ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

NANOPARTICLES AND NANOFIBERS OF POLY(ACRYLONITRILE-CO-ITACONIC ACID) / POLYTHIOPHENE COMPOSITES

M.Sc. THESIS

Havva BAŞKAN

Department of Textile Engineering

Textile Engineering Programme

JANUARY 2015

ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

NANOPARTICLES AND NANOFIBERS OF POLY(ACRYLONITRILE-CO-ITACONIC ACID) / POLYTHIOPHENE COMPOSITES

M.Sc. THESIS

Havva BAŞKAN
(503121805)

Department of Textile Engineering

Textile Engineering Programme

Thesis Advisor: Prof. Dr. Hale KARAKAŞ
Co-Advisor: Prof. Dr. A. Sezai SARAÇ

JANUARY 2015

İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

POLİ(AKRİLONİTRİL-KO-İTAKONİK ASİT)/POLİTİYOFEN KOMPOZİT YAPILARIN NANOPARTİKÜL VE NANOLİFLERİ

YÜKSEK LİSANS TEZİ

Havva BAŞKAN
(503121805)

Tekstil Mühendisliği Anabilim Dalı

Tekstil Mühendisliği Programı

Tez Danışmanı: Prof. Dr. Hale KARAKAŞ
Eş Danışman: Prof. Dr. A. Sezai SARAÇ

OCAK 2015

Havva BAŞKAN, a **M.Sc** student of ITU **Graduate School of Science Engineering and Technology** student ID **503121805**, successfully defended the **thesis** entitled "**NANOPARTICLES AND NANOFIBERS OF POLY(ACRYLONITRILE-CO-ITACONIC ACID) / POLYTHIOPHENE COMPOSITES**", which she prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

Thesis Advisor :	**Prof. Dr. Hale KARAKAŞ** Istanbul Technical University	.....
Co-advisor :	**Prof.Dr. A. Sezai SARAÇ** Istanbul Technical University	.....
Jury Members :	**Prof. Dr. Fatma KALAOĞLU** Istanbul Technical University	.....
	Doç. Dr. Emine Dilara KOÇAK Marmara University	.....
	Doç. Dr. Süleyman İlker MISTIK Marmara University	.....

Date of Submission : 15 December 2014
Date of Defense : 15 January 2015

To my family,

FOREWORD

First of all, I would like to thank my advisor Prof. Dr. Hale KARAKAŞ for continuous support, kindness and patience. Her wise words and helpful critics always motivated me to work harder. She has become more than an advisor. I express my profound sense of gratitude to my co-advisor Prof. Dr. A. Sezai SARAÇ for providing all the resources, usefull suggestions, discussions, kindness and patience. This work would not be completed without their support. I am grateful for their encouragement all the time.

Secondly, I would like to thank my laboratory friends Zeliha Güler, Timuçin Balkan, Burcu Sayınlı, Selin Gümrükçü, and Ezgi İşmar for their friendly manner, support and spirit of sharing.

In addition, my special thanks go to my colleagues İlkay Özsev Yüksek, Pelin Altay, Zehra Engin Sağırlı and my close friends Ayşegül Ekşi, Özlem Gedikli, Seda Öztürk and Emine Akbaş for their nice friendship, encouragement and favor.

Finally, I would like to thank my family. My mom and dad, Aynur-Ali Kemal Başkan, my dear sisters Ülkü Başkan, Serap İskenderoğlu, my brother-in-law Mustafa Başkan and Ali İskenderoğlu for their love, understanding and patience. I have accomplished everything in my life with their eternal love. It is very lucky for me to have a family like you.

January 2015

Havva BAŞKAN
(Textile Engineer)

TABLE OF CONTENTS

Page

ABBREVIATIONS

AN	**:** Acrylonitrile
AFM	**:** Atomic Force Microscopy
APS	**:** Ammonium Per Sulfate
DMF	**:** N,N Dimethylformamide
EDOT	**:** 3,4 Ethylenedioxythiophene
EDS	**:** Energy Dispersive Spectroscopy
FTIR-ATR	**:** Fourier Transform Infrared-Attenuated Total Reflactance
IA	**:** Itaconic Acid
MOT	**:** 3methoxythiophene
PAN	**:** Polyacrylonitrile
PEDOT	**:** Poly (3,4 ethylenedioxythiophene)
PMOT	**:** Poly (3methoxythiophene)
S	**:** Sulphur
SDBS	**:** Sodium Dodecyl Benzene Sulfonate
SEM	**:** Scanning Electron Microscopy
UV	**:** Ultra Violet

LIST OF TABLES

Page

LIST OF FIGURES

Page

NANOPARTICLES AND NANOFIBERS OF POLY(ACRYLONITRILE-CO-ITACONIC ACID) / POLYTHIOPHENE COMPOSITES

SUMMARY

Nanofibers and nanomaterials have become one of the most popular subject due to their special properties as distinct from their bulk phase. The popularity of them depends on the development in applications. This study also deals with the production and characterization of nanoparticles and nanofibers. The study consists of two parts. First one is achieving the P(AN-co-IA)/polythiophene composites and second one is achieving nanofibers via electrospinning technique. In the first stage, acrylonitrile (AN) and itaconic acid (IA) was copolymerized by emulsion polymerization in the presence of surfactant Sodium Dodecyl Benzene Sulfonate (SDBS). Ammonium Per Sulfate (APS) was selected as initiator and the polymerization was continued for three hours at the temperature 70 ^{0} C. At the end of the polymerization, emulsion latex was obtained. Without any initiator addition, three different amounts of 3,4 ethylenedioxythiophene (EDOT) and 3 methoxythiophene (MOT) were separately incorporated into the emulsion latexes. This copolymerization was lasted for 72 hours. At the end of the copolymerization, the emulsion latexes were precipitated by centrifuging, washed with ethanol and dried under vacuum oven at 60 ^{0} C. Finally, the powder of the nanoparticles were produced. For the characterization of nanoparticles, Ultra Violet (UV)-Visible Spectroscopy, Fourier Transfrom Infrared-Attenuated Total Reflectance (FTIR-ATR) Spectroscopy, Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM) was used. In order to analyze the nanoparticles in the UV-Visible spectroscopy the emulsion latexes were diluted to the optimum value and the range of 190-1100 nm was chosen for characterization. The increase of the peaks according to the increase in amounts of EDOT and MOT were clearly seen. The powder of the nanoparticles were characterized by SEM. According to the SEM images, cauliflower structure was observed. The powder of the nanoparticles were also analyzed by FTIR-ATR. Before AFM characterization spin coating was applied to the nanoparticles which had been treated with N,N Dimethylformamide (DMF) solvent. According to the AFM characterization results, it was seen that the surface roughness increased as the conductive monomer were added and as the amount of them were increased. In order to obtain nanofibers, nanoparticles were dissolved in DMF solvent and blended with polyacrylonitrile (PAN) which had been dissolved in DMF, too. The blending was performed for tuning the viscosity of the electrospinning solution. During the electrospinning experiments, the solution concentration, voltage, feed rate and distance from tip to collector was kept constant in order to compare the average fiber diameters of the electrospun nanofibers. Nanofiber characterization was fulfilled by SEM, Energy Dispersive Spectroscopy (EDS) and the electrochemical measurements were performed with Princeton Applied Research (PAR) Parstat 2263 potentiostat. Electrochemical measurements

was used to compare the resistance behavior of the nanofibers. EDS results proved that presence of Sulphur (S) in the structure shows the blending was successfully achieved. According to the SEM images, it was seen that the average fiber diameter does not differentiate very much among the nanofibers, it is much the same and in the range of 100-200 nm for all electrospun nanofibers. The electrospun nanofibers have sufficient fineness and smoothness. Nanoparticles and nanofibers obtained from this study can be a good candidate for applications where electroactivity is desired.

POLİ(AKRİLONİTRİL-KO-İTAKONİK ASİT)/POLİTİYOFEN KOMPOZİTLERİN NANOPARTİKÜL VE NANOLİFLERİ

ÖZET

Nanomalzemeler ve nanolifler sahip oldukları önemli özellikler sebebiyle oldukça popüler olan konulardandır. Son zamanlarda ortaya çıkan yeni kullanım alanlarında da sahip oldukları spesifik özellikler sebebiyle tercih edilmektedirler. Bu malzemeler üretilirken çeşitli polimerlerin bir araya getirilmesi de söz konusu olmaktadır. Nanolif ve nanomalzeme üretiminde yararlanılan bu polimerlere iletken polimerler de dahil edilebilir ve iletken polimerlerin tek başına proses edilebilme zorluklarından dolayı diğer polimerlerle sentezlenerek kullanımları son zamanlarda sıkça rastlanan örneklerdendir.

Bu çalışmada da, iletken monomerlerden olan iki adet tiyofen türevli monomerin akrilonitril (AN) ve itakonik asit (IA) ile kompozit yapı oluşumu gerçekleştirilmiştir. Bu çalışma iki kısımdan oluşmaktadır. Birinci kısım nanopartikül üretimi ve karakterizasyonu, ikinci kısım ise nanolif üretimi ve karakterizasyonudur. Birinci kısımda sulu ortamda emülsiyon polimerizasyonu yöntemi ile akrilonitril ve itakonik asidin kopolimerizasyonu gerçekleştirilmiş ve Poli (Akrilonitril-ko-Itakonik asit) lateksi elde edilmiştir. Emülsiyon polimerizasyonu için anyonik bir yüzey aktif madde olan sodyum dodesil benzen sülfonat (SDBS), başlatıcı olarak ise suda çözünebilen amonyum persülfat (APS) kullanılmış ve reaksiyon 3 saat boyunca 70 ºC de gerçekleştirilmiştir. Emülsiyon polimerizasyonu sonucu elde edilen lateks üzerine, polimerizasyon devam ederken, iletken monomer olan 3,4 etilendioksitiyofen (EDOT) ve 3 metoksitiyofen (MOT) damlaları ayrı ayrı üç farklı oranda ilave edilmiştir. Bu polimerizasyon için herhangi ilave bir başlatıcı kullanılmamıştır, ortamda bulunan başlatıcı ile reaksiyon sürdürülmüştür ve polimerizasyon 72 saat devam etmiştir. Ardından elde edilen P(AN-ko-IA)/PEDOT ve P(AN-ko-IA)/Poli(3 metoksitiyofen) santrifüj yöntemiyle çöktürülmüş, etanol ile yıkanmış ve vakum etüvünde 60 ºC altında yapısında bulunan su tamamen buharlaşıncaya kadar kurutulmuştur. Elde edilen nanopartiküllerin karakterizasyonu için UV-Görünür Spektroskopi, Fourier Dönüşüm Kızılötesi-Azaltılmış Toplam Yansıma Spektroskopisi (FTIR-ATR), Taramalı Elektron Mikroskobu (SEM) ve Atomik Kuvvet Mikroskobu (AFM) kullanılmıştır.

