ÖNEN and Prof. Dr. Mustafa ÖKSÜZ for their guidance and technical support.

In addition, I am thankful to all my colleagues and friends in this research especially to Ezgi İŞMAR, Mustafa Edhem KAHRAMAN, Mert Emre ÖZTOKSOY, Leyla YAĞMUR, Serha AYA, Ömer Faruk VURUR, Elif BAHAR and Salih GÜLŞEN for their assistance, encouragement and friendship.

Finally, I would like to thank to my parents; Fatma and Lütfü AYAZ for being with me and supporting me at every moment of my life.

January 2013

Onur AYAZ
(Textile Engineer)

TABLE OF CONTENTS

	<u>Page</u>
FOREWORD	vii
TABLE OF CONTENTS	ix
ABBREVIATIONS	xi
LIST OF TABLES	xiii
LIST OF FIGURES	xv
SUMMARY	xvii
ÖZET	xix
1. INTRODUCTION	1
1.1 Nanofibers	1
1.2 Production Methods of Nanofibers	3
1.2.1 Electrospinning	3
1.2.1.1 Multi-jet electrospinning	5
1.2.1.2 Coaxial electrospinning	6
1.2.2 Other nanofiber production methods	6
1.2.2.1 Drawing	6
1.2.2.2 Electroblowing	7
1.2.2.3 Meltblowing	7
1.2.3 Electrospinning parameters	7
1.2.3.1 Solution paramters	8
1.2.3.2 Ambient parameters	9
1.2.3.3 Process parameters	10
1.3 Overview of SEBS-g-MA	11
1.4 Cellulose	12
1.4.1 Cellulose nano whiskers	14
2. AIM OF THE STUDY	17
3. EXPERIMENTAL STUDIES	19
3.1 Materials	19
3.2 Equipment and Analysis	19
3.2.1 Infrared analysis (IR)	19
3.2.2 Scanning electron microscope (SEM)	20
3.2.3 Tensile loading machine	20
3.2.4 Thermogravimetric analysis (TGA)	22
3.3 Electrospinning Proecss	22
3.3.1 Solvent preparation	22
3.3.2 Preparation of cellulose nano whiskers (CNW)	23
3.3.3 Sample preparation	24
4. RESULTS AND DISCUSSION	27
5. CONCLUSION	41
REFERENCES	45
CURRICULUM VITAE	49

ABBREVIATIONS

CNW	: Cellulose Nano Whiskers
SEBS-g-MA	: Block-poly(ethylene-ran-butylene)-block-polystyrene graft- maleic anhydride
SEM	: Scanning Electron Microscope
FT-IR	: Fourier Transform Infrared
TGA	: Thermo Gravimetric Analysis
DMF	: Dimethylformamide
THF	: Tetrahydrofuran
MCC	: Microcrystalline Cellulose

LIST OF TABLES

	<u>Page</u>
Table 1.1 : Different terminologies used to describe cellulose micro and nano Particles.....	13
Table 3.1 : Electrospinning parameters of samples.....	24
Table 3.2 : Production methods and CNW contents of the samples.....	26
Table 4.1 : Solvent and spinning parameters and spinning results of the samples....	27
Table 4.2 : Average, minimum and maximum diameters of samples 5,8,12,13,14 and 15.....	31
Table 4.3 : Average, maximum and minimum diameters of fibers obtained from reference sample, single nozzle and coaxial nozzle.....	34
Table 4.4 : TGA analysis values of nanofibers and films.....	37
Table 4.5 : Mechanical test results of samples.....	38

LIST OF FIGURES

	<u>Page</u>
Figure 1.1 : Basic electrospinning setup [7].	4
Figure 1.2 : Molecular structure of SEBS-g-MA [37].	11
Figure 1.3 : Molecular chain formula of cellulose [41].	12
Figure 3.1 : Common stress-strain diagram [50].	21
Figure 3.2 : Conventional electrospinning system.	23
Figure 3.3 : Coaxial nozzle.	26
Figure 4.1 : SEM image of sample 1.....	29
Figure 4.2 : SEM image of sample 2.....	29
Figure 4.3 : SEM image of sample 3.....	30
Figure 4.4 : SEM image of sample 12.....	32
Figure 4.5 : SEM image of sample 13.....	32
Figure 4.6 : SEM image of sample 14.....	33
Figure 4.7 : SEM image of sample 15.....	33
Figure 4.8 : SEM micrographs of nanofibers (a) Reference N; (b) Single N; (c) Coaxial N.....	34
Figure 4.9 : FTIR: (a) comparison between Reference N (1) Single N (2); (b) comparison between Reference N (1) Coaxial N (2); (c) comparison between Reference F (1) and Composite F (2).....	36
Figure 4.10 : Thermogravimetric analysis (TGA) graphs: (a) TGA graphs of films, 1, Reference F, 2, Composite F; (b) TGA graphs of nanofiber webs, 1, Reference N, 2, Single N and 3, Coaxial N.....	37

PRODUCTION OF CELLULOSE NANOWHISKERS REINFORCED ELASTOMERIC NANOFIBERS WITH ELECTROSPINNING TECHNIQUE

SUMMARY

Nanotechnology is an emerging interdisciplinary technology that has been booming in many areas. Nanomaterials with their enhanced properties, promise a great future and many possibilities for developing technologies including textiles and fibrous materials.

Nanocomposite materials are gaining more application areas each day with the developing technology. Materials like carbon nano tubes (CNT), nano clays and carbon black are gaining more attention in scientific researches and high technology industrial applications.

Cellulose nanowhiskers (CNW) are one of the nano materials which have great potential of usage and application in nano composite area. Although some studies on cellulose nano whiskers (CNW) have been carried out in the last two decades, detailed investigations on the use of CNW in composite materials are quite recent. Cellulose is the most abundant biopolymer. It is also biodegradable, non-toxic, low cost. Cellulose nano whiskers have been successfully used as reinforcing fillers for both synthetic and natural matrices. CNW have great properties such as high aspect ratio, high modulus, high strength, renewability and biodegradability. But on the other hand lack of commercial availability, low yield production, agglomeration tendency are the main obstacles using CNW.

Fibers with the diameter under 1 micron are called nanofibers. With their high surface area, flexibility, superior mechanical and thermal properties, nanofibers have many current and potential application areas from filtration to the medical field.

In this study, nanofibers from 3 different elastomeric polymers (SEBS-g-MA, PS-Isoprene and SBS) have been produced with electrospinning method. Elastomeric polymers have been chosen due to their potential application areas such as wound dressing or filtration because of their elasticity and high surface area. Different type of solvents with different combinations and different production parameters have been tried to investigate the spinnability and fiber morphology of resultant nanofibers.

From the results it has been seen that, Toluene is not a suitable solvent for electrospinning process. Better results have been obtained from the studies with Cyclohexane, DMF and THF in certain ratios. Sample with the ratio of 10% SEBS-g-MA, 70% Cyclohexane, 20% DMF and 10%THF has shown the best results in the spinning process.

When the samples containing CNW were investigated, it has been seen that the presence of CNW results in a more uniform diameter distribution and also a decrease in the diameter of the each type of composite nanofibers, when compared with reference sample.

Also different nozzle types in the electrospinning system have been investigated. It was found that the single-component nozzle system resulted in more uniform and thinner nanofibers than the coaxial nozzle system. In the single nozzle system, CNW were dispersed in the polymer solution before electrospinning process. But in the coaxial system CNW were carried by water into the core of the nanofibers during spinning without being directly mixed with the polymer solution. Not directly mixing the CNW caused more agglomeration and non-homogenous placement of CNWs in the nanofiber matrix.

From the TGA analysis it has been seen that, addition of CNW decreases the thermal stability of the sample due to its low thermal stability. On the other hand presence of CNW increased the tensile strength around two-fold and modulus around three-fold of nanofibers.

SELÜLOZ NANOWHISKER İLE GÜÇLENDİRİLMİŞ ELASTOMERİK NANO LİFLERİN ELEKTROEĞİRME YÖNTEMİ İLE ÜRETİLMESİ

ÖZET

Nano teknoloji, tekstil alanından fibröz malzemelere pek çok alanda her geçen gün daha fazla uygulama alanı bulan ve gelişmekte olan disiplinler arası bir teknolojidir. Malzemelerin boyutları mikron seviyesinden mikron altı veya nano mertebelere indiği zaman, çok yüksek yüzey alanı/hacim oranı, yüzey fonksiyonelleştirmede esneklikler, yüksek fiziksel performans gibi çok önemli özellikler gözlenmektedir.

Geleneksel malzemelere kıyasla daha gelişmiş özellikler ve daha geniş bir kullanım alanı elde etmek amacıyla nanokompozit ürünlere yönelik çalışmalar ve endüstriyel uygulamalar her geçen gün önem kazanmaktadır. Karbon nano tüpler, killeri, karbon black gibi malzemeler nano kompozit alanında her geçen gün önem kazanan malzemelerdendir.

Selüloz nanowhisiker geniş bir kullanım ve uygulama alanı potansiyeline sahip nano malzemelerden biridir. Son yirmi yıldır selüloz nanowhisiker üzerine çeşitli çalışmalar gerçekleştirilse de bu malzeme üzerine detaylı yapılan çalışmalar oldukça yenidir. Biopolimerler canlı organizmaların içinde doğal olarak oluşan polimerlerdir. Selüloz nano whiskersın hammaddesi olan selüloz, doğada en çok bulunan biopolimerdir. Ayrıca doğada çözünebilir oluşu, toksik olmayışı ve ucuz bir malzeme oluşu çevresel ve ekonomik açıdan önemini daha da arttırmaktadır. Selüloz nanowhisikerler şu ana kadar yapılan çalışmalarda, hem doğal hem de sentetik matrislerde güçlendirici dolgu malzemesi olarak başarıyla kullanılmışlardır. Selüloz nanowhisikerler yüksek modülüs, yüksek mukavemet, yenilenebilirlik ve biyo-çözünürlük gibi pek çok avantaja sahiptir. Ancak diğer taraftan ticari kullanılabilirliğinin bulunmaması, düşük üretim verimliliği ve topaklanma gibi problemlere sahip olması bu malzemenin kullanılabilirliğinde karşılaşılan zorluklardır.

Çapı 1 mikronun altında kalan lifler nanolif olarak adlandırılmaktadır. Nanolifler de yüksek yüzey alanları, esneklikleri ve üstün mekanik ve termal özellikleriyle filtrasyondan yara örtücü yüzeylere pek çok alanda kullanım olanağı bulmaktadır.

Nanolifler, yüksek yüzey alanlarıyla gerek hava ortamından gerekse de sıvı ortamdan kirlenici partiküllerin filtrelenmesi konusunda yüksek filtreleme verimliliği sağlamaktadır. Pekçok teorik ve deneysel çalışma nanolif filtrelerin uçan partikülleri filtrelemede oldukça verimli olduğunu göstermektedir.

Medikal alanda da nanolifler her geçen gün daha fazla kullanım olanağı bulmaktadır. Özellikle ilaç salınım sistemlerinde nanolifler; daha efektif bir ilaç terapisi, azaltılmış yan etkiler ve hedeflenmiş ilaç salınımı sağlamaktadır. Doku mühendisliği de nanoliflerin kullanıldığı bir başka medikal alandır.

Elektro eğirme yöntemi en yaygın nanolif üretim metodudur. Bu yöntemle ilk filament üretimi 100 yıl kadar öncesine gitmektedir. Gene bu yöntem kullanılarak alınan ilk patent de 1930larda Formhals tarafından alınmıştır. Elektro eğirme yönteminin diğer yöntemlerden en önemli farkı, nanolif üretimi için elektro-statik kuvvetleri kullanmasıdır. Kurulumu oldukça basit olan bu sistem, bir adet pompa, şırınga, yüksek gerilim kaynağı ve toplayıcı plakadan oluşmaktadır.

Elektro eğirme yönteminde, yüzey geriliminin yardımıyla bir iğnenin ucunda tutulan polimer çözeltisi bir elektrik alanına maruz bırakılır. Elektrik alanının artmasıyla birlikte yüzey gerilimine karşıt bir kuvvet oluşur. İğnenin ucundaki polimer damlası Taylor Konisi denilen konik bir şekil alır. Elektriksel kuvvet yüzey gerilimini aştığında ise Taylor Konisi'nin ucunda yüklü bir jet oluşur. Malzeme iğne deliğinden püskürtüldükten sonra çözelti, malzeme toplayıcı plakaya gidene kadar buharlaşır ve toplayıcı plakada malzeme nanolif formunda toplanır.

Bu çalışmada, 3 farklı elastomerik polimerden (SEBS-g-MA, PS-Isoprene ve SBS) elektro eğirme yöntemi ile nanolif üretilmiştir. Elastomerik polimerler, elastikiyetleri ve yüksek yüzey alanları gibi üstün özellikleri dolayısıyla yara örtücülük veya filtrasyon gibi alanlardaki potansiyel kullanımları sebebiyle seçilmiştir. Farklı çözelti tipleri, bu çözeltilerin farklı oranlarda kombinasyonları ve farklı üretim parametreleri kullanılarak üretilen nanoliflerin çekilebilirlikleri ve lif morfolojileri incelenmiştir.

Yapılan testler neticesinde bu 3 polimer tipinin elektro eğirme işlemine uygunlukları SEM görüntüleri alınarak irdelenmiştir. Ayrıca elde edilen sonuçlara göre hangi çözeltilerin hangi oranlarda elektro eğirme işlemi için daha uygun olduğu araştırılmıştır. Bunun neticesinde ise işlem parametreleri üzerinde bir optimizasyona gidilerek en iyi nanolif morfolojisine sahip numuneyi üretecek parametreler tespit edilmiştir.