UV- Görünür spektroskobik analizler için elde edilen latekslerden alınan sıvılar belli bir oranda seyreltilmiş ve 190-1100 nm aralığında analiz edilmiştir. Bu analizler sonucunda hem görünür bölgede hem de ultraviyole bölgede iletken monomerlerin yapı içine girdiğini gösteren pikler 250, 255 ve 800 nm de gözlenmiştir. Ayrıca analiz sonuçlarından elde edilen eğrilerin eklenen iletken monomer madde artışına bağlı olarak genişlediği görülmüştür ve bu da EDOT ve MOT' un yapıya dahil olup P(AN-ko-IA)/PEDOT ve P(AN-ko-IA)/Poli(3 metoksitiyofen) kopolimerlerini oluşturduğunun ispatıdır.

Fourier Dönüşüm Kızılötesi-Azaltılmış Toplam Yansıma Spektroskopisi (FTIR-ATR) analizlerinde nanopartüküllerin çöktürülmüş ve kurutulmuş toz yapılarından faydalanılmıştır. P(AN-co-IA)/PEDOT'a ait FTIR-ATR spektrumunda 2244 cm^{-1} bandında C≡N gerilme piki, 2933 cm^{-1} bandında alifatik CH_2 gerilme piki, 1732 cm^{-1} bandında nanopartikül yapısındaki karboksil grubunun varlığından kaynaklanan karbonil gerilme titreşimi, 1453 cm^{-1} bandında –CH eğilme titreşimi, 1218, 1063, 1008 ve 771 cm^{-1} bantlarında C-S bağından gelen etilendioksi halkası görülmüştür. P(AN-co-IA)/PMOT'a ait FTIR-ATR spektrumunda da 2244 cm^{-1} bandında C≡N gerilme piki, 2933 cm^{-1} bandında alifatik CH_2 gerilme piki, 1733 cm^{-1} bandında nanopartikül yapısındaki karboksil grubunun varlığından kaynaklanan karbonil gerilme titreşimi, 1453 cm^{-1} bandında –CH eğilme titreşimi ve 1221 cm^{-1} bandında C-C bağına ait PMOT gerilme titreşimi görülmüştür.

Nanopartiküllerden elde edilen Taramalı Elektron Mikroskobu (SEM) sonuçlarında ise iletken polimer içeren nanopartiküllerin, matris polimerizasyonu sonucunda elde edilen nanopartiküllere göre daha gözenekli ve 'cauliflower' olarak isimlendirilen yapıya sahip oldukları tespit edilmiştir.

Atomik Kuvvet Mikroskobunda inceleme yapılmadan önce, toz halde elde edilen nanopartüküller N,N dimetilformamid (DMF) çözücüsü ile muamele edilmiş ve ardından döner kaplama yöntemi ile cam yüzey üzerine filmleri dökülmüştür. AFM analizlerinde ise hem düzgün yüzeye sahip olan film içermeyen cam yüzeyin ölçümü alınmış hem de film kaplı cam yüzeylerin ölçümü alınarak elde edilen yapıya ve yüzey pürüzlülüğüne bakılmıştır. Elde edilen verilere dayanarak, polimerizasyon esnasında ilave edilen EDOT ve MOT' un artışına bağlı olarak, filmlerin yüzey pürüzlülüğünün de arttığı gözlenmiştir. P(AN-ko-IA)/PEDOT numunelerinde yaklaşık çapı 100 nm olan partiküller görülmüştür. P(AN-ko-IA)/PMOT polimerine ait filmlerde ise düzgün olarak yerleşmiş üçgensel yapılar görülmüştür. Bu yapıların da 3 metoksitiyofenin yapısından kaynakladığı düşünülmektedir.

Elde edilen nanopartiküller, güç kaynağı, pompa, şırınga ve metal toplayıcı yüzeyden oluşan elektroeğirme cihazında nanolif haline getirilmiştir. Bunun için kütlece % 5 lik çözelti konsantrasyonu kullanılmıştır. Nanolif üretimi öncesinde çözelti hazırlanırken poliakrilonitril polimeri ile üretilen kopolimerlerin karışım yapılması tercih edilmiştir. Karışımın tercih edilme sebebi, elektroeğirme yöntemi için kullanılacak olan çözelti viskozitesinin en uygun şekilde ayarlanması ve buna bağlı olarak da lif elde edilebilmesini kolaylaştırmasıdır. Karışımda kullanılacak poliakrilonitril için de kütlece % 5 oranında çözelti hazırlanmıştır ve ayrı ayrı 2 saat karıştırılan çözeltiler bir araya getirilerek tekrar 2 saat karıştırma işlemine tabi tutulmuştur. Hazırlanan çözeltilerinin viskoziteleri karışımdan önce ve karışımdan sonra viskozimetre ile ölçülmüştür. Bu ölçümden alınan sonuçlara göre karışımdan önce PAN çözeltisinin viskozitesinin 48.8 mPa.s (22.7 ºC), üretilen P(AN-ko-IA)/PEDOT çözeltisinin viskozitesinin 2.09 mPa.s (23.3 ºC) olduğu görülmüştür. Karışım yapıldıktan sonra ölçülen viskozite değerinin ise 39.1 mPA.s (23.3 ºC) olduğu tespit edilmiştir. Tüm karıştırma işlemlerinin ardından farklı voltaj uygulamalarında, toplayıcı ile şırınga arasındaki uzaklık farkında değişik ön denemeler yapılmıştır. En düzenli ve damlacık içermeyen lifin görüldüğü çalışma şartları esas deney olarak uygulanmıştır. Sonuç olarak elektroeğirme prensibinde besleme hızı 1 ml/h, voltaj 15 kV, şırınga ile toplayıcı arasındaki mesafe ise 10 cm olarak belirlenmiştir. Eletroeğirme sonucunda elde edilen liflerin ortalama lif çaplarının kıyaslanabilmesi açısından elektroeğirme parametreleri tüm lifler için çözelti konstrasyonunda olduğu gibi sabit tutulmuştur. Elektroeğirme sonucunda

Taramalı Elektron Mikroskobu (SEM) ve Enerji Dağıtıcı Spektroskobi (EDS) ile karakterizasyon yapılmıştır. Bunlara ilaveten liflerin direnç davranışlarını görebilmek için de elektrokimyasal empedans ölçümleri gerçekleştirilmiştir. Elde edilen EDS sonuçlarına göre yapıda görülen kükürdün tiyofen halkasından geldiğini ve buna dayanarak P(AN-ko-IA)/PEDOT ve P(AN-ko-IA)/PMOT kopolimerlerinin PAN ile başarılı bir karışım oluşturduğunu söylemek mümkündür. Yapıdaki kükürdün diğer bileşenlere oranla daha az görülmesi ise karışımdaki kopolimerin PAN'a oranla daha düşük miktarda kullanılmasından kaynaklanmaktadır. SEM analizlerine değinilecek olursa, elde edilen nanoliflerin oldukça düzgün ve ince oldukları ve toplayıcı üzerinde homojen bir şekilde dağıldıklarını görülmektedir. mümkündür. Ortalama lif çapları 100-200 nm aralığında değişmektedir ve hemen hemen her karışımda yaklaşık olarak yakın lif çaplarının belirlendiğini belirtmek doğrudur. Lif dağılımlarına ait eğrilere ve standart sapmaya bakılacak olursa sapma miktarının % 30 larda olduğu ve bunun da literatürde görülen aralık içerisinde kaldığı söylenebilir.

Tüm bu sonuçlar değerlendirildiğinde, bu tezde gerçekleştirilmeye çalışılan nanopartikül ve nanolif eldesinin başarıyla sonuçlandığı ve elde edilen partikül ve liflerin tekstil sektörü için iletken kaplama uygulamaları, gaz sensörü, biyosensör, membran vb. elektroaktif özellik istenen uygulama alanlarında kullanımının uygun olacağını söylemek mümkündür.

1. INTRODUCTION

Composite structures are of great interest in recent years due to their advantages of gathering different polymers' properties in one composition [1]. For this purpose, conductive polymers and various derivatives of them are studied by researchers frequently. Polythiophene and its derivatives are among these conductive polymers preferred for composite structures [2-3].

Conductive polymers such as polythiophene, polypyrrole, polyaniline, polyacetylene, poly(p-phenylene) have many applications such as sensors, light emitting diodes, capacitors etc. due to their unique properties. However, difficulty in processing and brittle structure are among their disadvantages. In order to compensate the disadvantages, combination of these polymers with special structures named core-shell is gaining popularity [4-7].

Polyacrylonitrile is a significant polymer for the production of high performance materials such as carbon fibers. Several comonomers, such as itaconic acid, vinyl acetate, methyl acylate, butyl acrylate are used for the copolymerization of acrylonitrile. When acrylonitrile and these comonomers are copolymerized for obtaining core-shell morphology, their properties can be used more efficiently. Acrylonitrile, being an insulating material, can be used as core and conductive comonomers can be used as a shell [8-11].

In the literature, the copolymerization of acrylonitrile with vinyl acetate, methyl acylate, butyl acylate, itaconic acid have been investigated. In addition, various compositions of these copolymers along with the conductive monomer and polymers such as pyrrole, 3,4 ethylenedioxythiophene, polythiophene and other thiophene derivatives, polyacetylene, polyaniline have also been analyzed [12-16].

The main objective of this research is to produce core-shell structures by using acrylonitrile, itaconic acid and thiophene derivates, and combine the properties of these monomers in the composite structure. First of all, acrylonitrile was

copolymerized with itaconic acid via emulsion polymerization. At the end of this stage, P (AN-co-IA), which is defined as matrix polymer, was formed. Secondly, thiophene derivatives were incorporated into the matrix polymer and P (AN-co-IA)/Polythiophene composite structures were obtained. Finally, P (AN-co-IA)/Polythiophene composites were electrospun with Polyacrylonitrile (PAN) to achieve electroactive nanofibers for various fields such as gas sensors, nanocoatings, membranes etc.

2. THEORETICAL PART

2.1 Emulsion Polymerization

2.1.1 Definition and history of emulsion polymerization

Emulsion polymerization is a chemical unique complex process in which waterborne resins are produced in a heterogeneous system with various physicochemical properties [17].

This process consists of emulsification of the relatively hydrophobic monomer in water by an oil-in-water emulsifier, then initiation reaction with a free radical initiator which can be both water soluble or oil soluble. After the polymerization a milky fluid called ‘latex’, ‘synthetic latex’ or ‘polymer dispersion’ is achieved. The obtained latex may be organic or inorganic, generally containing 40-60 % polymer solids and 40-60 % polymer particles dispersed in the continuous aqueous phase. The size of the polymer particles obtained by emulsion polymerization ranges between 10 nm to 1000 nm in diameter [17,18].

In 1929, Dinsmore, who was working for the Goodyear Tire & Rubber Company produced a synthetic rubber and honoured with a patent since he was the first person using a soap as emulsifying agent. After this patent, a free-radical initiator was incorporated into the process and this led to the polymerization of the emulsified monomer. Then the name ‘emulsion polymerization’ occurred due to the addition of soap and the idea of polymerization in the emulsified monomer droplets [19].

In the mid 1930s, the usage of emulsion polymerization also boosted rapidly in industrial scale. However, the major developments in emulsion polymerization occurred during the World War II for producing synthetic rubbers from 1,3-butadiene and styrene. Studies between academia and industry revealed various types of latex in homopolymer and copolymer state. Different compositions with different monomers like butadiene, styrene, acrylic esters, acrylonitrile and vinyl acetate have been experimented during and after the World War II [19-21].

After the World War II, in the mid 1940s a great deal of books have been written about the mechanism, kinetics, applications and some formulations of emulsion polymerization. Moreover, since 1966 many conferences have been organized and the proceedings of them have been published on this unique process [20, 22].

Today, the final product of the emulsion polymerization is used in a wide range of applications such as synthetic rubbers, toughened plastics, paints, adhesives, paper coatings, floor polishes, sealants, cement and concrete additives, nonwovens, cosmetics, biomaterials, high-tech products etc [20,23].

2.1.2 Main ingredients and mechanism of emulsion polymerization

There are four basic ingredients in emulsion polymerization which are monomer, dispersion medium, emulsifier and initiator [23].

Besides the main ingredients, of course, there are some auxiliaries like buffers, acids, bases, biocids, transfer agents etc.[20].

Monomer: The monomers used in emulsion polymerization are generally butadiene, styrene, acrylonitrile, acrylic acid, vinyl chloride, acrylate ester, methacrylate ester monomers, vinyl acetate, methacrylic acid, etc. [20].

The common property of these monomers is being free-radical polymerizable monomer. Beyond this property, they are all different in terms of structure, chemical and physical properties that affects the polymerization [23].

The monomers used in emulsion polymerization can also be classified with respect to their solubility degree. For example; acrylonitrile having a solubility in water of 8 % has a good solubility in water whereas the monomers like methyl methacrylate and other acrylates with solubility of water 1-3 % have a moderate solubility degree. The other monomers such as butadiene, isoprene, styrene, vinyl chloride and etc. can be defined as insoluble in water [20].

Dispersion Medium: In emulsion polymerization, generally water is used as dispersion medium. Because water has some advantages over other dispersing liquids. First of all, water is cheap, inert and environmentally friendly. During the transfer of monomer droplets to polymer particles, initiator decomposition and

oligomer formation, it is the fundamental medium. It also takes part to be a good solvent for emulsifier, initiator and other ingredients [20].

Emulsifier: Emulsifiers are the surface-active agents and they are regarded as soap, surfactant, dispersing agent and detergents [24].

During the polymerization they take on important tasks. For instance; by the help of the emulsifier, the interfacial tension between the monomer and water is reduced, micelles are generated. Micelles are the ordered clusters of emulsifier molecules. They have two parts as oil-soluble and water-soluble and the oil-soluble part orients towards the center of the cluster and water-soluble part orients towards water.In addition, the emulsifier stabilizes both the monomer droplets and the final latex, helps to solubilize the polymer and also acts as chain transfer agents [25,26].

In order to mention in detail, emulsifiers can be anionic, cationic, zwitterionic or non-ionic and this classification comes from the nature of the water-soluble part of them. Sodium lauryl (dodecyl) sulfate, sodium doceyl benzene sulfonate, sodium dioctyl sulfosuccinate are the examples of anionic emulsifiers. Acetyl dimethyl benzyl ammonium chloride and hexadecyl trimethyl ammonium bromide are the examples of cationic emulsifiers. Alkylamino or alkylimino propionic acids are the examples of zwitterionic emulsifiers which show both anionic and cationic properties depending on the pH of the medium. Polyoxyethylenated alkylphenols, polyoxyethylenated straight-chain alcohols and polyoxyethylenated polyoxypropylene glycols are some of the examples of non-ionic emulsifiers and they do not carry any charge [20,27,28].

Among these four groups, especially anionic emulsifiers are selected for emulsion polymerization due to their property of being strong particle generator and stabilizing the latex particles.

Initiator: In emulsion polymerization initiator activates free-radicals which then compose the polymer molecules. The free radical initiators can be water-soluble or oil-soluble [29].

Persulfates also named as peroxodisulfates such as potassium-,sodium-,and ammonium-persulfate are the most commonly used water-soluble initiators.

Persulfate ion decomposes in dispersion medium generally in water and gives two sulfate radical anions that start the polymerization.

Benzoyl peroxide and azobisisobutyronitrile are the examples of thermal initiators where hydrogen peroxide and other peroxides are the thermal decomposition type initiators. Apart from these initiators persulfate-bisulfite systems are the parts of the redox initiators which produce free radicals at relatively low temperatures [20,29].

Except the main ingredients, there are some auxiliaries mentioned before. To give an example; chain transfer agents are the ones used for ordering the molar mass distribution of the latex polymer. Buffer is the other one used in order to regulate the pH of the polymerization. Moreover, plasticizers, antioxidants,UV-absorbers, pigments, fillers can be used according to the purpose of the polymerization system [20].

Emulsion polymerization is a type of free radical addition polymerization consisting of three steps: initiation, propagation and termination.

At the initiation stage, surfactant, dispersing medium (generally water), monomer and initiator is gathered together and surfactant helps to decrease the interfacial tension between the water and monomer surface. The free-radicals are decomposed and then they interact with the monomer and trigger the radical growth. The spontaneous latex particles begin to occur at this stage [24,30,31].

At the propagation stage the exact polymer molecules are generated. The number of monomer molecules decrease related with the increase of the number of the polymer particles [24,30,31].

At the termination in which the growing polymer chain is terminated and at the end of this stage a milky fluid is obtained [24,30,31].

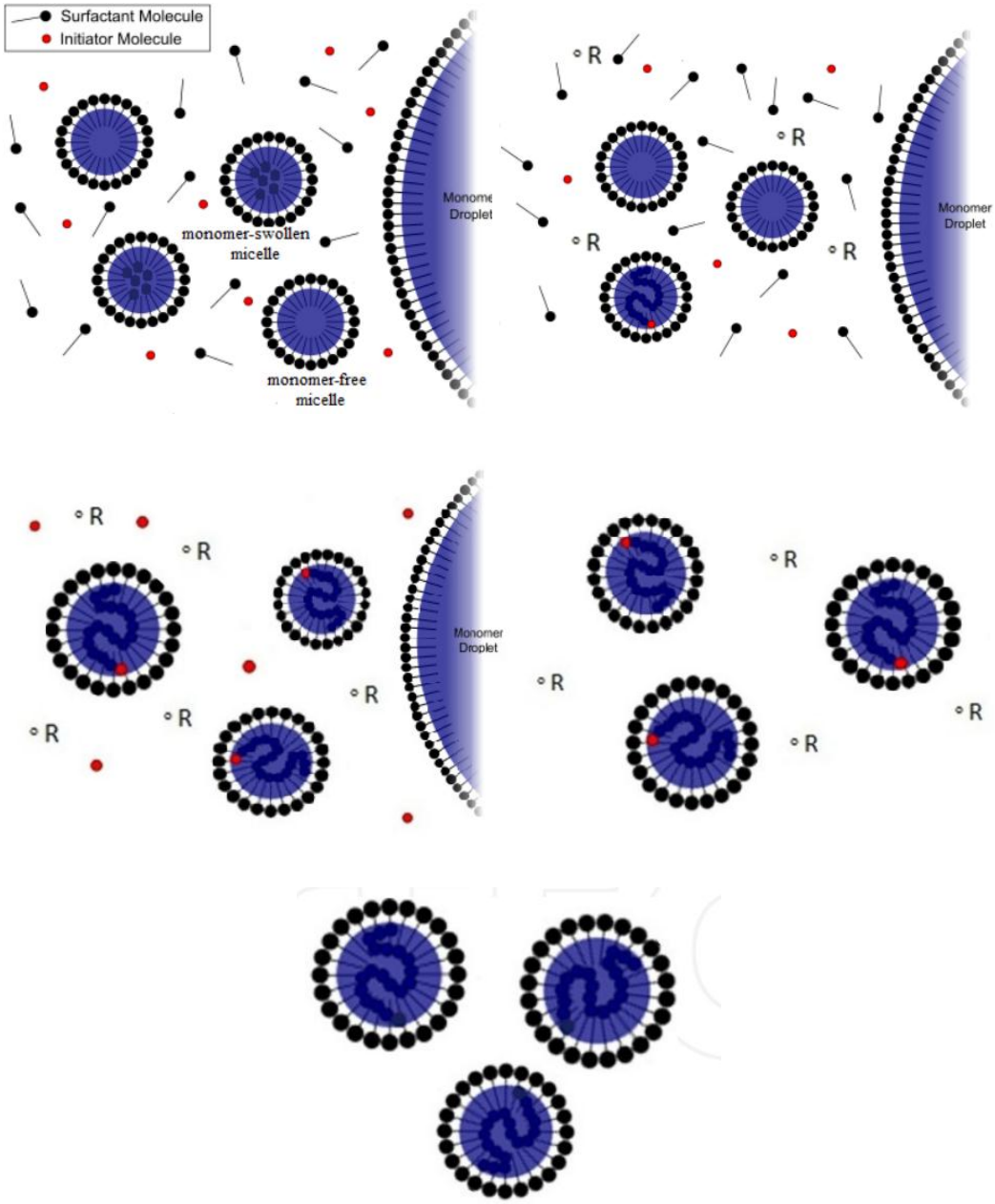


Figure 2.1: Schematic drawing of the emulsion polymerization [20].

2.1.3 Advantages and disadvantages of emulsion polymerization

Emulsion polymerization has some advantages over other polymerization systems. For example; in emulsion polymerization water is used as a dispersing medium, thereby the system is inexpensive, nontoxic and nonflammable. It gives the possibility of incorporating the ingredients at any stage of the polymerization with better temperature control. In addition to all these, particle size distribution can be achieved bu tuning the parameters. The viscosity of the latex is independent of the

molecular weight and the major advantage is the opportunity to obtain high molecular weight polymer at a high reaction rate.

Unfortunately, there are two overcomes which are the unavoidable contamination in the system because of the existence of emulsifiers and additional operations in order to separate the polymer from dispersion medium [19,20].

2.1.4 Monomers used in emulsion polymerization

Styrene/butadiene copolymers, vinyl acetate homopolymers and copolymers, polyacrylates, copolymers of ethylene, styrene, vinyl esters, vinyl chloride, vinylidene chloride, acrylonitrile and polyurethane are the most used monomers experimented in emulsion polymerization. Also using acids such as methacrylic, acrylic, maleic, fumaric or itaconic acid helps to stabilize the polymer particles related to their carboxylic groups [20].

If styrene copolymers is replaced by acrylonitrile elastic and solvent resistant copolymers can be obtained [20].

Acrylic monomers such as methyl-, ethyl-,butyl-,methylacrylate, methacrylic-acid are the most popular ones used for binders, textile products, papers, laminates, adhesives, elastomers etc [20].

The homopolymer and copolymers of these ester with styrene gives the opportunity to tune morphological designs, hydrophilicity and the film forming temperature [20].

PVC (polyvinylchloride) latexes which are used in daily life in a great deal of area (especially for packaging of food) can also be polymerized by emulsion polymerization [20].

The last but not the least one is the vinyl acetate which accounts 28 % of the total latexes. Vinyl acetate can be copolymerized with ethylene, acrylic esters, versatic ester, or vinyl chloride. The copolymers of vinyl acetate are generally used in coating and adhesive [20].