Daha sonraki selüloz nanowhiskeyer içeren çalışmalarda ise polimer olarak, yapısının uygunluğu ve yüksek eğirilebilme özelliğı sebebiyle SEBS-g-MA seçilmiştir. SEBS-g-MA termoplastik bir polimerdir. Genellikle polimer yapılarını modifiye etmek amacıyla, özellikle de Polipropilen ile beraber kullanılmaktadır. Polimerin yapısında bulunan Maleik Anhidrid grup orta bloğa graflanmıştır ve polimerin polar kaplamalarla olan etkileşimini arttırmaktadır. Polar yapıya sahip olan selüloz nano whisker ile yapılan denemelerde bu polimerin seçilmesinin ana sebeplerinden biri de budur.

Nanolif üretimi için 2 farklı iğne tipi seçilmiştir; tek uçlu ve coaxial. Tek uçlu sisteme göre daha yeni bir sistem olan coaxial uç, özellikle özlü yapıda veya içi boş liflerin üretilmesinde tercih edilen bir yöntemdir. Bu yöntemle fonksiyonallı edilmiş nano partiküller, nanolif yapısının içerisine veya dış yüzeyine yerleştirilebilir. Bu sayede katalizlerden gaz sensörlerine pek çok alanda kullanılabilir malzemeler üretilebilir. Coaxial yöntem aynı zamanda gelişkin optik, elektriksel ve mekanik özelliklere sahip konjüge polimerlerin eğirilebilme özelliğini de arttırmaktadır.

Tek uç ile yapılan deneylerde selüloz nano whisker polimer çözeltisine doğrudan katılırken, coaxial sistemde selüloz çözeltisi eğirme esnasında iç uçtan beslenmiştir. Yapılan çalışmalarda iki sistemin avantajları ve dezavantajları taramalı elektron mikroskobu (SEM) görüntüleri alınarak ortalama lif çapı ve çap dağılımı açısından incelenmiştir. Ayrıca yapıya katılan selüloz nano whiskerların lif morfolojisi üzerine etkileri de incelenmiştir. Özellikle tek uçlu sistemde selüloz nano whiskerların polimer çözeltisine doğrudan katılması ile coaxial yöntemde iç uçtan beslenmesinin sonuçlar üzerindeki etkileri irdelenmiştir.

Bunun dışında nanolif yapısıyla film yapısını kıyaslayabilmek adına selüloz nano whisker içeren nanokompozit film de üretilmiştir. Ayrıca hem film hem de nanolif numunelerinde selüloz nanowhiskers içermeyen referans numuneler de üretilmiştir.

Selüloz nano whisker içeren numunelerde, selülozun yapıdaki varlığı Fourier Dönüşümlü Kızıl Ötesi (FTIR) spektroskopisi sonuçları neticesinde, karakteristik tepe noktaları gözlemlenerek kanıtlanmıştır. Üretilen tüm numunelerde selülozun $3200\text{--}3550\text{ cm}^{-1}$ civarında görülen tipik -OH pikine rastlanmıştır.

TGA analizleri ile selüloz nano whiskerların malzemenin ısı dayanımına olan etkisi incelenmiştir. Ayrıca film ve nanolif numuneler de, termal dayanım yönünden karşılaştırılmıştır.

Selüloz nano whisker içeren ve referans nanolif ve film numunelerinin mekanik özelliklerini incelemek adına gerilim yükleme cihazı (Instron) kullanılmıştır. Bu sayede selüloz nano whiskerların malzemenin mukavemet, modülüs ve kopma uzaması gibi değerleri üzerine etkileri incelenmiştir. Özellikle eklendiği polimer çözeltisinin elektrik iletkenliği değiştirmesi, selüloz nano whiskerların nanoliflerin mekanik özelliklerinde dramatik bir gelişme sağladığı gözlenmiştir.

Sonuç olarak; 3 farklı polimer tipi kullanılarak yapılan elektro eğirme işleminde optimizasyon çalışmaları gerçekleştirilmiş. Bunun devamında elde edilen en uygun numunelerle nanokompozit bir yapı üretilmiştir. Yapıya katılan destekleyici selüloz nano whisker malzemesinin, nanolif ve film yapısı üzerindeki termal ve mekanik etkileri incelenmiştir. Tüm bunların dışında selüloz nano whisker içeren kompozit yapılara ait sınırlı sayıdaki literatür çalışmasına da katkı sağlamak amaçlanmıştır.

1. INTRODUCTION

1.1 Nanofibers

Nanotechnology is an emerging interdisciplinary technology that has been booming in many areas including textiles or fibrous materials. Fibers with a diameter less than 1μ are called nanofibers. In the nano scale, properties of substances dramatically change. With their high surface area, porous structure, flexibility and superior mechanical properties, nanofibers promise a great potential and these prominent properties make nanofibers suitable for versatile platforms from medical applications to the filtration [1, 2].

Spinning of synthetic filaments with the help of electrostatic force is a well-known process for more than a hundred years. First patents using the electrostatic force to produce filaments go to the 1930s by Formhals [3, 6]. Formhals' spinning process consists of a movable thread collecting device to collect the threads in a stretched condition, like a spinning drum in the conventional spinning. His process was capable of producing threads aligned parallel on to the receiving device. However, it was difficult to completely dry the fibers after spinning due to the short distance between the spinning and collection zones. Later the structure of jet and the droplet occurred during spinning has been investigated by Taylor in 1960s which is called later "Taylor Cone". Taylor studied the shape of the polymer droplet produced at the tip of the needle when an electric field is applied and showed that it is a cone and the jets are ejected from the vertices of the cone.

In the next years researchers focused on characterization and morphology of nanofibers by using devices such as; scanning electron microscopy (SEM), transmission electron microscopy (TEM), differential scanning calorimetry (DSC), wide-angle X-Ray diffraction (WAXRD). In 1980s, effects of electrospinning parameters on fiber morphology and jet stability have been understood [6]. In the last 20 years, ultrafine nanofibers have been able to produced with electrospinning

technique due to the increased knowledge. With the increased mechanical properties, investigations in new application areas of nanofibers are gaining interest.

Nanocomposite applications are one of the main applications of nanofibers. With their superior physical properties, they can be used as reinforcements with combination of conventional materials [3]. Especially carbon nanotubes and carbon nanofibers gather attention for nanocomposite applications. Besides this, new application areas for polymeric nanofibers have been exploring.

Filters have been widely used in both households and industry for removing substances from air or liquid. Filters for environment protection are used to remove pollutants from air or water. In military, they are used in uniform garments and isolating bags to decontaminate aerosol dusts, bacteria and even viruses, while maintaining permeability to moisture vapor for comfort. Electrospun nanofiber membrane provides dramatic increases in filtration efficiency at relatively small decrease in permeability. They also show great filtration efficiency at the same pressure drop compared with conventional filters due to their high diffusion, interception and high inertial impaction efficiency. As the result of experimental and theoretical works, it has been seen that nanofiber filters are very effective at airborne particle filtering. Besides solid particles, tiny liquid droplets within a liquid-liquid immiscible system can also be removed by a nanofiber membrane [4].

In medical area, electrospun nanofibers are being used more and more each day. In drug delivery systems, nanofibers provide more effective drug therapy, less side effects and targeted drug release [5]. Tissue engineering is another exciting area of electrospun nanofibers. So far, hundreds of papers have been published on using electrospun nanofiber mats as tissue scaffolds and related cell growth performance. Different type of polymers have been used in tissue engineering applications including synthetic and natural polymers, biodegradable and non-biodegradable polymers [4].

Another application area of nanofibers is sensors. Sensors have been widely used to detect chemicals for environment protection, industrial process control, medical diagnosis, safety, security and defense applications. Also small dimensions, high sensitivity, low production cost and selectivity are desired properties of a good sensor. The characteristics of the electrospun nanofibers match well with these

requirements. Therefore, a nanofibrous structures should be a promising materials to form a highly sensitive and fast response sensors [4].

Beside these application areas, using nano fibrous structures as catalysts are gathering attention in recent studies with their high surface area, adjustment to any substrate, offer more activity in chemical reactions [6].

Electrospun nanofibers offer a new option in the energy area to the conventional batteries. Batteries with the PVDF nanofiber membrane, with their high electrolyte uptake, provide larger battery life in thinner battery packs [7].

1.2 Production Methods of Nanofibers

There are several production methods for producing nanofibers such as; electrospinning, drawing, electroblowing, island in the sea, melt blowing.

1.2.1 Electrospinning

The term “electrospinning” is derived from “electrostatic spinning”. It is a process patented by Formhals (1934) which creates nanofibers through an electrically charged jet of a polymer melt or a polymer solution [8]. The main difference of electrospinning with other conventional methods is, electrospinning uses electrostatic forces to form nanofibers. Polymers are the most common materials in the electrospinning method but ceramic precursors are also being used in this technique without adding any polymeric material [9].

In the electrospinning process at laboratory level, the set-up is basically consist of a high voltage power supply, a feeding pump, a syringe, a flat tip needle and a conductor collector and can be seen from Figure 1.1.

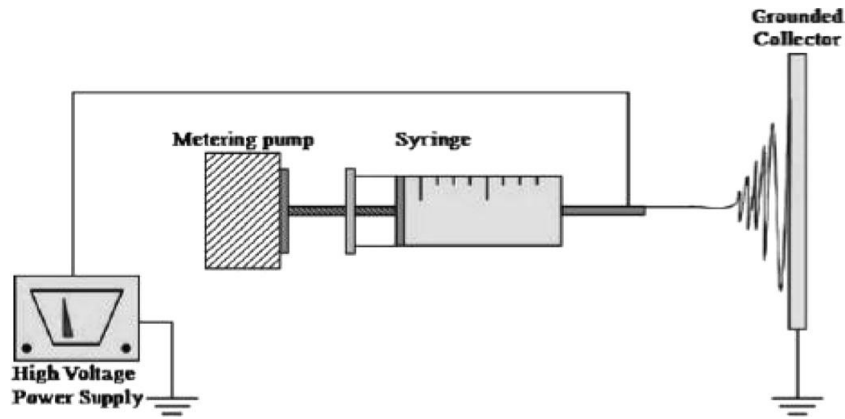


Figure 1.1 : Basic electrospinning setup [7].

During the process, an electric field is applied to the polymer solution, which is held by its surface tension at the end of a needle. An opposite force against surface tension occurs with the increase of the electrical field. The shape of the polymer drop at the end of the needle takes a conical shape, which is called Taylor cone. When the electrical forces overcome the surface tension, a charged jet at the tip of the Taylor cone occurs. Once ejected out of a metal spinneret with a small hole, the charged solution jets evaporated to become fibers, which were collected on the collector [3, 10].

So far, in the literature with more than 50 polymers, fibers with diameter under 1μ have been produced with electrospinning process from polymeric solutions or melts successfully. In some studies, fibers with the diameter as small as 3nm were able to produce. In addition to the polymers, carbon nanotubes, nanoplatelets and ceramic nanoparticles can also be dispersed in polymer solutions and then electrospun in order to form composite nanofibers [11].

The behavior of electrically driven jets, the shape of the jet-originating surface, and the jet instability are some of the critical areas in the electrospinning process that are the subject of many researches. From the studies of Taylor, it has been seen that Taylor cone with an angle of 49.3° is formed when a critical potential is reached to disturb the equilibrium of the polymer drop at the tip of the needle. As the jet travels in its trajectory continues to thin down. This type of jet is called electrohydrodynamic cone-jet. The charges in the jet lead the polymer solution in the direction of the electric field towards the collector, for closing the electrical circuit. As the jet travels to the collector it goes under a chaotic motion which is called

bending instability. At first, it was thought that, as the fiber diameter decreases due to the simultaneous stretching of the jet and the evaporation of the solvent, the increased charge density splits the jet into smaller jets. However, recent studies suggested that the rapid growth of a nonaxisymmetric or whipping instability causes the stretching and bending of the jets [6].

There has been a substantial amount of research carried out on the fundamental aspects of electrospinning. The main issue is the scaling-up of the process to a commercial level. Electrospinning apparatus is simple in construction, and since the last decade, there has been no major change in the design of the electrospinning set-up. Scientists have been modifying their electrospinning setups to obtain the nanofibers with the desired properties. For example in some studies, a parallel plate has been placed to overcome the problem of a nonuniform electric field.

1.2.1.1 Multi-jet electrospinning

In addition to the single nozzle systems, multi-jet systems are also being used in order to increase the productivity and covering area of electrospinning. Using the multi-jet systems, enables to produce multi component nanofibers with polymers which cannot be dissolved in the same solvent or cannot be kept in the same container such as poly(vinyl alcohol) (PVA) and Cellulose acetate (CA) [12].

Multi-jet electrospinning is usually achieved with a porous tubular system. A polymer solution is pumped in a cylindrical porous tube and Taylor jets occur on the outer surface of the cylinder when the solution is charged. These cylindrical tubes can be produced with different materials from polymers to ceramics. But there are very few literature studies about multi-jet electrospinning systems due to its complexity and possible clogging problems [13]. Another problem in multi-jet systems with multiple needles is, due to using different solutions, the current distributed on the needles might be varies. Because of this variation, the real current on the jet must be calculated [12]. Also jets might push each other because of their mutual Coulomb forces. This situation causes the jets at the edges miss the collector plate. This problem might be overcome with the arranging optimum inter nozzle distance [14].

1.2.1.2 Coaxial electrospinning

Coaxial electrospinning enables to produce core-sheath and hollow nanofibers and core-shell nanoparticles. By this method, functionalized nanoparticles can be placed inner and outer surfaces of the nanofibers. By depositing these nanoparticles, nanofibers can be used in many applications from catalysis to gas sensors [15].