2.2 Polyacrylonitrile and Copolymers of PAN

2.2.1 PAN (Polyacrylonitrile)

Acrylonitrile (AN) and the polymers based on acrylonitrile are efficiently used in order to produce acrylic fibers. Acrylonitrile and acrylonitrile based polymers have a wide range of applications in industry such as plastics, synthetic fibers, rubbers ad so many composites [32].

There are three different methods for synthesizing acrylonitrile.

First method is the Sohio process which proceeds from propylene and ammonia.

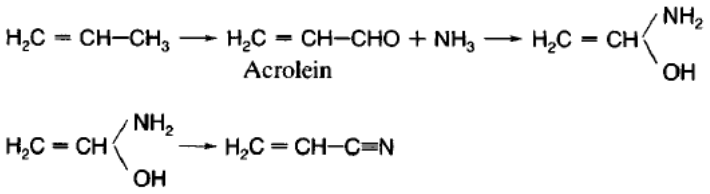


Figure 2.2: Sohio process [32].

Second method is the Two Phase Process which starts with ethylene oxide and hyrogen cyanide.

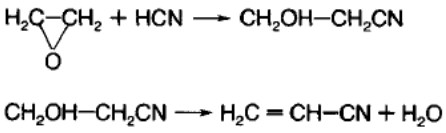


Figure 2.3: Two phase process [32].

Third method is the direct addition of hydrogen cyanide to acetylene.

Figure 2.4: Direct addition of hydrogen cyanide to acetylene [32].

Polyacrylonitrile (PAN) produced from acrylonitrile (AN) is a polymer with a molecular formula of [C3H3N] and includes a chain of carbon connected to one

another is hard, horny, relatively insoluble and a high-melting material. The high-melting point (Tm~320 ° C) of PAN is attributed to the strong dipole-dipole interactions between nitrile (-CN) groups [33,34].

PAN homopolymer consists highly polar groups,and this causes some difficulties during spinning, therefore PAN copolymers are generally used to disorder the nitrile-nitrile interactions,which causes better chain alignment [35].

Çetiner mentioned that,'Thermal stability of homopolymer of AN is improved after being copolymerized.' He also said that while heating homopolymer of AN and its copolymers cylization of nitrile groups, which is an exothermic reaction, occurs and this convert the structure of PAN to ladder type. For that reason adding some monomer to acrylonitrile give the property of weakening the dipolar interactions,decreasing melting point or increasing decomposition temperature of the PAN based copolymers [12].

PAN is one of the mostly used polymer in manufacturing of synthetic fibers. Since PAN has high carbon yield (up to 56 %), ability to modify the final structure of carbon nanofibers (CNFs) and the ladder structure for obtaining stabilized products, it is most commonly used as a precursor for gaining carbon nanofibers [36].

Carbon nanofibers (CNFs) produced from PAN has unique properties and used in many applications such as garments, energy storage devices, insulators, filtration barriers, material reinforcements and etc. For instance; by the help of physical trapping and adsorption nanofiber membranes consisting sheets of randomly oriented nanofibers show an efficient removal method with a high rejection rate of airborne particles. In future, beyond the current usage of PAN-based nanofibers, there will be many more applications in a wide range of scientific disciplines [37].

2.2.2 Polyacrylonitrile based copolymers

The use of PAN as homopolymer is not preferred since the homopolymer of PAN fibers have low hygroscopicity and dye uptake depending on the molecular structre of the polymer and also its high glass transition temperature. For fiber manufacturing studies have focused on the copolymerization of acrylonitrile with various comonomers [38].

In the case of copolymerization of acrylonitrile with a suitable monomer, melting point decreases and decomposition temperature increases related with the distruption of the bipolar interactions between the –CN groups [12].

Methyl acrylate, vinyl acetate, methyl methacrylate are the most commonly used comonomers which are at the same time neutral comonomers copolymerized with acrylonitrile and this copolymerization provides increase in the dye uptake.Bhanu et al. has studied on the copolymerization of acrylonitrile/ methylacrylate (AN/MA) by changing the parameters of the polymerization. Han et al. and Çetiner et al. are the other examples of researchers who has made studies on the production and characterization of acrylonitrile with methacrylate and vinyl acetate. By the use of vinyl acetate with acrylonitrile, the solubility of the polymer in spinning solutions increases and the fiber morphology becomes different [12].

The dye absorption also increases when ketones, esters, alcohols are used because they are nonionizable comonomers [10, 39].

In order to talk about other comonomers, acrylic acid (AA) and itaconic acid (IA) can be good examples that they can improve the hygroscopicity. These acidic comonomers differ from other comonomers since their help to the cyclization of nitrile groups of AN for changing the structure from the ordered one to the ladder type [40].

2.3 Polyacrylonitrile-itaconic acid copolymers

Polyacrylonitrile is copolymerized with various monomers, but among these comonomers itaconic acid (IA) is the most commonly used one because of its two carboxylic groups. Polyacrylonitrile is an important precursor for obtaining carbon fibers; however in the process for producing carbon fibers there must be an intermediate stabilization step nearly at temperatures between 180-400 ° C. At this stage the structure of polyacrylonitrile converts to the ladder type as a result of the changes of nitrile groups. If polyacrylonitrile is copolymerized with an acidic comonomer like itaconic acid the polymer backbone can be stabilized in the cyclization process [40,41,42] .

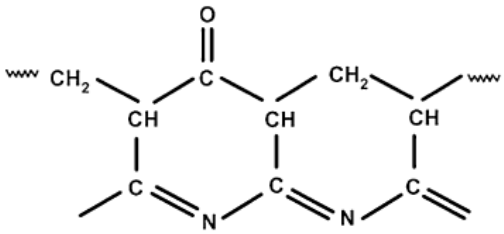


Figure 2.5: Ladder type structure of polyacrylonitrile (PAN) [32]

Because of having two carboxylic groups, itaconic acid has the chance to increase the possibility of interaction between the carboxylic group and nitrile group during the cyclization process, thereby it is advantageous to choose IA as a comonomer over acidic monomers.

Devasia et al. studied on the cyclization reaction in poly(acrylonitrile / itaconic acid) copolymer with DSC and they evaluated that IA initiates the cyclization reaction via an ionic mechanism. Further the temperature of the initiation of cyclization reaction can be lowered to 180-200 ° C which means that the DSC exotherm becomes less intense and broader [40].

Tsai et al. studied the effect of itaconic acid on the exothermic reaction and revealed that by increasing the molar content of itaconic acid the exothermic peak has become more complex and showed several distinct peaks. In addition it has been mentioned that the cyclization reaction rate is largely depends on the distribution of the comonomer in polyacrylonitrile copolymers [42].

Acrylonitrile and itaconic acid has been copolymerized with several polymerization techniques. Zhao and coworkers tried the aqueous deposited polymerization system with water-soluble initiator ammoniumpersulfate (APS). In this aqueous deposited polymerization system it has been demonstrated that the temperature of the polymerization is also an important parameter except the amount of itaconic acid and affects the monomer reactivity ratios effectively [43].

Devasia et al. copolymerized acrylonitrile with itaconic acid using solution polymerization method and used dimethylformamide (DMF).In this study when the molar concentration of itaconic acid has increased to 10-15 mol %, the retardation problem of copolymerization has occured. In order to eliminate the dilemma the triethylamine (TEA) was incorporated into the polymerization system [44].

Later studies has made on the copolymerization of acrylonitrile with itaconic acid in the presence of DMF/water mixture. As distinct from other polymerization techniques here water was used and the existence of water caused retardance both in the reactivity of itaconic acid amd polymerization rate [45].

In 2009 Yu et al. experimented the copolymeriztion of acrylonitrile with itaconic acid by suspended emulsion polymerization. They selected the potassiumpersulfate (KPS) as an initiator, PVA as a dispersing medium and Span80 as an emulsifier. The obtained copolymers of AN/IA showed porous structure with low particle density. They mentioned that the more KPS concentration leads the less particle size and narrower particle size distribution can be obtained. Even more with increasing water amount the particle size distribution becomes wider [46].

2.4 Conductive Polymers

Polymers with another name plastics are one of the most used materials in the world and their usage differs in a wide range from containers to clothing. They are used as insulating materials since they have good typical properties like strength, flexibility, elasticity, stability, mouldability, ease of handling etc. They are typically utilized in electrical and electronic applications as insulators where advantage is taken of their very high resistives. For example;metal cables are coated in plastic to insulate them [47].

Polymers are much more easily be processable compared to metals. For example; using a spin-coated polymer solution, large surfaces can be covered easily.Most of the polymers can be deformed reversibly, hovewer, this is not the case for metals. Polymers can be shaped into complex multipolymers and all of these makes them to be perfect materials for novel applications and new products [48].

What is Conductivity?

Conductivity can be simply described by Ohm’s Law, whose formula is V=I.R, where V is the applied voltage, I is the current and R is the resistance.

All materials contain electrons and conductivity exactly depends on the number of electrons and their mobility. Metals are known as conducting materials and all the

outer electrons in a metal is accepted to be free to carry charge, as they can bump in to each other. In contrast to metals, insulators have tightly bound electrons, therefore no electron flow occurs so they offer high resistance to charge flow. Shortly, it can be said that free electrons must be in a material to make it conductive [49].

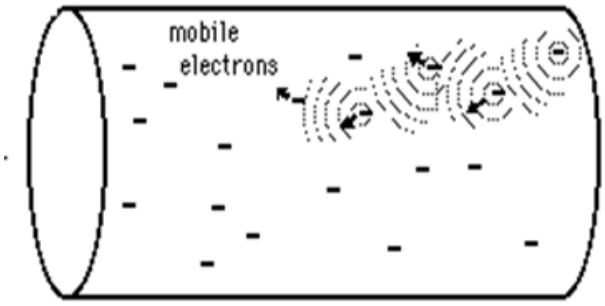


Figure 2.6: Mobile electrons in a metal [49].

In 1977, a polymer chemist, an inorganic chemist and a physicist namely Hideki Shirakawa, alan MacDiarmid and Alan Heeger admitted their new discovery 'polyacetylene' which is the simplest conducting polymer in the ChemComm paper. In 2000, the discovery of conducting polyacetylene was recognised by the award of the Chemistry Nobel Prize.After this discovery a new field' conducting materials' occured in the chemisty world that organic materials known as insulators can also behave as metal sor semiconductors [50] .

2.4.1 Electron conducting polymers

Conducting polymers can be classified in three groups:

1. Electron-conducting polymers
2. Proton-conducting polymers
3. Ion-conducting polymers

In order to become electrically conductive, a polymer's electrons need to be free to move and not bound to the atoms [51,52]. There are two conditions to be electrically conductive:

First Condition: The polymer itself can comprise of alternating single and double bonds called conjugated double bonds. Every bond contains a localised sigma bond which forms a strong chemical bond. Beyond this, every double bond contains pi bond and this bond is less strongly localised compared to the sigma bonds [53].

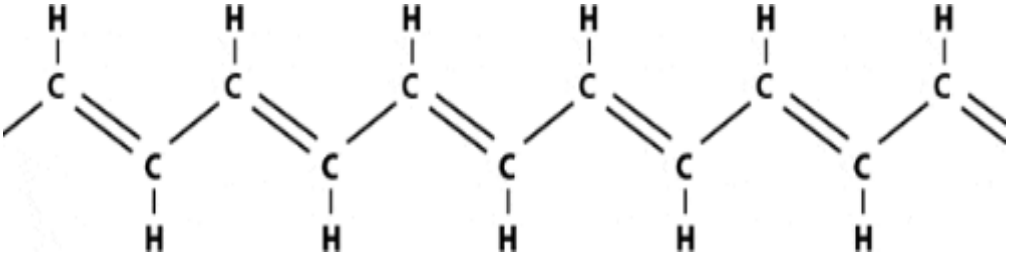


Figure 2.7: Single and double bonds [53].

Second Condition: By extracting electrons from the material(oxidation) or by incorporating them to the material (reduction) conductivity can be obtained. This process is called as Doping [53].

There are two types of doping process:

1. p-doping (oxidation with halojen)

$$(CH_n) + \frac{3x}{2} I \rightarrow (CH_n)^{+} + I_3^{-}$$

2. n-doping (reduction with alkali metal)

$$(CH_n) + xNa \rightarrow (CH_n)^{x-} + xNa^{+}$$

As mentioned above, after the discovery of polyacetylene (first conducting polymer) in 1977, the term conducting polymers have received expressive attention from the scientist and studies on conducting polymers obtained incredible acceleration [54].

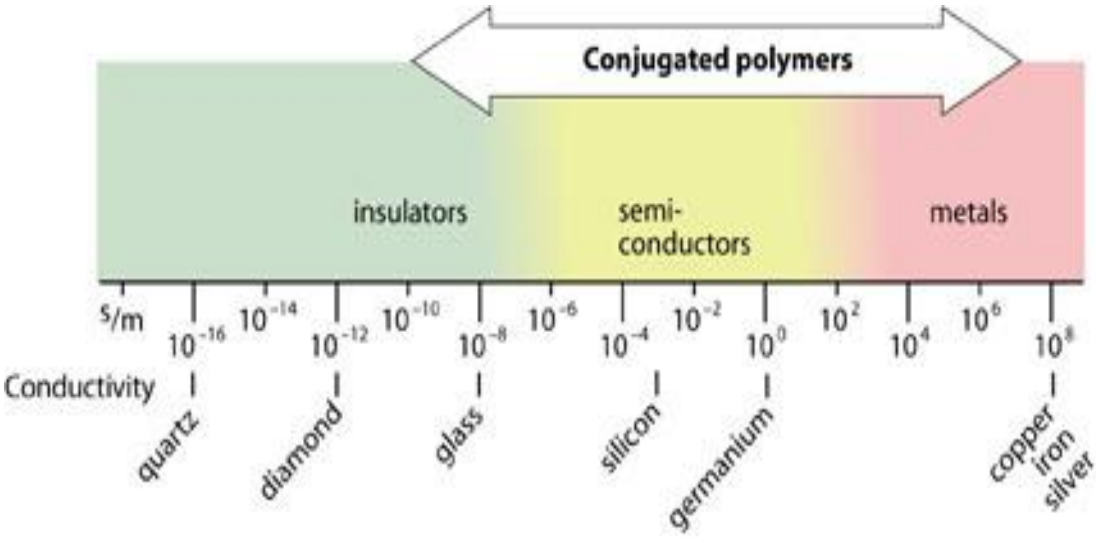


Figure 2.8: Conductivity level of conjugated polymers [53].

Polyacetylene, poly(p-phenylene), polypyrrole, polythiophene, polyaniline and their derivatives are the examples of conjugated conducting polymers.

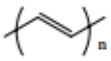
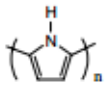
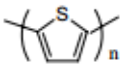
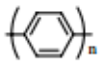
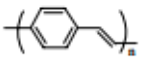
Polymer (date conductivity discovered)	Structure	d-d* gap (eV)	Conductivity# (S/cm)
I. Polyacetylene and analogues			
Polyacetylene (1977)		1.5	$10^3 - 1.7\times10^5$
Polypyrrole (1979)		3.1	$10^2 - 7.5\times10^3$
Polythiophene (1981)		2.0	$10 - 10^3$
II. Polyphenylene and analogues			
Poly(paraphenylene) (1979)		3.0	$10^2 - 10^3$
Poly(p-phenylene vinylene) (1979)		2.5	$3 - 5\times10^3$
Polyaniline (1980)		3.2	30 – 200

Figure 2.9: Some electron conducting polymers with their structure [53].

2.4.1.1 Polythiophene and its derivatives

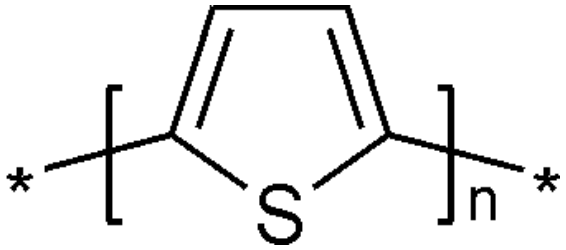


Figure 2.10: Repeating unit of thiophene [53].

Studies on polythiophene and its derivatives have come out over the last three decades. As seen from the Figure 2.10 it has aromatic structure with five membered rings. Polythiophene has rigid backbone therefore like many other linear polyaromatic structures it is insoluble in organic solvents. It has good thermal and chemical stability.In order to make the polymer soluble it is necessary to exchanging in the 3 and/or 4 position. It has been said that with the substitution in the 3 position, lots of different regioisomers can be obtained. The regioisomers can be classified in three groups as, head-to head, tail-to-tail, and random configurations. Regioregularity is a siginificant case that all changes the polymer chemistry and exist even in polystrene and poly(methyl methacrylate) which are simple linear polymers [53].

Polythiophenes retain their electroactivity upon ring substitution unlike the majority of conjugated polymers. They display very interesting optical properties like strong electroluminescence in the undoped state. If polythiophene structurally defined it can be evaluated that the less degree of crosslinking the more charge-transport [55].

Studies on regioregular polythiophenes show that inceasing stereoregularity also incerases the crystallinity.For regiorandom polymers conductivity and optical nonlinearities has been determined to be in the range of 7-9 [53].

In addition to the structure of polythiophenes, it should be said that there is an interesting case with the substitiuted polythiophenes, which is the temperature dependence of the UV absorption. If the temperature increases, it leads the ƛmax to alter to the shorter wavelengths. Depending upon the solvent and the temperature two distinct structures can be obtained. The first is the coplanar structure in an aggregated from at low temperatures and a disordered non-planar structure at a high temperature [53].

In 1980 s PEDOT which is a derivative of polythiophene has been popular with its applications. Since PEDOT exhibits high conductivity,lower oxidation potential when compared with polythiophenes, high stability at the doped state, low band gap, it is preferred for many applications.Not only PEDOT but also other polythiophene derivatives with their nanofiber and nanocomposite from are considerably chosen for the application of organic electronics due to the high surface area. For instance; El-Aufy, studied PEDOT/PSS nanofibers and nanocomposites using PAN as a spinnable carrier for PEDOT/PSS [56, 57].

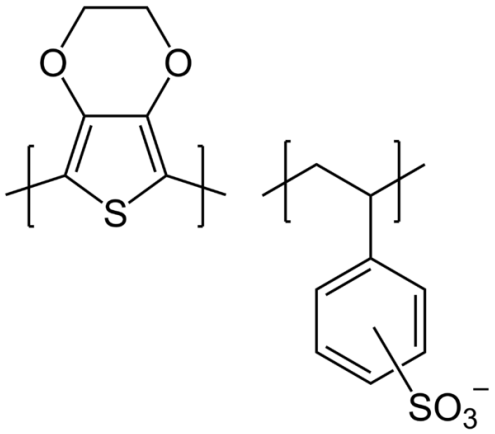


Figure 2.11: Image of PEDOT/PSS [56].

Single walled carbon nanotubes (SWCNTs) can also be successfully integrated into PEDOT/PAN blend and electrospun together in the aim of developing functions of electrospun yarn produced without SWCNT. PEDOT/PAN nanofibres can be used as an attractive material for wearable electronics [48].

Ngyven et al. used PVP as a polymer matrix in order to prepare electrically conductive PEDOT nanofiber [48].

By utilizing one pair of the PEDOT nonwoven web an electrochemical capacitor was designed and electrochemical behaviour of the capacitor was observed and it was concluded that PEDOT nonwoven web is an appropriate material for producing electrochemical capacitors [58].

Bianco et al. produced pure poly-3-dodecylthiophene (P3DDT) nanofibers and poly-3-dodecylthiophene (P3DDT) /PEO composite nanofibers via electrospinning [48, 59].

Poly(3-hexylthiophene) is a polymer generally used in organic electronics specifically in photovoltaic devices. It can be used for for the production of photovoltaic devices both in pure and association with PEO.Uniform regioregular poly(3-hexylthiophene) nanofibers and their composites with PCL was also studied by Lee. Furthermore, using PMMA as a core and poly(3-hexylthiophene) as a shell electropsun sensory fibers were produced by Kuo and coworkers [60,61].

Besides these usages of thiophene derivatives thiophene itself is suggested for preparing conducting thin films with controlled film thickness. To cite an example in 1987 Heeger's team had made the first attempt into device applications with making a diode by cating a polythiophene film from solution onto electrodes [50,62] .

2.4.2 Some special features of conducting polymers

2.4.2.1 Molecularity and disorder

Electrically conducting polymers don't have long range order as in inorganic semiconductors instead they are molecular in character. Electronic motion is created by the molecular character of polymers in one-dimensional along the macromolecules. Fermi surface instabilities which ocur in one and two dimensional systems affect the electronic properties of a polymeric material even if it is perfectly crystalline solid.

Bakhshi and Bhalla said that ' The occurence of disorder in polymers leads to the concept that even the intrinsic electronic states in these materials may be localized'. As the dimensionality of the system is reduced, the consequences of disorder are boosted [53].

2.4.2.2 Nature of doping process

The nature of doping processes exhibits some difference between the polymers and inorganic semiconductors. For the organic conjugated polymers, the doping process is a charge transfer reaction where for inorganic semiconductors it is not a charge transfer reaction instead the doping brings electron-rich or electron-deficient sites.

Figure 2.12: Oxidation (p-doping) process [53].

Figure 2.13: Reduction(n-doping) process [53].

X=I_2,Br_2,AsF_5,..., M=Na, Li,…

The reaction shown above is generally exist in polymers which are unsaturated with π electrons since they can be easily removed or added to the polymeric chains to form polyions.

2.4.2.3 Solitons, polarons and bipolarons as charge carriers

By the discovery of polyacetylene (PA) and polyparaphylene (PPP) it has been proved that the conductivity was obtained with the formation of self-localized excitations whose names are solitons, polarons and bipolarons.