Coaxial electrospinning technique also increases the spinnability of conjugated polymers which have great electrical, optical and mechanical properties [16]. This method requires a polymer solution which forms the shell and another polymer solution or a non-polymeric Newtonian liquid or a nanoparticle to form the inner structure. A Taylor cone occurs with a core-shell structure at the tip of the coaxial system. Nanofiber formation mechanism is similar with the ordinary electrospinning [16, 17].

1.2.2 Other nanofiber production methods

Although electrospinning is the most popular method for producing micro and nanofibers, there are many other production methods like drawing, electroblowing and meltblowing.

1.2.2.1 Drawing

In drawing method, a micropipette with a diameter of few micrometers is dipped to the polymer melt. After that, micropipette is drawn back from the liquid at the speed about 10^{-4} ms^{-1} and nanofibers are formed. This drawing motion repeats in every drop several times [18]. In the drawing method, the material must have a required viscoelastic behavior to endure the strong deformation and cohesive property to overcome the stresses during drawing by the micropipette [18, 19].

Solidification and fiber formation occurs during pulling. If the drops are prepared by the melt method, solidification is done by cooling. In dry spinning, solidification is obtained by evaporating the solvents [19]. The morphology of the resultant fiber is deeply depends on the drawing rate, evaporation or the cooling rate and the type of the material.

1.2.2.2 Electroblowing

Electroblowing process can be simply described as a blowing-assisted electrospinning, which blows the air around spinneret. This technique is developed to overcome some problems occurred in electrospinning. The blowing air decreases the size of drops at the tip of the needle and Taylor cone forms easily. Also air flow increases the evaporation of the solvent. As a result the production rate and stability of electrospinning processes increases. Besides thinner and more uniform fibers are obtained [20, 21].

1.2.2.3 Meltblowing

Meltblowing is one of the most common methods for producing the fibers at micron and submicron level. Fibers produced by meltblowing method find many application areas from filtration to hygiene [22].

In meltblowing process, a polymer melt is extruded through a linear die with small orifices with approximately 0.4mm diameter and 20-30 holes/inch. The melt filaments are drowned down with a jet of hot air [23, 24].

Meltblowing process is widely used in the industry due to its versatility, cost-effectiveness. It is also an environmentally friendly technique [23]. There are many commercially available products produced with melt spinning process.

1.2.3 Electrospinning parameters

Electrospinning is a process that many parameters determine the morphology of nanofibers and affect the efficiency of production. These parameters can be divided into three main groups; solution parameters, ambient parameters and process parameters.

- Solution parameters
- Ambient parameters
- Process parameters

1.2.3.1 Solution paramters

Solution viscosity

Viscosity is the characterization of the intermolecular interactions in polymer solution. Solution viscosity is dependent to the solution concentration and one of the biggest determinants of fiber diameter and morphology when spinning polymeric nanofibers. There is an optimum viscosity value for each solution. If the viscosity is below that value, fiber formation does not occur. When the viscosity of the solution exceeds that value, diameter of the fibers becomes thicker. There is a direct proportion between the solution viscosity and fiber diameter [25, 26]. It is also seen that as the viscosity increases, drop at the tip of the needle changes from hemispherical to conical [27].

At low viscosities, viscoelastic force is smaller than the Coulombic force which over stretches and breaks the jet before formation a fiber and this causes electrospraying. On the other hand at high viscosity, viscoelastic force become bigger than the Coulombic force and that prevents the breaking of the jet [25].

Solvent type

In electrospinning process, solvent is one of the main contributors to the properties like conductivity, surface tension etc. Solvents with high vapor pressure lead to nanofibers with porous structures [28]. The charged ions in the polymer solution are highly active in jet formation. The ions increase the charge carrying capacity of the jet, thereby subjecting it to higher tension when the electric field is applied. Using solvents with high dielectric constant enables the high conductivity of the solvent and this leads to finer and smoother fibers. Otherwise, beaded fibers might be observed. Also solvents with high evaporation rate, causes to increase in the jet instabilities in the electrospinning [29].

Soltuion tempertature

Solution temperature is another important solution parameter in electrospinning process. From the studies it has seen that, with the increase of the solution temperature, viscosity and surface tension of the polymer solution decreases. As the solution temperature increases, polymer molecules expand and degree of chain entanglements reduce. This causes to a decrease in viscosity. Reduction in the

viscosity means reduction in the viscoelastic force against to the Coulombic force. As a result thinner fibers are obtained [30, 31].

Polymer molecular weight

To understand the effect of the polymer molecular weight on the nanofiber morphology, a critical chain overlap concentration (c^*) was determined. It has been found that, there is an inverse ratio between c^* and polymer molecular weight. In the electrospinning process as the molecular weight increased, the number of beads and droplets reduced [7].

1.2.3.2 Ambient parameters

Humidity

Humidity is one of the major parameters which directly affect the fiber morphology. From the studies it has been seen that presence of humidity increases the number of pores in nanofiber structure. Higher humidity also increases the diameter of pores [32].

Decrease in the humidity leads to the thinner fibers. Water vapor has more conductivity than the air and this causes the discharging of surface charges of electrospun fibers. At low humidity higher electrical charges stretches the fibers more and this reduces the fiber diameter [33].

Temperature

Higher ambient temperature leads to thinner fibers because of the decrease in the viscosity. At high temperatures, polymer chains have more space to move, which decreases the viscosity of solvent and at low viscosity, stretching forces opposed to viscous forces will stretch the film more to form thinner fibers.

On the other hand, evaporation rate of the solvent changes with the temperature exponentially. At low temperatures and low evaporation rate, it takes more time for the jet evaporation and jet will elongate more. This will also decrease the diameter of nanofibers [32].

1.2.3.3 Process parameters

Voltage

Voltage can be seen as the most essential parameter in electrospinning process. During electrospinning, as the applied voltage to the polymer solution increases, a charge against surface tension occurs. When this charge overcomes the surface tension, jet at the tip of the needle occurs.

With the increase of the applied voltage, shape of the droplet may change. Change in the shape of the droplet causes a reduction in the balance of the jet and alters the morphology of the resultant fiber. Also beaded structure may occur in this unbalanced situation. Besides that increase in the voltage changes the shape of the nanofiber.

Increase in the applied voltage generally causes decrease in the fiber diameter but in some cases it increases the diameter. It has been seen that the smallest diameters have been obtained at the optimum level of the voltage which is in the middle range [34].

When all the other parameters held constant, with the increase in the voltage increases the flow of the mass from tip of the capillary to the grounded collector [35].

Feed rate

To obtain a Taylor cone there must be a minimum value of the polymer solution at the end of the capillary. With different feeding rates, nanofibers in different morphologies can be obtained. Feeding rate influences the jet velocity and the material transfer rate [6].

At high feed rates, feeding rate of the solution exceeds the amount of the solution delivered with the electric field. This causes some spraying and shots of tiny drops on the collector. At low feeding rate the amount of the solution removed by the electrical field is bigger than the feeding rate of the solution to the tip of the needle. This causes unstable jets and beads in the nanofiber morphology [36]. So there must be a constant and optimum amount of the feeding rate during the electrospinning.

Tip to collector distance

The structure and morphology of electrospun fibers is easily affected by the nozzle to collector distance because of their dependence on the deposition time, evaporation rate, and whipping or instability interval. It has been found that a minimum distance is required between the tip and the collector to allow sufficient time to fibers to dry before reaching the collector. If the distance is too low the nanofibers cannot completely stabilized and cross-sections of nanofibers become flat [36]. On the other hand at high distances the electrical field may not be strong enough to form a jet.

From the studies it has been seen that regardless of the concentration of the solution, lesser nozzle-collector distance produces wet fibers and beaded structures. Also aqueous solvents require more distance than the volatile organic solvents to form a dry fiber formation. Changing in the distance changes the electrical field, thereby the diameter of the electrospun nanofibers may change with the distance [34].

1.3 Overview of SEBS-g-MA

Polystyrene-block-poly(ethylene-ran-butylene)-block-polystyrene-graft-maleic anhydride (SEBS-g-MA) is a thermoplastic elastomer generally used for modifier for polymers, especially for polypropylene which can be seen from Figure 1.2. Maleic anhydride is grafted on the mid-block to increase compatibility with polar coatings and increase interaction with substrates [37]. In polymer blends presence of SEBS-g-MA increases the impact strength and fracture toughness but reduces their stiffness [38].

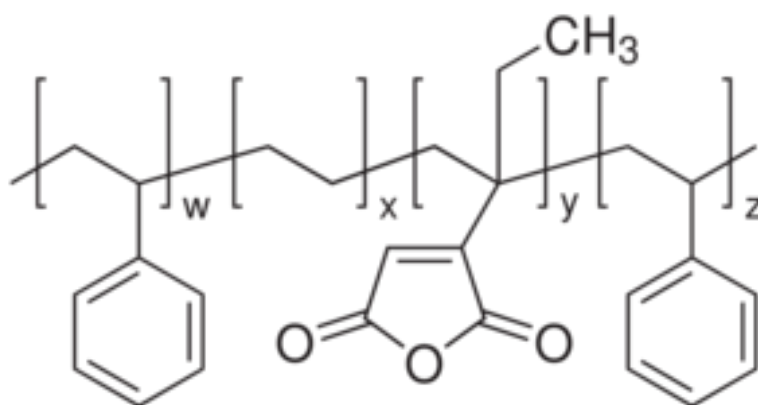


Figure 1.2 : Molecular structure of SEBS-g-MA [37].

Thermoplastic polymers have some prominent advantages over conventional thermoset polymers. Thermoplastics are easy to process, recyclable, have lower energy cost at production, and they also have uniform grades.

Styrene copolymers are the lowest priced copolymers. These block copolymers are produced with hard polystyrene segments interconnected with soft segments of a matrix such as ethylene-butylene.

These materials show low tensile strength but high elongation. They resist water, alcohols, and dilute alkalis and acids. They can be solved in strong acids, chlorinated solvents, esters, and ketones.

These block copolymers have many application areas such as, medical products, food packaging, tubing, sheet, belting, mallet heads, shoe soles, coatings and cable isolations [39].

1.4 Cellulose

Cellulose is the most abundant biopolymer because it serves as the main component of plants and also produced by some sea animals in smaller scale. In nature, cellulose chains have a DP of approximately 10000 glucopyranose units in wood cellulose and 15000 in native cellulose. Cotton cellulose has both crystalline and amorphous phases in its structure [40]. Each monomer bears three hydroxyl groups. These hydroxyl groups and their ability to form hydrogen bonds is important for crystalline packaging direction and physical properties of cellulose. Figure 1.3 shows generally accepted chemical constitution of the cellulose chain molecule.

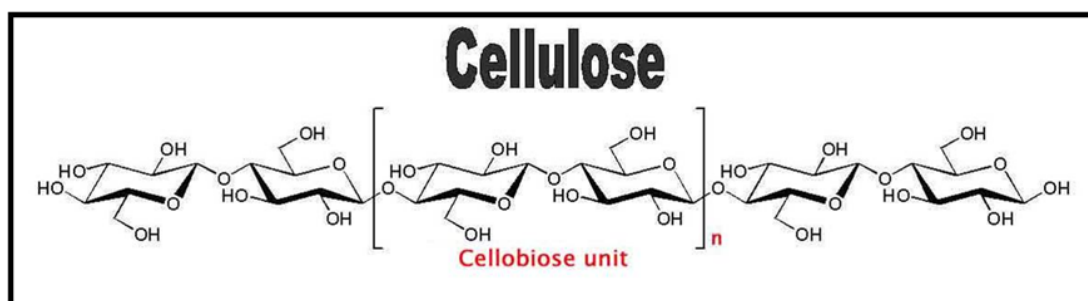


Figure 1.3 : Molecular chain formula of cellulose [41].

Cellulose is insoluble in water and in a lot of common organic liquids. But some systems have been developed for dissolving cellulose such as calcium and sodium thiocyanate, lithium chloride/N,N-dimethylacetamide (LiCl/DMAc) and NaOH/urea [42]. These developments open new possibilities to produce cellulose composites through a solution processing. Low cost, low density, high stiffness, renewable nature and biodegradability are main advantages of cellulose and major reasons to find new application areas. However, there are some difficulties in using cellulose such as low yield production, agglomeration in process, and difficulty of using it in systems, which are not water based and polar, because of its strong hydrogen bonding and polarity.

Cellulose consists of two main polymorphs which are called cellulose I and cellulose II. Native cellulose, namely cellulose I, is the crystalline cellulose. Cellulose II is also known as regenerated cellulose is used to refer to cellulose precipitated out of solutions. Cellulose I governs the mechanical properties due to its high modulus and crystallinity [41]. In addition to its crystalline phase, native cellulose also contains some amorphous, disordered domains.

Recently the interest on the biopolymers has been growing due to new environmental approaches of both consumers and producers. Compared with the fossil fuel base plastics, biopolymers have a less harmful effect on our environment. They are based on renewable resources and reduce the production of carbon dioxide, water and biomass [43]. Besides that, using biopolymers as a reinforcing element in the materials are gathering attention. Cellulose is a classic example of a reinforcement material. Some examples to the different terminologies used to describe cellulose micro and nano particles is shown in Table 1.1.

Table 1.1 : Different terminologies used to describe cellulose nano and micro particles

Acronyms	Name	Source	Process
CNW	Cellulose nanowhiskers	Ramie	H ₂ SO ₄ hydrolysis
		MCC	H ₂ SO ₄ hydrolysis
		MCC	H ₂ SO ₄ hydrolysis
		Grass fiber	H ₂ SO ₄ hydrolysis
		MCC	LiCl:DMAc

Table 1.1 (continued) : Different terminologies used to describe cellulose micro and nano particles

CNXL	Cellulose Nanocrystals	Cotton Whatman filter paper	H ₂ SO ₄ hydrolysis
		Bacterial cellulose	H ₂ SO ₄ hydrolysis
		Cotton (cotton wool)	H ₂ SO ₄ hydrolysis
		MCC	H ₂ SO ₄ hydrolysis
		MCC	Sonication
CNW-HCl	Cellulose nanowhiskers	Cotton linters	HCl hydrolysis
Wh	Whiskers	Cellulose fibers	H ₂ SO ₄ hydrolysis
NF	Nanofibers	Wheat straw	HCl + Mechanical Treatment
NCC	Nanocrystalline cellulose	MCC	H ₂ SO ₄ hydrolysis
MFC	Microfibrillated Cellulose	Pulp Gaulin	Homogenizer
		Pulp Daicel	-
		Pulp Daicel	-
NFC	Nanofibrillated cellulose Cellulose nanofibrils	Sulfite pulp	Mechanical
MCC	Microcrystalline cellulose	Alpha-cellulose fibers	Hydrolysis
-	Cellulose Crystallites	Cotton Whatman filter paper	H ₂ SO ₄ hydrolysis
-	Nanocellulose	Sisal fibers	H ₂ SO ₄ hydrolysis
-	Cellulose Microcrystal	Cotton Whatman filter paper	HCl hydrolysis
-	Nanofibers	Soybean pods	Chemical treatment + high pressure defibrillator

1.4.1 Cellulose nano whiskers

Cellulose in the form of nanometric monocrystals are called cellulose nano whisker (CNW). Cellulose whiskers are obtained by acid hydrolysis with sulphuric acid or hydrochloric acid. In last two decades, there are some investigations on CNW as reinforcing material in order to produce fully renewable and biodegradable nanocomposites. Cellulose nano whiskers have been successfully used as reinforcing fillers for both synthetic and natural matrices [43].

Cellulose nano whiskers (CNW) have great properties such as high aspect ratio, high modulus, high strength, renewability and biodegradability. But on the other hand

lack of commercial availability, low yield production, agglomeration tendency in processes and in order to its strong hydrogen bonding and its polarity difficulty of using it in systems which are not water based and polar are the main obstacles in using CNW [44].

Agglomeration problem can be solved with using surfactant or dispersing cellulose whiskers in a solvent. There are several studies involving transferring whiskers from water to other solvent [44].

Properties of cellulosic nanocomposites are dependent to the morphological aspects and interfacial behaviors of matrix and CNW. Both synthetic (poly(vinylchloride) (PVC), polypropylene, waterborne epoxy) and natural (starch, silk fibroin and cellulose acetate butyrate (CAB)) polymers have been investigated as matrix. Processing techniques have important effect on the final properties of the composites [45]. Also it has been seen that, mechanical properties of the composites were dependent not only on the filler/filler interactions, but also on the quality of the dispersion [46].

Cellulose nano whiskers act as filler in polymer composites. Additions of cellulose nanowhiskers to the matrix, enhance the mechanical and thermal properties of the composites. It has potential applications at low filler loadings. In the nanocomposite field, up to now, cellulose whiskers were only used as cellulosic filler and no practical industrial application has seen. Practical applications of such fillers and transition into industrial technology require a favorable ratio between the expected performances of the composite material and its cost. There are still significant scientific and technological challenges to take up [45].

2. AIM OF THE STUDY

In this study, spinnability properties of three different elastomeric polymers have been investigated. Elastomeric polymers have been chosen due to their potential application areas such as wound dressing or filtration because of their elasticity and high surface area.

Literature studies indicate that there are few studies related with composite nanofibers with CNW. Although CNW have a potential for contribution of mechanical properties of polymer matrix. From the studies it can be seen that, CNW can be used as a nanofiller in nano and micro composites as reinforcement material. Thus mechanical properties of the composite enhances. For the further studies SEBS-g-MA has been chosen as polymer matrix. The elastomeric polymer is not compatible with the polar CNWs but the maleic anhydride groups provide compatibility between CNWs and the polymer matrix. Production of the nanofiber composites have been carried out with single and coaxial nozzle systems in order to compare advantages and disadvantages of these systems. Also cast films have been produced to investigate the differences between nanofibers and cast films.

In this study, besides contribution to the scientific studies related with the composites with CNW, improvements on mechanical and thermal properties of the composites by adding CNWs to the structures are intended.

3. EXPERIMENTAL STUDIES

3.1 Materials

SEBS-g-MA (polystyrene-block-poly(ethylene-ran-butylene)-block-polystyrene-graft-maleic anhydride from Sigma Aldrich) is an elastomeric polymer used as polymer matrix. Beside SEBS-g-MA, two other polymers are also used for nanofiber production with electrospinning technique. These are Polystyrene-block-polyisoprene-block-polystyrene from Sigma Aldrich (called as PS-ISOPRENE) and Styrene-butadiene block copolymer from BASF (it was called as SBS). These thermoplastic elastomers are chosen due to their high durability and elasticity [47]. Toluene (Merck), Acetone, (Merck), Cyclohexane (Merck), Dimethylformamide (DMF, Merck) and Tetrahydrofuran (THF, Merck) were used as solvents. Microcrystalline Cellulose (MCC) (FMC Biopolymer) was used to produce cellulose nano whiskers (CNW) to be used as reinforcement. Sulfuric acid (Merck) 95-97% and sodium hydroxide (Aldrich) were also used during the production of CNW.

3.2 Equipment and Analysis

3.2.1 Infrared analysis (IR)

Infrared (IR) spectroscopy is one of the mostly used characterization technique in chemistry. Simply, it is the absorption measurement of different IR frequencies by a sample positioned in the path of an IR beam. IR spectrum is characteristic for every molecule because some groups of atoms give peaks at certain frequencies regardless of the structure of the rest of the molecule. Using various sampling accessories, IR spectrometers can accept a wide range of sample types such as gases, liquids, and solids.

The range of the infrared radiation is about $13,000$ to 10 cm^{-1} , or wavelengths from 0.78 to $1000\text{ }\mu\text{m}$. This radiation is absorbed and converted into the energy of

molecular vibration by an organic molecule. IR absorption positions are generally expressed as wavenumber (cm^{-1}) which is number of waves per unit length. Also band intensities can be showed as transmittance (T) or absorbance (A).

Fourier transform infrared (FTIR) spectrometry contains radiation all IR wavelengths (about $500\text{--}4000\text{ cm}^{-1}$). FTIR method contains some advantages such as; all radiation range is passed through the sample at the same time, which provides a time saving. FTIR offers a high resolution. With very small samples, excellent results can be obtained [48].

In this study, infrared analyses were performed with Thermo Scientific Nicolet IS10 FT-IR Spectrometer.

3.2.2 Scanning electron microscope (SEM)

Scanning electron microscope (SEM) is the most widely used electron microscopic technique. SEM provides very wide range of magnification. It gives also opportunity to easy sample preparation. Today SEMs can obtain image resolutions in the range of 0.5 nm. In this microscope, during scanning an electron beam is passed through the surface of the sample and this beam induces some changes in the sample. The electrons interact with the atoms that make up the sample producing signals which gibes information from the surface of the specimen [49].

In this study, the images of the samples are obtained from scanning electron microscope (SEM) with JEOL Model JSM-5910LV to observe the distribution of CNW in nanofiber matrix and measurement of the diameters of nanofibers.

3.2.3 Tensile loading machine

Tensile test is one of the major mechanical tests applied to the materials. It gives information about how the material will react to forces being applied in tension. This test consists of applying a gradually increasing force of tension at one end of a sample length of the material. It is a simple and inexpensive test. From the test results, elastic modulus, elongation, tensile strength, yield point, yield strength and other informations could be obtained. Tensile test gives results as load-elongation curve which is then converted into a stress versus strain curve. Each material has its own unique stress-strain curve.

A typical stress-strain curve can be seen from Figure 3.1. The initial behavior of the stress-strain curve is linear. This part is called linear elastic region and it indicates that no plastic deformation has occurred. This means that, at this region after the load is removed, material goes to its original shape. The slope of this line gives Young's modulus or modulus of elasticity. Young's modulus gives the stiffness of the material. To compute the modulus of elastic, simply divide the stress by the strain in the material.

Yield point can be defined as the point where the plastic deformation begins to occur during loading. After this point, the material does not return to its original shape when the load is removed, the deformation is permanent. But in brittle materials, the material shows no plastic deformation and it breaks near the end of the linear-elastic portion of the curve.

The tensile strength is the maximum engineering stress level reached in a tension test. In brittle materials tensile strength is at the end of the elastic region. In ductile materials tensile strength will be at the plastic region of the stress-strain curve.

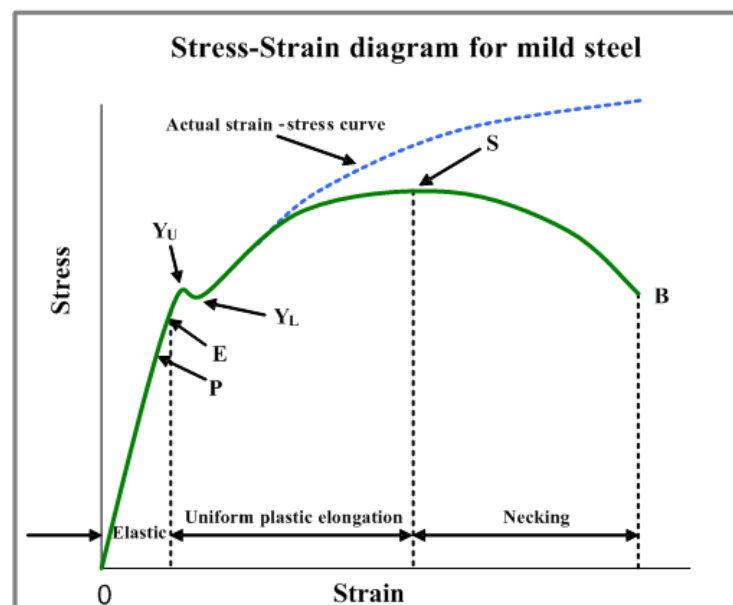


Figure 3.1 : Common stress-strain diagram [50].

In this study, Instron 3345 Tensile Tester was used to determine the Young's modulus, elongation at break and strength properties. The dimensions of the

materials were to 35mm x 5mm. Load cell was 100 N and cross head speed was 10 mm/min. The gage length was 15 mm, and at least 10 specimens were tested for each sample.

3.2.4 Thermogravimetric analysis (TGA)

Thermogravimetric analysis is a method used for comparing the thermal stability of the polymers. TGA provides quantitative measurement of mass change in materials associated with transition and thermal degradation. Measurements are used mainly to determine the composition of materials and to predict their thermal stability at temperatures up to 1000°C. Thermogravimetric analysis gives the weight loss or gain due to oxidation, dehydration or decomposition. With the thermogravimetric analysis, composition and thermal stability of materials, oxidative stability, estimated lifetime, decomposition kinetics and moisture content of the materials can be known.

In this study, thermal stability was evaluated using a Q50 TGA from TA Instruments. Film samples of 5–10 mg were placed in the scale and heated from 25 °C to 900°C under N₂ (flow rate: 90 mL/min) at an applied heating rate of 20°C /min. During the heating period, the weight loss and temperature difference were recorded. Thermogravimetric analyses were performed with a TA TGA Q50 instrument at a heating rate of 20 °C/min [51].

3.3 Electrospinning Process

3.3.1 Solvent preparation

In this study three different commercial elastomeric polymers, Polystyrene-block-poly(ethylene-ran-butylene)-block-polystyrene-graft-maleic anhydride, which is called SEBS-g-MA, Polystyrene-block-polyisoprene-block-polystyrene from Sigma Aldrich (called as PS-ISOPRENE) and Styrene-butadiene block copolymer from BASF (it was called as SBS) are used to produce nanofibers. Different type of solvents with different combinations and different production parameters have been tried to investigate the spinnability and fiber morphology of resultant nanofibers. Solvents and polymers have been mixed by weight ratio and solutions were prepared at room temperature. Besides that, effect of CNW on the nanofiber morphology has been investigated by adding CNW in the different amounts to the solvents.

Electrospinning process has been done with a conventional electrospinning system shown in Figure 3.2. Solution fed by syringe pump (Sino mdt, sn-50c6/c6t) and electric field is applied by Matsusada high power supply. Aluminum collector and steel needle (gauge 0.8 x 38 mm) was used. All experiments were carried out at the room temperature in air.



Figure 3.2 : Conventional electrospinning system.

Two type of nozzles used in experiments to obtain web of composite nanofibers; single nozzle and coaxial nozzle.

3.3.2 Preparation of cellulose nano whiskers (CNW)

CNW was produced from microcrystalline cellulose powder (Avicel Type GP1030) (MCC) at the laboratory by acid hydrolysis method, which is similar method applied in literature [52]. 5g of MCC was hydrolyzed in 43,75 ml of 51 wt% sulfuric acid at 45°C for 60 minutes. After hydrolysis, 170ml of deionized water added and the solution was kept between 17 and 24 hours. Then sulfuric acid removed by centrifugation of the solvent with repeated 9 cycles. Each cycle last 40 min at 8000 rpm. The supernatant was removed from the sediment and was replaced by deionized water. After centrifugation, the supernatant became blurry. To decrease acidity of the

solution, 5 wt% NaOH was added into the solution until 8th cycle. The final suspension had a pH value of 9.

3.3.3 Sample preparation

At first, various solvents have been prepared with three polymers with different amount and type of solvents and with different process parameters in order to obtain nanofibers at best morphology. The parameters of the study can be seen from the Table 3.1.

Table 3.1 : Electrospinning parameters of samples.