Solitons, polarons and bipolarons are the quasi-one-dimensional particles arises from a strong interaction between the charge on the chain and the molecular structure.When quasi-particles namely solitons, polarons and bipolarons can move freely throught the material, charge carrying species in doped organic conjugated polymers are not free electrons or holes.Bakhshi and Bhalla mentioned that ‘ In polymers with degenerate ground state such as, trans-polyacetylene, charged solitons are the charge carriers, whereas in polymers with non-degenerate ground state such as cis-polyacetylene, polypyrrole,polythiophene or poly(p-phenylene), initially polarons are formed on doping’. After that these polarons come together to generate bipolarons acting as the charge carriers. Because of the Coulomb repulsion between two similar charges, the formation of one bipolaron is thermodynamically more stable than two seperated polarons [53].

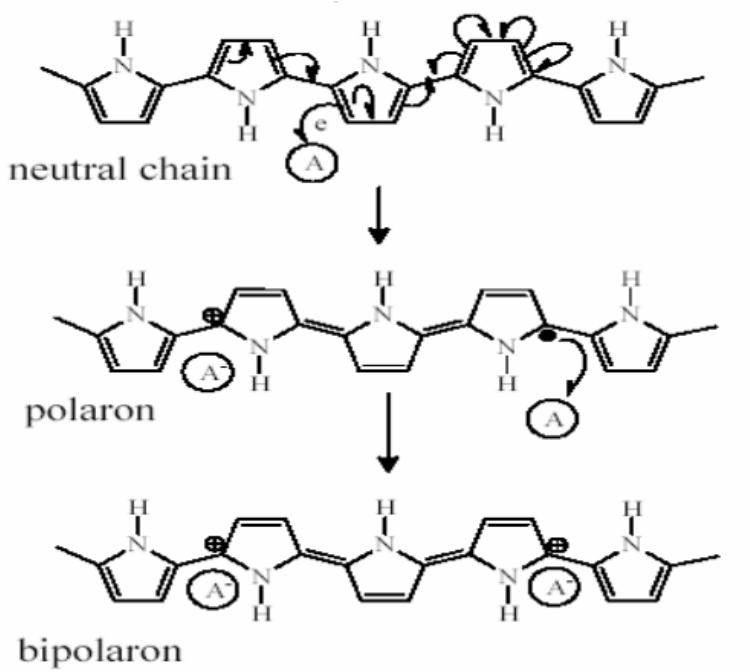


Figure 2.14: Polaron and bipolaron states for polypyrrole.

2.4.3 Applications of conducting polymers

The discovery of electrically conducting polymers has brought a new perspective and so many different applications. Light weight and rechargeable batteries, solid state batteries, electromagnetic shielding, molecular electronics, chemical, biochemical and thermal sensors, electromechanical actuators, welding plastics, light emitting diodes (LED) are the major applications based on conducting polymers [63-68].

For the polymers which have both p and n doping, they can be used as both positive and negative electrodes in the same battery system.To give an example polypyrrole-lithium cell operates by the oxidation and reduction of the polymer backbone. In these batteries lithium ions are collected on the lithium surface, and simultaneously oxidizes anions balances the created charge. At the time of discharging, electrons are removed from the lithium, thus lithium ions remigrate the electrolyte [69,70].

Of course, polymer electrodes have some advantages over conventional ones.For example;their shelf-life is longer, they do not have any toxic materials, thus dilemmas are diminished. They could be used to produce an electric car depending

on the unique properties. The last one is that they can be combined with solar cells and used as a power source [71].

Solid state batteries generated from conducting polymers have reliability and high durability. They may also supply plasticity. For example polypyrrole/ polyimide conducting composite is experienced for the application as a solid polymer electrolyte for lithium ion batteries [53].

Conducting polymers can show good properties about electromagnetic shielding depending on the dissipative abilities. The radiation can be eliminated by coating the plastic case with a conductive surface [53].

2.5 Core-shell polymer nanocomposites

Scientists studied with bulk materials until they discovered single nanoparticles. After this discovery, they started to make experiments on single nanoparticles since their better properties. This situation ended in the late 1980s with the discovery of heterogeneous, composite or sandwich colloidal semiconductor particles. Because they supply some better and new properties compared to single nanoparticles. Moreover,in the early stage of 1990s researchers produced concentric multilayer semiconductor nanoparticles in order to develop the properties of semiconductor materials. Accordingly the perception of ‘core-shell’occured. The core-shell nanostructures become an important research area since their advantages and a broad applications as biological, electronical and industrial [72].

2.5.1 Core-shell structure of polymer nanocomposites

The core-shell structure can be defined as two layer, the core meaning inner part of the material and the shell meaning outer part of the material.

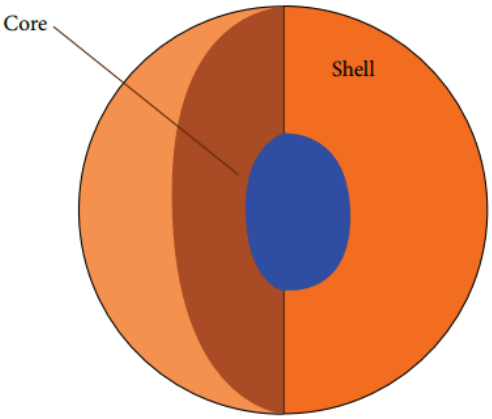


Figure 2.15: Core-shell structure [72].

The size and the shape of the core-shell nanocomposites can differ in the meaning of thickness and surface morphology [72,73].

The shapes can be spherical, centric, eccentric, star-like or tubular.

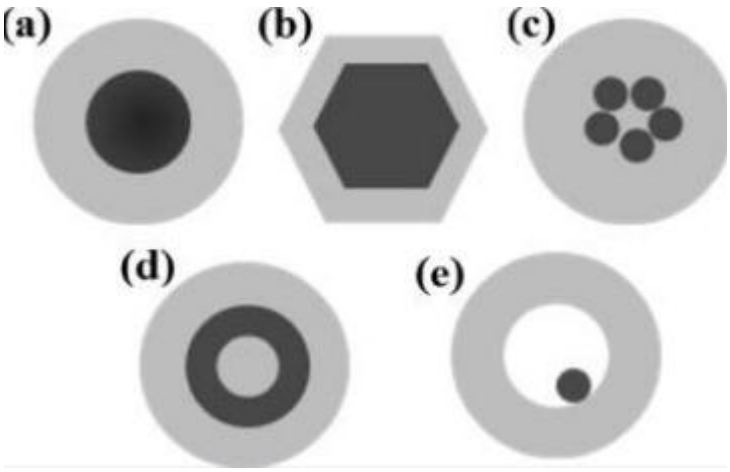


Figure 2.16: Different core-shell nanoparticle shapes: (a) spherical; (b) hexagonal; (c) multiple small core materials coated by single shell materials; (d) nanomatryushka material; (e) movable core within hollow shell [72].

It can be said that concentric spherical core-shell nanoparticles are the most common one. In this shape a spherical core particle is completely coated by a shell of a different material.

The types of core-shell structures can be classified into six categories [72].

1. Metal core and different metal shell

2. Metal core and nonmetal shell

3. Metal core and polymer shell

4. Nonmetal core and nonmetal shell

5. Polymer core and nonmetal shell

6. Polymer core and polymer shell where two polymers are different

Hydrothermal synthesis, solvothermal synthesis, sol-gel method, emulsion polymerization, microemulsion polymerization are the synthesis methods used to produce core-shell structures [13,72,73]

Paria emphasized that there are two approaches depending on the obtention of the core particles. In the first one, the core particles are seperately synthesized, purified and dried. After that surface modification is applied for coating the shell material in the reaction mixture. In the second one, firstly the core particles are sythesized using suitable reactants in the presence of inhibitor and then more reactants are added to form the shell particle *in situ*. However, in the second system there is a dilemma that some impurity from the reaction media may be trapped between the core and shell layer [73].

2.5.2 Use of core-shell polymer nanocomposites as conductive polymers

Polymer and semiconductor core-shell have attracted considerable interest with applications in various electronics including organic ligth emitting diodes (OLEDs), organic photovoltaics (OPVs), sensors etc [73].

The advantages of having a polymer coating on another polymer or conducting monomer is to modify the physical, mechanical and electrical properties. For instance; a high Tg core material has the impcat of improving the mechanical stability whereas a low Tg shell material improves the film-forming ability [74].

Conjugated polymers are often brittle in nature and therefore it is very difficult to make a film from them. Core-shell conductig composites have two advantages. Depending on the type of insulating polymer used as core, conducting polymer coated nanoparticles can show excellent mechanical properties and the amount of

conducting polymer used can be greatly reduced without much loss of conductivity [74].

Arman and Saraç studied on the core-shell structure of poly(acrylonitrile-co-vinylacetate)/ pyrrole and they showed that the high degree of homogeneity and molecular order induced by molecular dispersion of conjugated polymer on copolymer matrix can improve the transport properties and stability of conjugated polymers [75].

Palkovits and coworkers studied on the SiO_2/PMMA nanocomposites. Here the advantage of using silica is reducing the bulk conductivity and increasing the suspension stability of the core particles [76].

Crespilho et al. experimented core –shell structure Au as core and polypyrrole as shell in order to combine the properties of two different materials and enhancing the final properties of obtained material [77].

2.6 Electrospinning

As the science and technology developed, the term nanometer has come into prominence. Related to the nanometer scale, the term ‘nanofiber’ has gained a lot of attention. As the diameter of the fibers reduces from the micrometer to nanometer several advantages occur [78].

Nanofibers have high surface area to volume ratio, high tensile strength and stiffness and flexibility in surface functionalities. These excellent properties lead them to be used in many industrial applications [79].

In the past several processing techniques were used to obtain nanofibers. Drawing, template synthesis, phase seperation, self-assembly, electrospinning are the processes used [80,81,82].

In 1934, Formhals declared a series of patents describing the production of nanofibers via an electrostatic force. After these patents the electrospinning process became popular. By using the electrospinning process nanofibers of small pore size and high surface area can be obtained. The process is also advantageous in economical terms that it is low-cost. However, there are two disadvantages. One of

them is the repeatability, the process sometimes can be a big problem and the other one is beading [78].

Electrospinning process consists of basic experimental setup. A high voltage supplier, a needle, polymer solution and collector are the components of this setup [83,84].

A polymer solution is prepared and a high voltage is applied to this polymer solution and charges are generated in the solution. When the charges reaches to a critical amount, Taylor cone forms at the tip of the needle and a fluid jet will erupt from the droplet.The fluid jet moves toward to the collector which have lower potential and evaporates simultaneously [78,85,86].