Sample	Polymer	Polymer Concentration (%)	Solvents (% ratio)	Process parameters
1	SEBS-g-MA	15 %	80%Toluen 15%DMF, 5%Aseton	20 KV 1,5 ml/h 15cm
2	PS-Isoprene	15 %	80%Toluen 15%DMF 5%Aseton	20 KV 1,5 ml/h 15cm
3	SBS	15 %	80%Toluen 15%DMF 5%Aseton	20 KV 1,5 ml/h 15cm
4	SEBS-g-MA	15 %	80%Toluen, 10% THF 10% Aseton	20 KV 1,5 ml/h 15cm
5	SEBS-g-MA	15 %	80%Cyclohexane 10%THF 10% Aseton	20 KV 1,5 ml/h 15cm
6	SEBS-g-MA	17 %	80%Cyclohexane 10%THF 10% Aseton	20 KV 1,5 ml/h 15cm
7	SEBS-g-MA	15 %	80%Cyclohexane 15%THF 5% Aseton	20 KV 1,5 ml/h 15cm
8	SEBS-g-MA	15 %	80%Cyclohexane 15%DMF 5% Aseton	20 KV 1,5 ml/h 15cm
9	SEBS-g-MA	15 %	70%Cyclohexane 30%DMF	--
10	SEBS-g-MA	15 %	70%Cyclohexane 20%DMF 10%THF	20 KV 1 ml/h 15cm
11	SEBS-g-MA	13 %	70%Cyclohexane 30%DMF	20 KV 1 ml/h 15cm
12	SEBS-g-MA	10 %	70%Cyclohexane 20%DMF 10%THF	20 KV 1 ml/h 15cm

Table 3.1 (continued) : Electrospinning parameters of samples.

13	SEBS-g-MA	10 %	70%Cyclohexane 20%DMF 10%THF	25 KV 1 ml/h 15cm
14	SEBS-g-MA	10 %	70%Cyclohexane 20%DMF 10%THF	20 KV 0.5 ml/h 15cm
15	SEBS-g-MA	10 %	70%Cyclohexane 20%DMF 10%THF	20 KV 1 ml/h 20cm

In the samples with the CNW, SEBS-g-MA was used as polymer matrix. To produce a web using the single-component nozzle system, a mechanical homogenizer (WiseTis Homogenizer-HG-15D) was used to mix CNW in the SEBS-g-MA solution at 9000 rpm for 15 minutes. The applied voltage to the system was 20kV, feeding rate was 1.5ml/h and the distance between the nozzle and the collector was 15cm. The electrospun nanofibers produced by single nozzle contain 20% CNW.

Nanofiber webs were also produced using a coaxial system and the set-up can be seen from the Figure 3.3. The outer and inner diameters of the inner nozzle are 0.8 mm and 3.3. mm, respectively. The inner diameter of the outer nozzle is 4 mm. Electrospinning parameters were 15kV and 15cm. Due to the maintaining the processibility, the applied voltage was lower than the single nozzle system. In this coaxial system, SEBS-g-MA and CNW were fed through the two individual nozzles. SEBS-g-MA solution was consisting of 10wt % SEB-g-MA. Cyclohexane, dimethylformamid (DMF) and tetrahydrofuran (THF) are used as solvents and were mixed in the ratio of 70:20:10 (70% Cyclohexane, 20% DMF, and 10% THF). 20% CNW dispersed in the 80% water, this solution was fed through the inner nozzle, and the solution of SEBS-g-MA was fed through the outer nozzle. The two feeding rates were selected to obtain a CNW to SEBS-g-MA ratio of 20:80 (20% CNW and 80% SEBS-g-MA). The feeding rate of SEBS-g-MA solution was 0.8 ml/h, and the feeding rate of CNW was 0.1 ml/h.



Figure 3.3 : Coaxial nozzle.

Addition to the electrospun nanofiber webs, films by solvent casting and compression molding has been prepared to study the influence of processing methods on their morphological, mechanical and thermal properties. To produce composite films, CNW were added to the 10% SEBS-g-MA solution such that the ratio was maintained at 20:80 (20% CNW and 80% SEBS-g-MA), by ultrasonic sonification (Bandelin Sonopuls) for 15 minutes. Then, the solution was cast in petri dishes and left for evaporation in a drying oven at 80°C for one day. Then the samples were placed between two Teflon sheets and pressed at 140°C for 2 minutes with a pressure of 60 bars (6.08 MPa). In addition, samples without CNW were produced with the same method to investigate the effects of CNW. CNW contents and production methods of the samples can be seen from the Table 3.2.

Table 3.2 : Production methods and CNW contents of the samples.

Sample	Production Method	CNW content (wt %)
Reference Nanofiber	Electrospinning	0
Single Nozzle	Electrospinning	20
Coaxial Nozzle	Electrospinning	20
Reference Film	Film	0
Composite Film	Film	20

4. RESULTS AND DISCUSSION

In this thesis, three different types of polymers have been used with different electrospinning parameters. Spinnability of polymers and solvents and effect of solvent ratios and spinning parameters on spinnability have been investigated. Fiber morphologies of these samples have been investigated in SEM. Besides that, effect of CNW in the nanofiber webs have been investigated. Finally, nanofibers produced with single and coaxial nozzle and composite film produced with solvent casting method have been compared with mechanical and thermal properties. From the Table 4.1 solvent and spinning parameters and the spinning results of the samples can be seen.

Tablo 4.1 : Solvent and spinning paramteres and spinning results of the samples.

Sample	Polymer	Polymer Concentration (%)	Solvents (% ratio)	Process parameters	Result
1	SEBS-g-MA	15 %	80%Toluen 15%DMF, 5%Aseton	20 KV 1,5 ml/h 15cm	Electrospraying
2	PS-Isoprene	15 %	80%Toluen 15%DMF 5%Aseton	20 KV 1,5 ml/h 15cm	Fibers together with beads and spraying
3	SBS	15 %	80%Toluen 15%DMF 5%Aseton	20 KV 1,5 ml/h 15cm	Fine fibers with beads and spraying
4	SEBS-g-MA	15 %	80%Toluen, 10% THF 10% Aseton	20 KV 1,5 ml/h 15cm	Electrospraying
5	SEBS-g-MA	15 %	80%Cyclohexane 10%THF 10% Aseton	20 KV 1,5 ml/h 15cm	Electsopun fibers which diameters is from few micron to nanometer. Often clogging of needles tip due to solvent evaporation
6	SEBS-g-MA	17 %	80%Cyclohexane 10%THF 10% Aseton	20 KV 1,5 ml/h 15cm	Electrospinning could not be carried out
7	SEBS-g-MA	15 %	80%Cyclohexane 15%THF 5% Aseton	20 KV 1,5 ml/h 15cm	Because of solvent evaporation, electrospinning could not be carried out

Table 4.1 (continued) : Solvent and spinning parameters and spinning results of the samples.

8	SEBS-g-MA	15 %	80% Cyclohexane 15% DMF 5% Acetone	20 KV 1.5 ml/h 15cm	Electrospun fibers which diameters is from few micron to nanometer.
9	SEBS-g-MA	15 %	70% Cyclohexane 30% DMF	--	Solution at tip of needle could not be drawn towards collector between 20 kV-30 kV
10	SEBS-g-MA	15 %	70% Cyclohexane 20% DMF 10% THF	20 KV 1 ml/h 15cm	Occasionally clogging of needle's tip
11	SEBS-g-MA	13 %	70% Cyclohexane 30% DMF	20 KV 1 ml/h 15cm	Occasionally clogging of needle's tip
12	SEBS-g-MA	10 %	70% Cyclohexane 20% DMF 10% THF	20 KV 1 ml/h 15cm	Electrospun fibers which diameters is from few micron to nanometer.
13	SEBS-g-MA	10 %	70% Cyclohexane 20% DMF 10% THF	25 KV 1 ml/h 15cm	Electrospun fibers which diameters is from few micron to nanometer.
14	SEBS-g-MA	10 %	70% Cyclohexane 20% DMF 10% THF	20 KV 0.5 ml/h 15cm	Electrospun fibers which diameters is from few micron to nanometer.
15	SEBS-g-MA	10 %	70% Cyclohexane 20% DMF 10% THF	20 KV 1 ml/h 20cm	Electrospun fibers which diameters is from few micron to nanometer.

During the spinning process, samples with Toluene (boiling point 111°C, dielectric constant 2.38) generally resulted with fail. Samples with Toluene contain beads and balls in their morphology or spinning process resulted with spraying which means no fiber formation occurred.

However when we compare the first three samples, PS-Isoprene resulted the best and SEBS-g-MA was the worst sample. This shows that when all the parameters are kept constant, different elastomeric polymer type can have different results in electrospinning process. It has been seen that Toluene is not very suitable solvent for electrospinning process due to low dielectric constant and high boiling point. This result can also be seen from the sample 4, 5 (Table 4.1).



Figure 4.1 : SEM image of Sample 1.

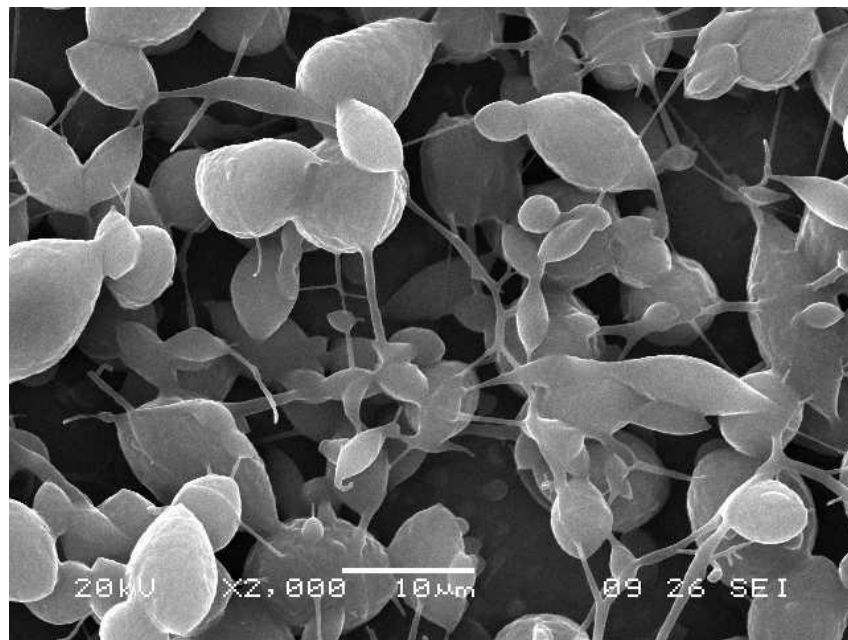


Figure 4.2 : SEM image of Sample 2.

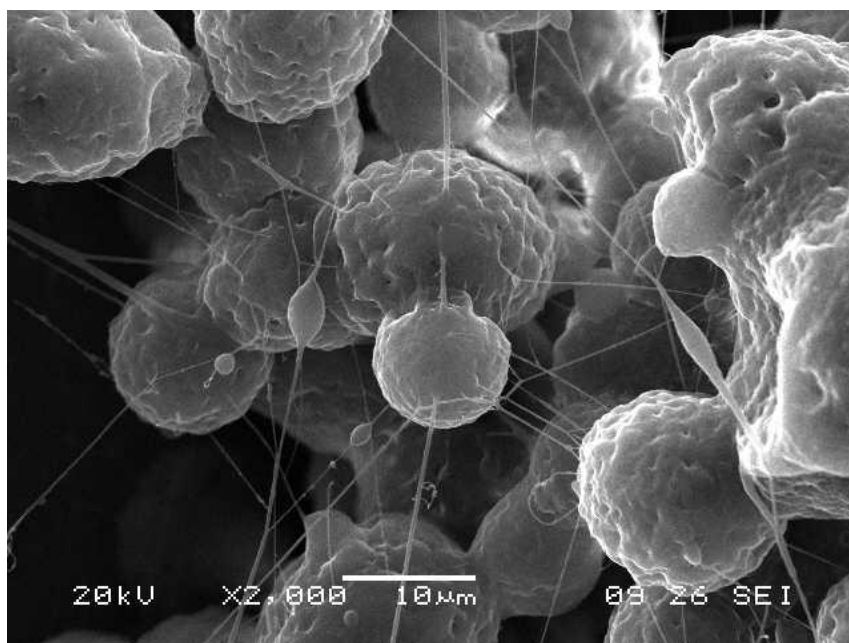


Figure 4.3 : SEM image of sample 3.

When Cyclohexane (boiling point 81°C, dielectric constant 2,02) was used instead of Toluene, fibers which diameters is in the range from few micron to nanometer could be produced successfully at the same experimental conditions. Low boiling point of Cyclohexane might be the reason of this. This shows the importance of the solvent type in electrospinnability.

During the spinning process, clogging of needle has been occasionally observed. Clogging problem may be caused from rapid evaporation of solvent at the needle's tip during process. Electrospun nanofibers could be obtained by 15 % SEBS-g-MA (sample 5, Table 4.1), when the ratio of SEBS-g-MA increased to 17% (sample 6, Table 4.1), it could not be possible to produce fibers because of evaluated viscosity of the solution and evaporation of the solvent.

The ratio of the Acetone (boiling point 56°C, dielectric constant 21) has been decreased from 10% to 5% and the ratio of THF (boiling point 66°C dielectric constant 7,5) has been increased from 10% to 15% with the aim of decreasing solvent evaporation. However, it has been observed that electrospinning could not have been done because of excessive solvent evaporation leading to clogging of needle's tip. When we used DMF (boiling point 153°C, dielectric constant 38) instead of THF, electrospun fibers could be obtained due to higher boiling point and dielectric constant of DMF. However when DMF is used instead of THF, the

diameter of the electrospun fibers increased due to higher viscosity resulted from use of DMF and high boiling point leading less evaporation.

When the ratio of Cyclohexane is decreased from 80% to 70 % and the ratio of DMF is increased from 15% to 30 % (sample 8, 9 Table 4.1), the solution at the end of needle could not be drawn towards collector at the voltage between 20 kV-30 kV. However, when the ratio of DMF decreases to 30% and 20% and THF is added to the solution, solution at the tip of the needle could be drawn towards collector even though clogging of needle's tip is observed frequently.

It has been observed that viscosity of the solution with 15 % SEBS-g-MA (70 % Cyclohexane, 30 %DMF, sample 9) is too high to be drawn, may be due to low solvent (Cyclohexane) and high DMF ratio. Thus, concentration of sample 9 (15% SEBS-g-MA, 70% Cyclohexane, 30% DMF) has been decreased from 15 % to 13 % (sample 11, 13% SEBS-g-MA, 70% Cyclohexane, 30% DMF). Thereby, solution at the tip of needle could be drawn towards collector.

Samples 12 (20kV, 1ml/h, 15cm), 13 (25kV, 1ml/h, 15cm), 14 (20kV, 0.5ml/h, 15cm) and 15 (20kV, 1ml/h, 20cm) were produced in order to see the effect of process parameters (voltage, feed rate and distance). From the Table 4.2 and Figures 4.4 and 4.5 can be seen that an increase of applied voltage (sample 12 and 13) results to an increase of diameter. This may be caused by drawn of more solution from the tip of the needle to the collector by higher voltage. Reduction in the feed (sample 14) rate and increase in the distance (sample 15) resulted a decrease in diameter, compared to reference sample (sample 12) which can be seen from Table 4.2. As the distance increased, the time for evaporation of solvents and drawing also increased and this leads to decrease of the diameter.

Table 4.2 : Average, minimum and maximum diameters of samples 5,8,12,13,14 and 15.

Sample	Average diameter (micron) %CV	Minimum diameter (micron)	Maximum diameter (micron)
Sample no: 5 10%SEBS-g-MA, 80% Cyclohexane, 10% THF, 10% Acetone 20 KV , 1,5 ml/h , 15cm	1,52 38 %	0,425	2,87
Sample no: 8 10 % SEBS-g-MA, 80% Cyclohexane 15% DMF, 10% Acetone 20 KV, 1,5 ml/h , 15cm	2,68 35 %	1,05	5,63

Table 4.2 (continued) : Average, minimum and maximum diameters of samples 5,8,12,13,14 and 15.

Sample no: 12 (reference) 10 % SEBS- g-MA ,70% Cyclohexane, 20% DMF, 10% THF 20 kV, 15 cm, 1 ml/h	0,645 52 %	0,22	2,02
Sample no: 13 10 % SEBS-g-MA, 70% Cyclohexane, 20% DMF, 10% THF 25 kV, 15 cm, 1 ml/h	1,13 45%	0,34	2,04
Sample no: 14 10 % SEBS-g-MA, 70% Cyclohexane, 20% DMF, 10% THF 20 kV, 15 cm, 0.5 ml/h	0,636 52 %	0,11	1,36
Sample no: 15 10 % SEBS-g-MA, 70% Cyclohexane, 20% DMF, 10% THF 20 kV, 20 cm, 1 ml/h	0,603 45 %	0,27	1,22

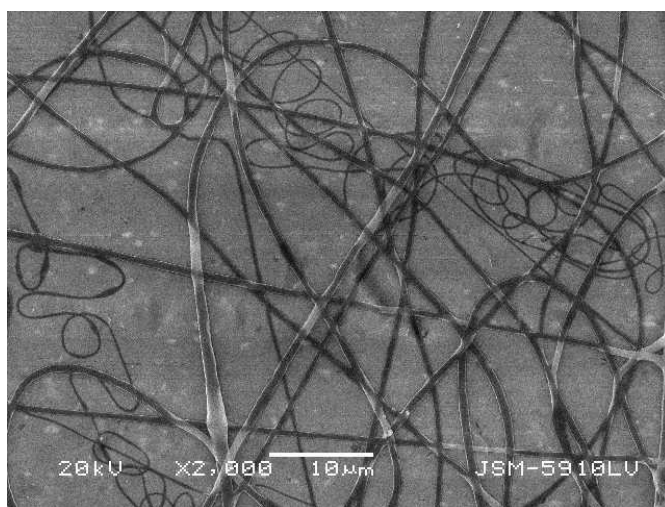


Figure 4.4 : SEM image of sample 12.

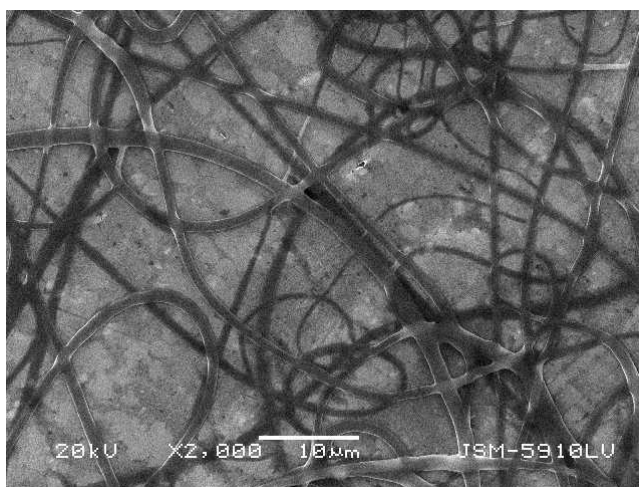


Figure 4.5 : SEM image of sample 13.

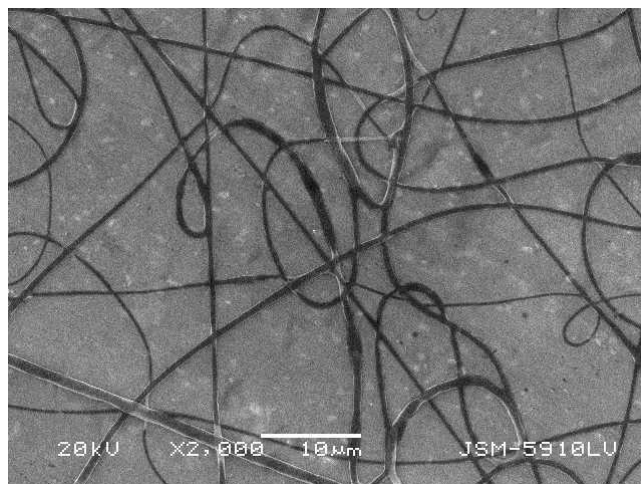


Figure 4.6 : SEM image of sample 14.

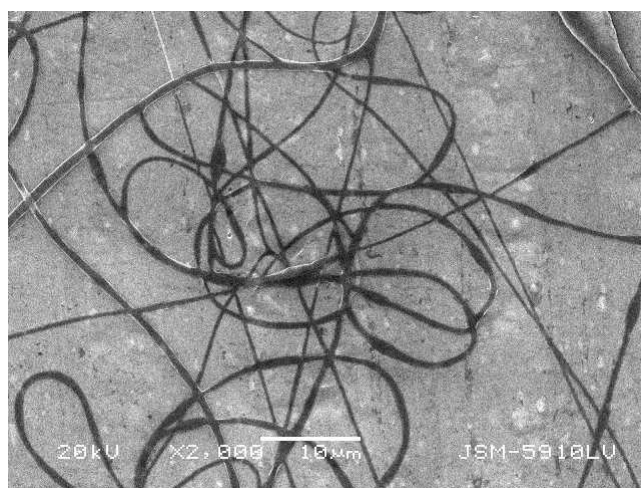


Figure 4.7 : SEM image of sample 15.

When the samples containing CNW were investigated, it has been seen that the presence of CNW results in a more uniform diameter distribution and also a decrease in the diameter of the each type of composite nanofibers, when compared with reference sample (Table 4.3 and Figure 4.8). Decrease in the diameter and increase in the uniformity might be accomplished through increased electrical conductivity of solution by addition of CNW [53].

It was found that the single-component nozzle system resulted in more uniform and thinner nanofibers than the coaxial nozzle system. In the single nozzle system, CNW were dispersed in the polymer solution before electrospinning process. On the other hand in the coaxial system CNW were carried by water into the core of the nanofibers during spinning without being directly mixed with the polymer solution.

Not directly mixing the CNW caused more agglomeration and non-homogenous placement of CNWs in the nanofiber matrix.

Table 4.3 : Average, maximum and minimum diameters of fibers obtained from reference sample, single nozzle and coaxial nozzle.

Sample	Average diameter (micron) %CV	Maximum diameter	Minimum diameter
Reference	0,971 58%	2,571	0,095
Single Nozzle	0,272 34%	0,473	0,071
Coaxial Nozzle	0,512 55%	1,38	0,095

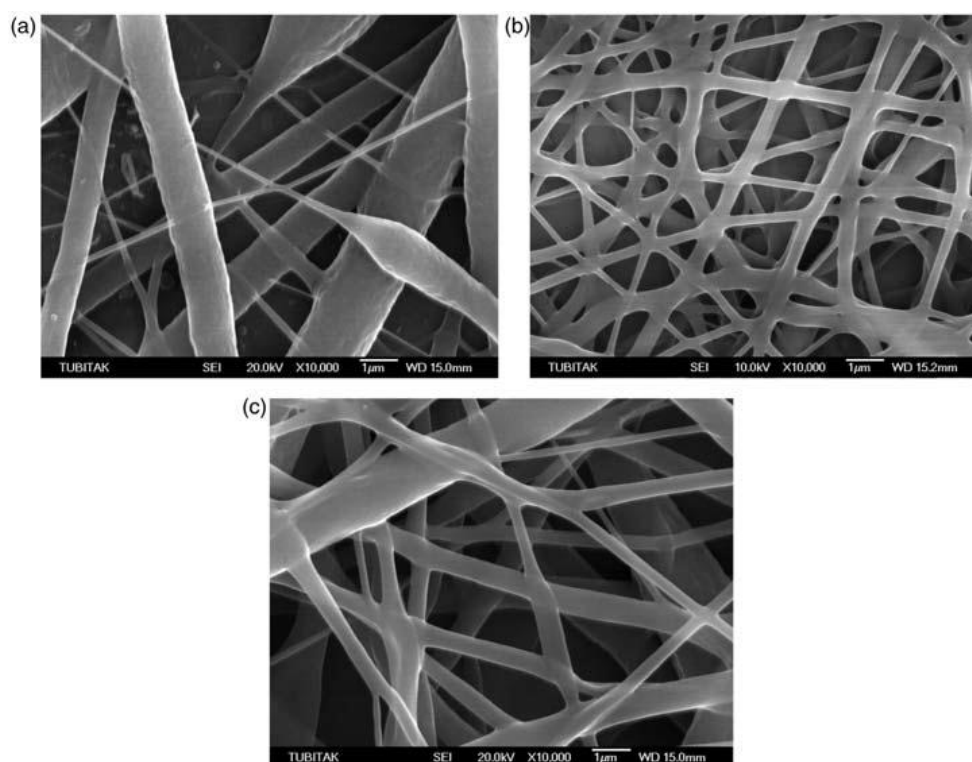


Figure 4.8 : SEM micrographs of nanofibers: (a) Reference N; (b) Single N; (c) Coaxial N.

In the results, high variability in fiber diameter has observed. High variability in the samples is the result of instabilities or uncontrolled jet movements in electrospinning. There are many major forces acting on the charged jet such as gravitational force, drag force, viscoelastic force, surface tension and electrostatic forces. All of these forces have an effect on the diameter and the distribution of diameter. Generally well-balanced forces result in a narrow distribution of the diameter. Addition to the

unbalanced forces, evaporation of solvent during the electrospinning process might cause fluctuation in viscosity and this leads to the variation in the fiber diameter [54].

From FTIR results in Figure 4.9 characteristic band of stretching –OH in the zone of 3200–3550 cm^{-1} can be seen [55]. This stretching confirms the presence of CNWs in the composite nanofibers.