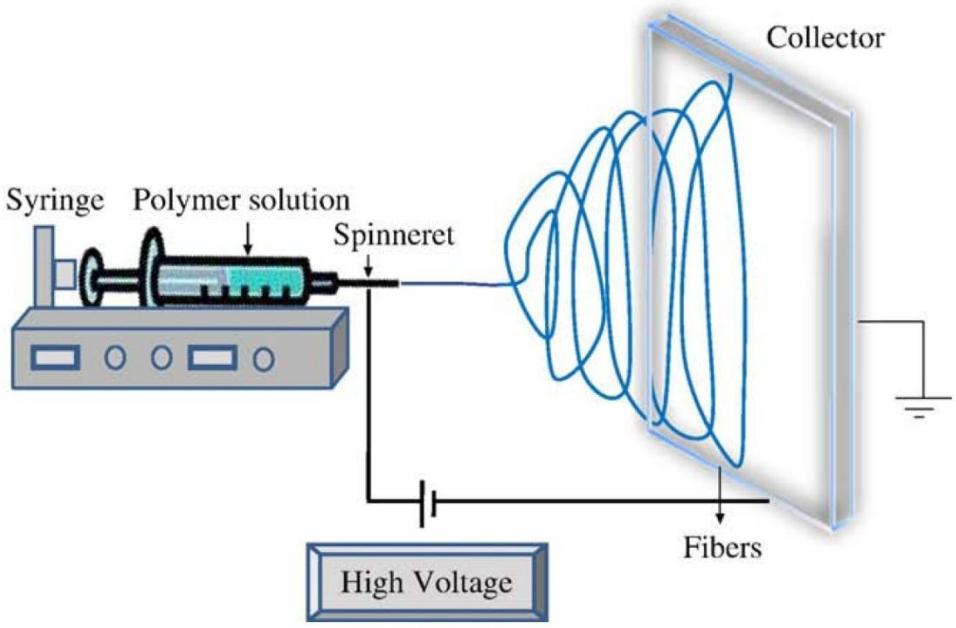


Figure 2.17: Experimental set-up of electrospinning

2.6.1 Electrospinning parameters

The factors that affecting the electrospinning process can be divided into three groups as polymer, solution and process parameters. These three groups can also be divided into several parameters. For instance; polymer parameters consist of molecular wieght, concentration, crosslinking, isomeric structure of the polymer. Solution parameters include the type of solvent, viscosity, electrical conductivity,

surface tension of the solution used in electrospinning. Process parameters covers the applied voltage, distance between the tip of the needle and the collector, flow rate, solvent evaporation rate, collection technique, relative humidity of the laboratuary and the temperature [87,88,89].

Concentration:

The concentration of the polymer used in electrospinning process plays very critical role in the formation of fibers.

When the concentration is very low, electrospray occurs instead of electrospinning, especially due to the high surface tensions of the solution. Generally micro particles are obtained in the case of low concentration. As the concentration is a little big higher fibers will be obtained with beads. When the concentration and also the viscosity is optimum, fibers with excellent diameter can be generated. If the concentration is too high, micro-ribbons can be obtained instead of nanofibers [90,91].

The fiber diameter increases with increasing the concentration of the solution.

Molecular Weight:

Molecular weigth affects the morphology of the resultant fibers and directly relates with the viscosity of the solution. If the concentration of the solution does not change, decreasing the molecular weight of the polymer results with beads, not fibers. At the same condition, by increasing the molecular weight of the polymer smooth fibers can be achieved. If molecular weight is increased too much, instead of fibers ribbons will be obtained [78].

Viscosity:

Viscosity of the solution, polymer concentration and molecular weight are all related to each other. At very low viscosity, smooth fibers cannot be produced. At very high viscosity, the solution will not be ejected from the tip of the needle. In order to obtain smooth fibers with finer diameters optimum viscosity should be used [78,92].

Surface Tension:

In the aim of producing smooth fibers, the surface tension of the solution should bereduced. By changing the mass ratio of the composition, the surface tension can be adjusted into a suitable value [78,92].

Voltage:

Among the other electrospinning parameters, it can be said that the voltage is the most important one. In the case of generating Taylor Cone, the applied voltage must be higher than the threshold voltage. There has been several studies on the relationship of the applied voltage and the fiber diameter. Some research groups defends that higher voltages causes the fiber diameter be bigger. However, some of them asserts that there is a linear relationship between the fiber diameter and the voltage. It can be concluded that the affect of the voltage on fiber diameter largely depends on the polymer worked and the process applied [78] .

Flow rate (Feed rate):

If the feed rate is very high, the time for the fiber in order to reach the collector can be short and this can result with the beaded fibers with higher diameters. Thus, generally lower flow rate are preferred to obtain smooth fibers with finer diameters [78].

Distance Between the Tip of the Needle and the Collector:

If the distance is very short, the fiber cannot solidify while approaching to the collector. If the distance is too long, beads or beaded fibers can be obtained. Like in the other parameters, optimum condition should be used for thinner and smoother fibers [78].

Relative Humidity and Temperature:

The humidity and the temperature are also effective parameters in the fiber formation. Low humidity can be advantageous in the meaning of the drying of the solvent. In the contrary, high humidity can cause charges and this can result in thick fiber diameter [78].

For the temperature, it should be recommended that with higher temperature thinner fiber diameter will be obtained. Mituppatham and coworkers studied on the polyamide-6 fiber and they evaluated that by increasing the temperature, the viscosity of the solution decreases that this gives thinner and smoother fibers [78].

2.6.2 Applications of electrospun nanofibers

The polymer nanofibers can be used in a wide range of applications. For example; they can be implemented in military protective clothing, nano-sensors such as thermal sensors, optical and biochemical sensors, wound dressing, drug delivery, tissue engineering and other biological applications, cosmetics, electromagnetic shielding, photovoltaic devices, micro/nano electronic devices, LCD devices, gas filtration, molecule or air filtration etc [93].

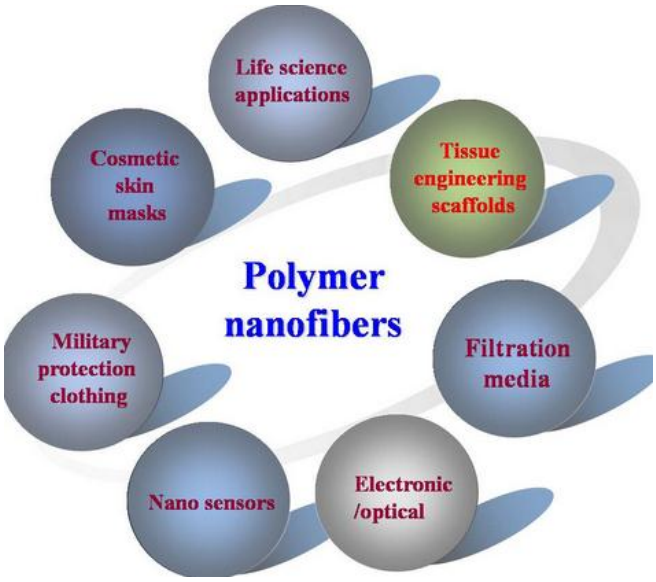


Figure 2.18: Application fields of polymer nanofibers

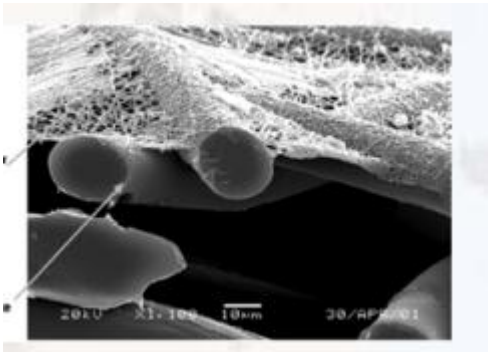


Figure 2.19: Filtration [94].

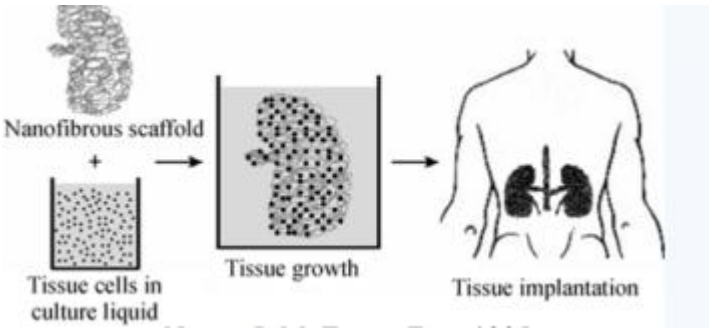


Figure 2.20: Tissue engineering [94].

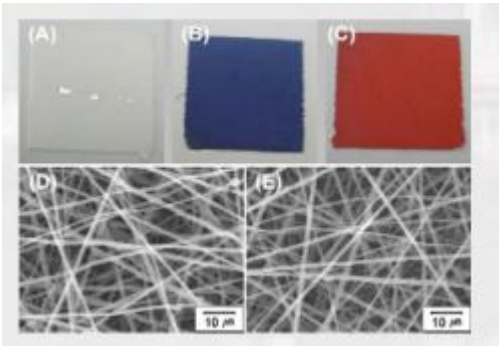


Figure 2.21: Gas sensors [94].

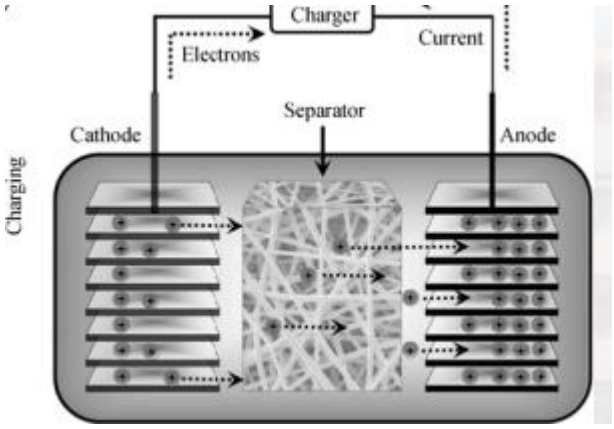


Figure 2.22: Energy storage [94].

3. EXPERIMENTAL PART

3.1 Materials

Acrylonitrile (> 99.5 %) was provided by the Aksa Acrylic Chemistry Company. Itaconic acid (> 99.5 %), 3,4 ethylenedioxythiophene (EDOT > 97 %), 3 methoxythiophene (> 98 %), sodium dodecyl benzene sulfonate (SDBS) and polyacrylonitrile (PAN) with average molecular weight 150,000 were purchased from Sigma Aldrich. Ammonium persulfate (APS), N,N dimethylformamide (DMF), ethanol were all Merck reagents. All these reagents were used without further purification.

3.2 Method

3.2.1 Copolymerization of acrylonitrile (AN) with itaconic acid (IA)

AN and IA were copolymerized by emulsion polymerization system using sodium dodecyl benzene sulfonate (SDBS) as a surfactant and ammonium persulfate (APS) as an initiator. During the polymerization, 0.1 mol monomer mixture in total was used and the feed ratio of AN to IA was selected as 99 % mol. 200 ml of polymerization medium was copolymerized in a three necked flask. In the first stage, the surfactant SDBS was dissolved in 150 ml pure water and stirred for 15 minutes. The ratio of surfactant to total momoner was experimented as 20 wt %. The monomers IA and AN were incorporated into the solution and stirred for approximately 30 minutes respectively. Until this process 5.3831 g monomer was consumed. In the second stage, the polymerization temperature was set at 70 ° C and the polymerization medium was heated to this temperature in the flask, while being stirred. A condenser was attached to this flask. When the temperature reached 70 ° C, the initiator APS, which had been dissolved in 10 ml. distilled water, was fed into the system. The ratio of APS to monomers in feed was 15 % wt. The reaction was continued for 3 hours and at the end of 3 hours, copolymerization was stopped by

closing the heater. Finally, poly (acrylonitrile-co-itaconic acid) milky-fluid latex was obtained.