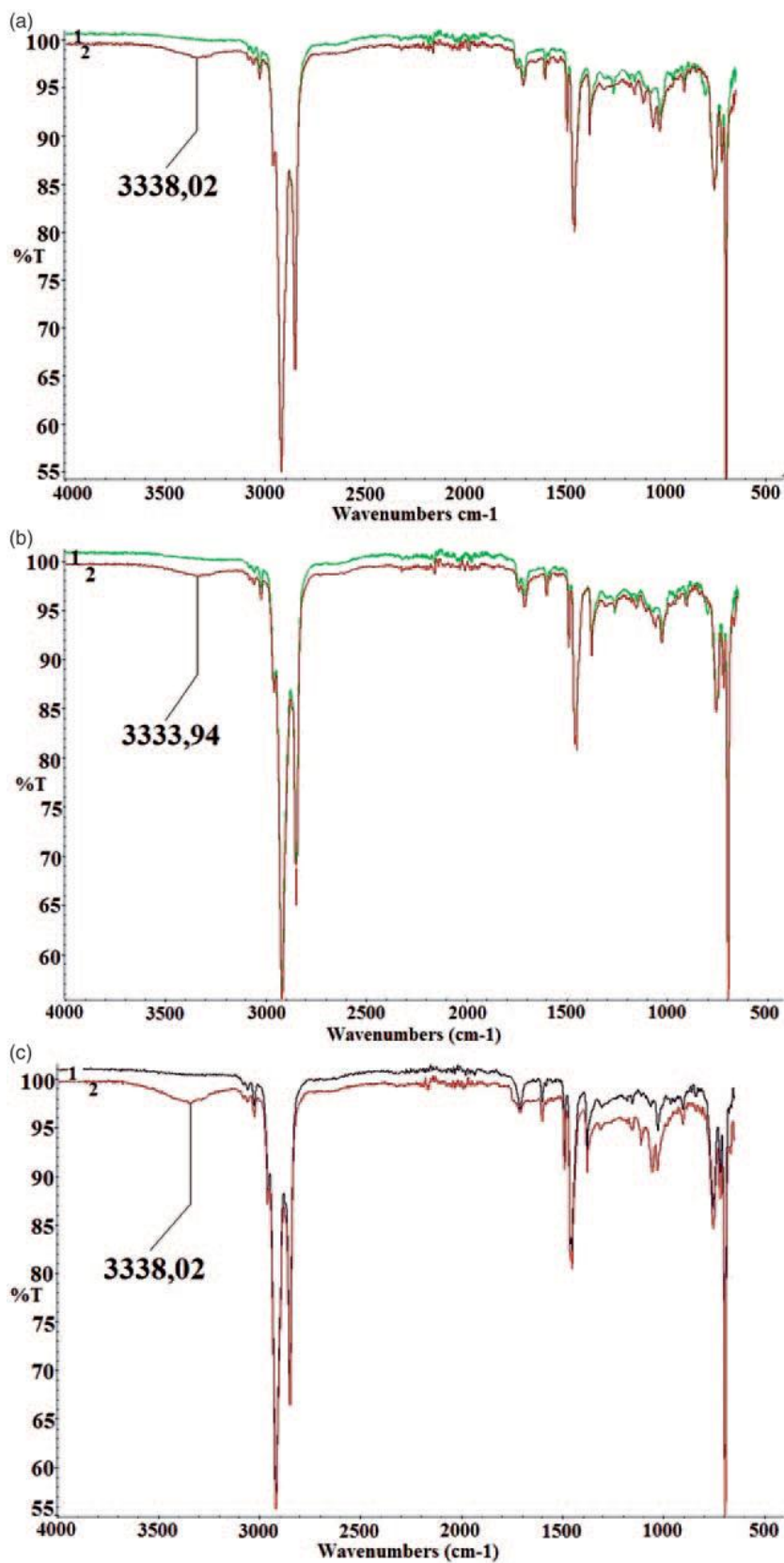


Figure 4.9 : FTIR: (a) comparison between Reference N (1) and Single N (2); (b) comparison between Reference N (1) and Coaxial N (2); (c) comparison between Reference F (1) and Composite F (2).

Table 4.4 : TGA analysis values of nanofibers and films.

Sample	Reference Nanofiber	Single Nozzle Nanofiber	Coaxial Nanofiber	Reference Film	Composite Film
5% loss temperature(T_{05}), °C	384	379	340	404	374

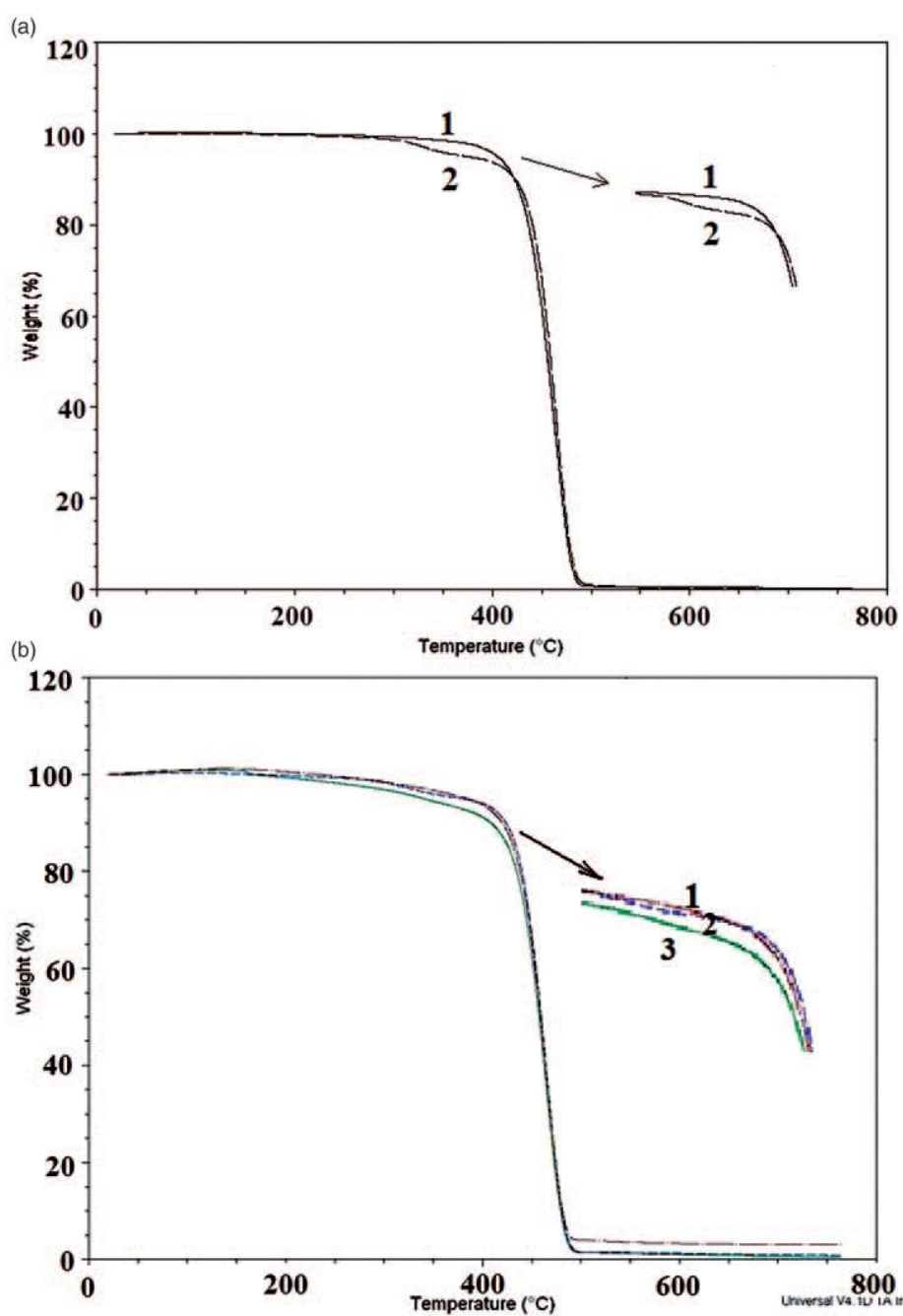


Figure 4.10 : Thermogravimetric analysis (TGA) graphs: (a) TGA graphs of films, (1) Reference F,(2) Composite F; (b) TGA graphs of nanofiber webs, (1) Reference N, (2) Single N and (3) Coaxial N.

TGA curves of the CNW containing film shows two separate bending points. First of them is around 290-300°C and shows the beginning of decomposition of CNW and the second of them is around 380-400 °C and it is related to the decomposition of polymer matrix. Observing only one bending point in the reference sample confirms the presence of CNW decreases the temperature corresponding to 5% weight loss (T_{05}), because of the lower thermal endurance of CNW.

The same inference can also be said for the nanofiber samples. Reference nanofiber (without CNW) shows lower degradation temperature than reference film. This might be caused by porous structure and low packing density of nanofiber webs. Nanofibers containing CNW starts to degrade at lower temperatures compared with others. Especially sample produced with coaxial spinning has much lower 5% loss temperature (340°C, Table 4.4). The reason behind this might be the poor distribution of CNW in the nanofiber matrix. Because coaxial system uses water to place the CNW in the core of forming nanofiber.

Table 4.5 : Mechanical test results of samples.

Sample	Strength (MPa)(CV%)	Breaking elongation (%) (CV%)	Modulus (MPa)(CV%)
Reference N	2.8 (24%)	582 (16%)	0.65 (12%)
Single N	5.8 (16%)	489 (20%)	1.79 (20%)
Coaxial N	1.7 (28%)	548 (24%)	0.69 (24%)
Reference F	30.3 (13%)	1204 (13%)	5.54 (10%)
Composite F	11.4 (30%)	514 (16%)	2.49 (15%)

Result of the tensile tests can be seen from the Table 4.5. The strength of the film samples is higher than the nanofiber webs. This is mainly due to the porous structure of nanofibers. In addition, random orientation of nanofibers in the matrix and lack of incorporation between fibers might cause lower strength. As seen from Table 4.5 presence of CNW decreased the strength of the film sample (11.4 MPa). The decrease in the breaking strength was about 60% compared with the reference film without CNW (30.3 MPa). On the other hand, presence of CNW in the nanofibers produced with single nozzle system resulted in an increase in the breaking strength (approximately 100%, 5.8 MPa) and modulus, and a decrease in the breaking elongation. The reason behind this may be unlike the coaxial nozzle electrospinning and composite film; CNW and SEBS-g-MA during electrospinning are forced to be

drawn under high voltage in single nozzle system. Therefore, agglomeration tendency for single component nozzle electrospinning is less than other samples.

Coaxial system has the lowest breaking strength. In this system, water carries the CNW through the inner nozzle; this caused to gather CNW particles mostly in the core region of the nanofiber rather than well disbursed in the polymer matrix. Therefore, more agglomeration occurred in nanofiber structure. This decrease in the breaking strength was about 40% compared with the reference nanofibers without CNWs. Nanofibers produced with single nozzle system have more uniform CNW distribution in the fiber web. This uniform distribution enhances the reinforcing mechanism by increasing the strength about 100% due to restricted molecular mobility of the polymer matrix. Results indicate that, both single nozzle and coaxial systems have important roles in the nanofiber morphology and properties.

5. CONCLUSION

In this study, three different polymers are used for nanofiber production with electrospinning technique. During the spinning process, different electrospinning parameters have been applied to the samples. In this study condition, it has been seen that Toluene is not very suitable solvent for electrospinning process due to low dielectric constant and high boiling point.

When Cyclohexane was used instead of Toluene, much better results have been obtained in the studies. Low boiling point of Cyclohexane might help to the formation of nanofibers. This shows the importance of the solvent type on spinnability.

Clogging of the needle is an important problem, which has been encountered during the experiments. Rapid evaporation of the solvents in the tip of the needle is one of the main reasons of clogging. Replacing DMF with THF prevented the clogging of the needle. However, increased viscosity of solvent with the use of DMF caused an increase in fiber diameter.

Concentration of the solution, which is an important parameter, has been examined in some trials. With different concentrations from 15% to 10%, nanofibers have been produced. Best results have been obtained with the 10% of concentration.

An increase of applied voltage (sample 13) results to an increase of diameter may be due to drawing more solution from the tip of needle to the collector by higher voltage. An increase in the distance and decrease in the feed rate resulted to thinner fibers.

For the further experiments, SEBS-g-MA has been chosen as polymer due to high spinnability and grafted maleic anhydride in its structure can improve compatibility between CNW and elastomeric polymer, which is originally incompatible with CNW.

Adding CNW to the nanofiber structure leads to finer nanofibers in both single nozzle and coaxial systems. Particularly in single nozzle system, addition of CNW increased the electrical conductivity and this leads to the formation of more uniform fibers in the fiber web.

When the single nozzle and coaxial systems are compared, nanofibers produced with single nozzle system are more uniform and thinner. Dispersing CNW in the polymer solution before spinning resulted better than using water to carry CNW during the spinning. Coaxial electrospinning can be used for some specific applications where materials mechanical properties are not the main issue.

Because of having lower thermal stability, addition of CNW to the nanofibers decrease the thermal stability of the fibers as measured by the temperature of 5% weight loss in TGA analysis. Nanofibers produced with coaxial system have the lowest thermal stability due to the damaging effect of uneven distribution of CNWs in the nanofibers.

Addition to the nanofibers, films with and without CNW have been produced with solvent casting in order to compare the nanofiber and film structures. In TGA analysis porous structure of nanofiber webs results in a lower temperature of 5% weight loss compared with the dense structure of cast films.

Dense structure of films leads to higher tensile strength of the film samples. This difference is mainly caused by their structural differences. Porous structures and being consist of unaligned individual fibers resulted with lower tensile strength of nanofiber samples.

Addition of CNW with the ratio of 20% increased the tensile strength around two-fold and modulus around three-fold of nanofibers produced with single nozzle system. On the other hand, with the nanofibers produced with coaxial nozzle and with the films no improvement in their mechanical properties observed. The reason behind this is ununiformed distribution of CNW for both coaxial nanofibers and cast films.

In coaxial nozzle system, CNW places in the core part of the resultant fiber instead of a uniform distribution. Mechanical properties of these nanofibers are 40% lower than the fibers without CNW. Good distribution of CNW in the spinning solution in single nozzle system resulted with enhanced mechanical properties of nanofibers.

As a result, solvent type is an important parameter in electrospinning as effecting spinnability and clogging problem. In addition, parameters like concentration, voltage, feed rate and distance effect the resultant fiber morphology. Finally, CNW decreases the fiber diameter with the increased conductivity and improves the mechanical properties if a good distribution is obtained in polymer matrix. It also decreases the thermal stability of the material.

REFERENCES

- [1] Lowery, J., Panseri, S., Cunha, C., Gelain, F. (2009). Electrospinning for tissue engineering applications, in *Electrospun Nanofiber Research, Recent Developments*. Ed. Haghi, A.K., Nova Science Publishers, NewYork.
- [2] Graham, K., Ouyang, M., Raether, T., Grafe, T., McDonald, B., Knauf, P. (2002). Polymeric nanofibers in air filtration applications. *Fifteenth Annual Technical Conference & Expo of the American Filtration & Separations Society*, Texas, USA, April 9-12.
- [3] Huang, Z. M., Zhang, Y. Z., Kotaki, M., Ramakrishna, S. (2003). A review on polymer nanofibers by electrospinning and their applications in Nanocomposites. *Composites Science and Technology*. **63**, 2223-2253.
- [4] Fang, J., Niu, H. T., Lin, T., Wang, X. G. (2008). Applications of electrospun nanofibers. *Chinese Science Bulletin*. **53**, 2265-2286.
- [5] Xu, X., Yang, L., Xu, X., Wang, X., Chen, X., Liang Q., et al. (2005). Ultrafine medicated fibers electrospun from w/o emulsions. *Journal of Controlled Release*. **108**, 33 -42.
- [6] Subbiah, T., Bhat, G. S., Tock, R. W., Parameswaran, S., Ramkumar, S. S. (2005). Electrospinning of nanofibers. *Journal of Applied Polymer Science*. **96**, 557-569.
- [7] Kulkarni, A., Bambole, V. A., Mahanwar, P. A. (2010). Electrospinning of polymers, their modeling and applications. *Polymer-Plastics Technology and Engineering*. **49**, 427-441.
- [8] Ramakrishna, S., Fujihara, K., Teo, W. E., Lim, T. C., Ma, Z. (2005). *An introduction to electrospinning and nanofibers*. World Scientific Publishing, Singapore.
- [9] Teo, W. E., Ramakrishna, S. (2006). A Review On Electrospinning design and nanofibre assemblies. *Nanotechnology*. **17**, 89-106.
- [10] Doshi, J., Reneker, D. H. (1993). Electrospinning process and applications of electrospun fibers. *Journal of Electrostatics*. **10**, 1698-1703.
- [11] Ko, F. K. (2004). Nanofiber technology: bridging the gap between nano and macro world in *NATO ASI on Nanoengineered Nanofibrous Materials*. Kluwer Academic Publishers.
- [12] Ding, B., Kimura, E., Sato, T., Fujita, S., Shiratori, S. (2004). Fabrication of blend biodegradable nanofibrous nonwoven mats via multi-jet electrospinning. *Polymer*. **45**, 1895-1902.

- [13] **Dosunmu, O. O., Chase, G. G., Kataphinan, W., Reneker, D. H.** (2006). Electrospinning of polymer nanofibers from multiple jets on a porous tubular surface. *Nanotechnology*. **17**, 1123-1127.
- [14] **Varesano, A., Rombaldoni, F., Mazzuchetti, G., Tonin, C., Comotto, R.** (2010). Multi-Jet nozzle electrospinning on textile substrates: observations on process and nanofibre mat deposition. *Polym Int*. **59**, 1606-1615.
- [15] **Li, D., McCann, J. T., Xia, Y.** (2005). Use of electrospinning to directly fabricate hollow nanofibers with functionalized inner and outer surfaces. *Small*. **1**, 83-86.
- [16] **Li, D., Babel, A., Jenekhe, S. A., Xia, Y.** (2004). Nanofibers of conjugated polymers prepared by electrospinning with a two-capillary spinneret. *Adv.Mater*. **16**, 2062-2066.
- [17] **Bazilevsky, A. V., Yarin, A. L., Megaridis, C. M.** (2007). Co-electrospinning of core-shell fibers using a single-nozzle technique. *Langmuir*. **23**, 2311-2314.
- [18] **Cui, W., Li, X., Zhou, S., Weng, J.** (2007). Investigation on process parameters of electrospinning system through orthogonal experimental design. *Journal of Applied Polymer Science*. **103**, 3015-3112.
- [19] **Ondarçuhu, T., Joachim, C.** (1998). Drawing a single nanofibre over hundreds of microns. *Europhys. Lett*. **42**, 215-220.
- [20] **Kong, C. S., Yoo, W. S., Lee, K. Y., Kim, H. S.** (2009). Nanofiber deposition by electroblowing of pva (polyvinyl alcohol). *J Mater Sci*. **44**, 1107-1112.
- [21] **Peng, M., Sun, Q., Ma, Q., Li, P.** (2008). Mesoporous silica fibers prepared by electroblowing of a poly (methyl methacrylate)/tetraethoxysilane mixture in n,n-dimethylformamide. *Microporous and Mesoporous Materials*. **115**, 562-567.
- [22] **Zhao, R., Wadsworth, L. C.** (2003). Attenuating PP/PET bicomponent melt blown microfibers. *Polymer Engineering and Science*. **43**, 463-469.
- [23] **Zhang, D., Sun, C. Q., Song, H.** (2004). An investigation of fiber splitting of bicomponent meltblown/microfiber nonwovens by water treatment. *Journal of Applied Polymer Science*. **94**, 1218, 1226.
- [24] **Ellison, C. J., Phatak, A., Giles, D. W., Macosko, C. W., Bates, F. S.** (2007). Melt blown nanofibers: fiber diameter distributions and onset of fiber breakup. *Polymer*. **48**, 3306-3316.
- [25] **Mit-uppatham, C., Nithitanakul, M., Supaphol, P.** (2004). Effects of solution concentration, emitting electron polarity, solvent type, and salt addition on electrospun polyamide-6 fibers: a preliminary report. *International Union of Pure and Applied Chemistry*. **216**, 293-299.
- [26] **Yamashita, Y., Tanaka, A., Ko, F.** (2006). Characteristics of elastomeric nanofiber membranes produced by electrospinning. *Journal of Textile Engineering*. **53**, 137-142.

- [27] **He, J., Wan, Y., Yu, J.** (2008). Effect of concentration on electrospun polyacrylonitrile (pan) nanofibers. *Fibers and Polymers*. **9**, 140-142.
- [28] **Wannatong, L., Sirivat, A., Supaphol, P.** (2004). Effects of solvents on electrospun polymeric fibers: preliminary study on polystyrene. *Polymer International*. **53**, 1851-1859.
- [29] **Veleirinho, B., Rei, M. F., Lopez-da-Silva, J. A.** (2008). Solvent and concentration effects on the properties of electrospun poly(ethylene terephthalate) nanofiber mats. *Journal of Polymer Science*. **46**, 460-471.
- [30] **Mit-uppatham, C., Nithitanakul, M., Supaphol, P.** (2004). Ultrafine electrospun polyamide-6 fibers: effect of solution conditions on morphology and average fiber diameter. *Macromol. Chem. Phys.* **205**, 2327-2338.
- [31] **Supaphol, P., Mit-uppatham, C., Nithitanakul, M.** (2005). Ultrafine electrospun polyamide-6 fibers: effect of emitting electrode polarity on morphology and average fiber diameter. *Journal of Polymer Science*. **43**, 3699-3712.
- [32] **De Vrieze, S., Van Camp, T., Nelvig, A., Hagström, B., Westbroeck, P., De Cleck, K.** (2009). The effect of temperature and humidity on electrospinning. *J Mater Sci*. **44**, 1357-1362.
- [33] **Kim, G. T., Lee, J. S., Shin, J. H., Ahn, Y. C., Hwang, Y. J., Shin, H. S., et al.** (2005). Investigation of pore formation for polystyrene electrospun fiber: effect of relative humidity. *Korean J. Chem. Eng.* **22**, 783-788.
- [34] **Heikkilä, P., Harlin, A.** (2008). Parameter study of electrospinning of polyamide-6. *European Polymer Journal*. **44**, 3067-3079.
- [35] **Deitzel, J. M., Kleinmeyer, J., Harris, D., Beck Tan, N. C.** (2001). The effect of processing variables on the morphology of electrospun nanofibers and textiles. *Polymer*. **42**, 261-272.
- [36] **Jalili, R., Hosseini, S. A., Morshed, M.** (2005). The effects of operating parameters on the morphology of electrospun polyacrylonitril nanofibres. *Iranian Polymer Journal*. **14**, 1074-1081.
- [37] <<http://www.sigmaaldrich.com/catalog/product/aldrich/432431?lang=en®ion=TR>>, date retrieved 10.07.2012.
- [38] **Kusmono, Z. A., Ishak, M., Chow, W.S., Takeichi, T., Rochmadi.** (2008). Influence of SEBS-g-MA on morphology, mechanical, and thermal properties of PA6/PP/Organoclay nanocomposites. *European Polymer Journal*. **44**, 1023-1039.
- [39] <<http://machinedesign.com/article/thermoplastic-elastomers-1115>>, date retrieved 15.07.2012.
- [40] **Marcovich, N.E., Auad, M. L., Bellesi, N. E., Nutt, S.R., Aranguren, M. I.** (2006). Cellulose micro/nanocrystals reinforced polyurethane. *J. Mater. Res.* **21**, 870-881.

- [41] **Siqueira, G., Bras, J., Dufresne, A.** (2010). Cellulosic bionanocomposites: a review of preparation, properties and applications. *Polymers*. **2**, 728-765.
- [42] **Han, D., Yan, D.** (2010). Preparation of all-cellulose composite by selective dissolving of cellulose surface in PEG/NaOH aqueous solution. *Carbohydrate Polymers*. **79**, 614-619.
- [43] **Petersson, L., Kvien, I., Oksman, K.** (2007). Structure and thermal properties of poly(lactic acid)/cellulose whiskers nanocomposite materials. *Composites Science and Technology*. **67**, 2535-2544.
- [44] **Bahar, E., Ucar, N., Onen, A., Wang, Y., Oksuz, M., Ayaz, O., et al.** (2012). Thermal and mechanical properties of polypropylene nanocomposite materials reinforced with cellulose nano whiskers. *Journal of Applied Polymer Science*. **125**, 2882-2889.
- [45] **Samir, A. S. A., Alloin, F., Dufresne, A.** (2005). Review of recent research into cellulosic whiskers, their properties and their application in nanocomposite field. *Biomacromolecules*. **6**, 612-626.
- [46] **Ljungberg, N., Bonini, C., Bortolussi, F., Boisson, C., Heux, L., Cavaille, J. Y.** (2005). New nanocomposite materials reinforced with cellulose whiskers in atactic polypropylene: effect of surface and dispersion characteristics. *Biomacromolecules*. **6**, 2732-2739.
- [47] **Chuangchote, S., Sirivat, A., Supaphol, P.** (2006). Electrospinning of styrene-isoprene copolymeric thermoplastic elastomers. *Polymer Journal*. **38**, 961-969.
- [48] **Silverstein, R.M., Webster, F.X.** (1998). Spectrometric identification of organic compounds. 6th edition, (John Wiley and Sons, New York, USA), pp. 76-77.
- [49] **Pradeep, T.** (2007). Nano: The Essentials. (Tata McGraw-Hill Publishing Company Limited, New Delhi), pp. 23-25.
- [50] <http://www.substech.com/dokuwiki/doku.php?id=tensile_test_and_strain-stress_diagram>, date retrieved 18.07.2012.
- [51] <<http://www1.chm.colostate.edu/Files/CIFDSC/TGA-MS.pdf>>, date retrieved 23.07.2012
- [52] **Marcovich, N.E., Auad, M.L., Bellesi, N.E., Nutt, S.R., Aranguren, M.I.** (2006). Cellulose micro/nanocrystals reinforced polyurethane. *J. Mater. Res.*, **21**.
- [53] **Peresin, M.S., Habibi, Y., Zoppe, J.O., Pawlak, J.J., Rojas, O.J.** (2010). Nanofiber composites of polyvinyl alcohol and cellulose nanocrystals: manufacture and characterization. *Biomacromolecules*. **11**: 674-681.
- [54] **Rojas, O.J., Montero, G.A., Habibi, Y.** (2009). Electrospun nanocomposites from polystyrene loaded with cellulose nanowhiskers. *J Appl Polymer Sci*. **113**: 927-935.
- [55] **Lu, P., Hsieh, Y.L.** (2009). Cellulose nanocrystal-filled poly (acrylic acid) nanocomposite fibrous membranes. *Nanotechnology*. **20**: 1- 9.

CURRICULUM VITAE

Name Surname: Onur Ayaz

Place and Date of Birth: İstanbul – 22.04.1988

Address: Sahrayıceddid Mah. Feritbey Sok. 19/6 Erenköy/İstanbul

E-Mail: onur.ayaz@yahoo.com

B.Sc.: Istanbul Technical University

M.Sc. : Istanbul Technical University

List of Publications and Patents:

PUBLICATIONS/PRESENTATIONS ON THE THESIS

- **Ucar, N., Ayaz, O., Bahar, E., Wang, Y., Oksuz, M., Onen, A., Ucar, M., Demir, A.,** 2012. Thermal And Mechanical Properties Of Composite Nanofiber Webs And Films Containing Cellulose Nanowhiskers. Textile Research Journal.
- **Ucar, N., Ayaz, O., Oksuz, M., Onen, A., Bahar, E., Ucar, M., Demir, A., Ilhan, M., Wang, Y.,** 2011. Production of Elastomeric Polymer Fiber Web By Electrospinning Process. Tekstil ve Konfeksiyon.
- **Karasule, S., Kara, I., Delibas, M., Ucar, N., Ayaz, O., Bahar, E.,** 2011, “Properties Of Woven Fabric Coated With Nanofiber Web And Non-Textured Film”, ICONTEX 2011 International Congress of Innovative Textiles, Istanbul.
- **Ayaz, O., Ucar, N., Bahar, E., Oksuz, M., Ucar, M., Onen, A., Demir, A., Demir, A.,** 2011. Production And Analysis Of Composite Nanofiber And Heat Applied Nanofiber. ICONTEX 2011 International Congress of Innovative Textiles, Istanbul.
- **Ayaz, O., Ucar, N., Bahar, E., Ucar, O., Oksuz, M., Onen, A., Ucar, M., Ismar, E., Demir, A.,** 2012. Properties of Composite Nanofiber Produced by Single and Coaxial Nozzle Method used for Electrospinning Technique. Engineering and Technology. 61.