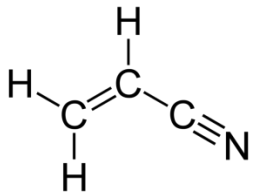


Figure 3.1: Chemical structure of acrylonitrile (AN)

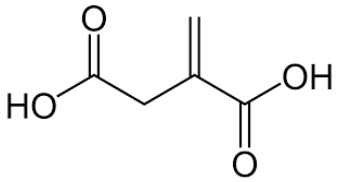


Figure 3.2: Chemical structure of itaconic acid (IA)

Figure 3.3: Experimental set-up of emulsion polymerization

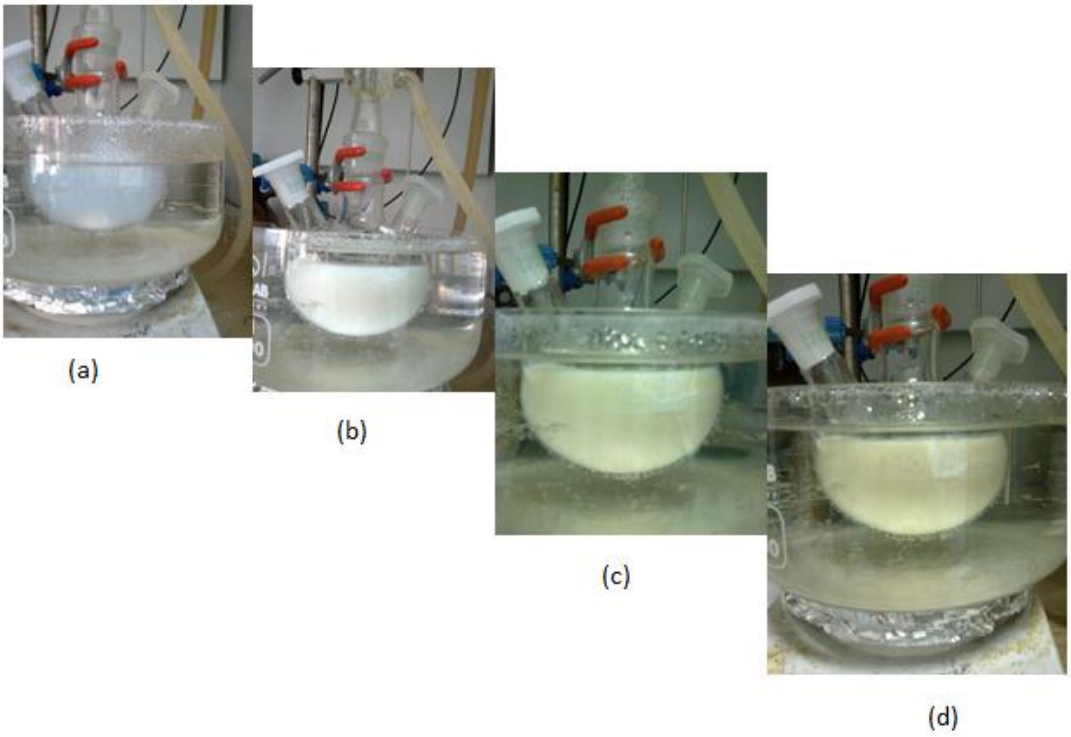


Figure 3.4: Copolymerization steps: (a) At the beginning of the copolymerization; (b) After 1 hour of the copolymerization; (c) After 2 hours of the copolymerization; (d) After 3 hours of the copolymerization

3.2.2 Producing core-shell structure of P(AN-co-IA) with EDOT and MOT

3,4 ethylenedioxythiophene (EDOT) and 3 methoxythiophene were used in order to produce core-shell structure. At the end of the copolymerization of poly (AN-co-IA), the temperature was turned off for cooling from 70 ° C to room temperature while the latex was being stirred continuously. Then the 200 ml synthesized copolymer solution was divided into 10 containers, each containing 20 ml of solution. With no initiator addition into the containers, EDOT and MOT were incorporated into the emulsion medium seperately and the reaction was maintained for 72 hours. Three different amounts of EDOT as 83.3, 125, 166.6 microliters and three different amounts of MOT as 77.6, 116.4 and 155.2 microliters were added into the containers.

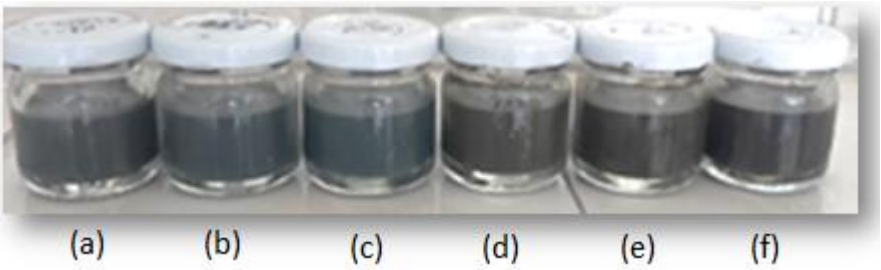


Figure 3.5: Copolymers of P(AN-co-IA)/ polythiophene composites: (a) P(AN-co-IA)/PEDOT with 83.3 µl; (b) P(AN-co-IA)/PEDOT with 125 µl; (c) P(AN-co-IA) /PEDOT with 166.6 µl; (d)P(AN-co-IA)/PMOT with 77.6 µl; (e) P(AN-co-IA) / PMOT with 116.4 µl; (f) P(AN-co-IA) / PMOT with 155.2 µl

3.2.3 Electrospinning of composite structures

In order to make nanofibers of produced composite structures, electrospinning method was used. During the electrospinning process, blends of composite structures with polyacrylonitrile (PAN) were used for tuning the viscosity of the electrospinning solutions due to the inadequacy of the viscosity of copolymer solutions.

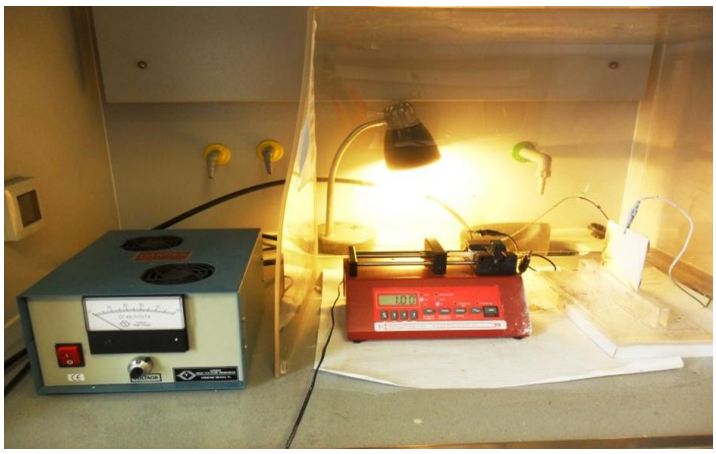


Figure 3.6: Electrospinning setup

The studied electrospinning parameters were mentioned below:

Voltage: 15 kV

Solution concentration: 5 % wt

Distance from tip to collector: 10 cm

Feed rate: 1.0 ml/h

In the blend, the ratio of the copolymer to PAN was 20 % in milliliters.

Table 3.1: EDOT consisting solutions used for electrospinning

Polymer	**Solvent**	**Solution Concentration (%wt)**	**Added EDOT Amount (µl)**
PAN	DMF	5	-
PAN/P(AN-co-IA)	DMF	5	-
PAN/P(AN-co-IA)PEDOT	DMF	5	83.3
PAN/P(AN-co-IA)PEDOT	DMF	5	125.0
PAN/P(AN-co-IA)PEDOT	DMF	5	166.6

Table 3.2: PMOT consisting solutions used for electrospinning

Polymer	Solvent	Solution Concentration (%wt)	Added 3methoxythiophene Amount (µl)
PAN	DMF	5	-
PAN/P(AN-co-IA)	DMF	5	-
PAN/P(AN-co-IA) PMOT	DMF	5	77.6
PAN/P(AN-co-IA) PMOT	DMF	5	116.4
PAN/P(AN-co-IA) PMOT	DMF	5	155.2

First of all, PAN solutions were stirred at 400 rpm for 2 hours and simultaneously solutions containing produced copolymers were stirred at 400 rpm for 2 hours. They are then blended and stirred again for 2 hours. The solutions were then loaded into a 2.5 ml syringe and pumped. The electrospinning device contains a syringe pump (NE-500 model, New Era Pump Systems Inc., USA) and DC power supplier (ES50 model, Gamma High Voltage Inc., USA).

3.2.4 Spin-coating for atomic force microscopy

In order to observe the morphology of the nanoparticles, spin-coating was applied. For this process, precipitated and dried nanoparticles were treated with N,N dimethylformamide (DMF) and the treated solution was dripped to pure glass and spin-coated for one minute. The concentration for spin-coating was selected as 5 wt %.

3.3 Characterization

Characterization process can be examined in two stages. First is the nanoparticle characterization and second is the nanofiber characterization.

3.3.1 Nanoparticle characterization

The latex obtained from emulsion polymerization and the solutions comprising EDOT and MOT were diluted to the optimum value and the absorbance fluctuation results were tested with UV-Visible Spectrometer (Perkin Elmer, Lambda 45).

The solutions were precipitated with ethanol, washed with ethanol and water for five times. Then, they were dried under vacuum oven at 60^0C approximately for 18 hours. The FTIR-ATR analysis of precipitated and dried copolymers were carried out FTIR-ATR reflectance spectrophotometer (Perkin Elmer, Spectrum One, with a universal ATR attachment with a diamond and ZnSe crystal).

The precipitated and dried nanoparticles were examined by Scanning Electron Microscope (FEI Quanta FEC 250).

The dry copolymers were then dissolved in N,N dimethylformamide solvent and surface morphology of the dissolved polymers were observed by Atomic Force Microscopy (AFM, Nanosurf Easy Scan 2).

3.3.2 Nanofiber characterization

The polymer solutions were blended with polyacrylonitrile (PAN) solution in order to obtain nanofibers. For this reason electrospinning set-up (NE-500 Model, New Era Pump System Inc., USA) and DC power supplier (ES 50 Model, Gamma High Voltage Inc., USA) was used.

In order to determine the viscosity of the solutions ‘And Vibro Viscometer SV-10’ was used. The measurements were carried out in the range of 0.3-10000 mPa.s.

Scanning Electron Microscope (SEM) and Energy Dispersive Spectroscopy (EDS) images of nanofibers were completed with FEI Quanta FEC 250 instrument.

Electrochemical measurements (EIS measurements) were performed with a Princeton Applied Research (PAR) Parstat 2263 potentiostat. The impedance measurements were fullfilled by scanning in the frequency range 10 mHz-100 kHz with applied AC signal amplitude of 10 mV using Power Sine.

4. RESULTS AND DISCUSSION

4.1 Nanoparticle characterization

4.1.1 SEM analysis of nanoparticles

The precipitated, washed and dried nanoparticles were characterized morphologically by Scanning Electron Microscope (FEI Quanta FEC 250). Before the measurement, the samples were coated with gold (Ion Sputter Metal Coating Device, Quorum).

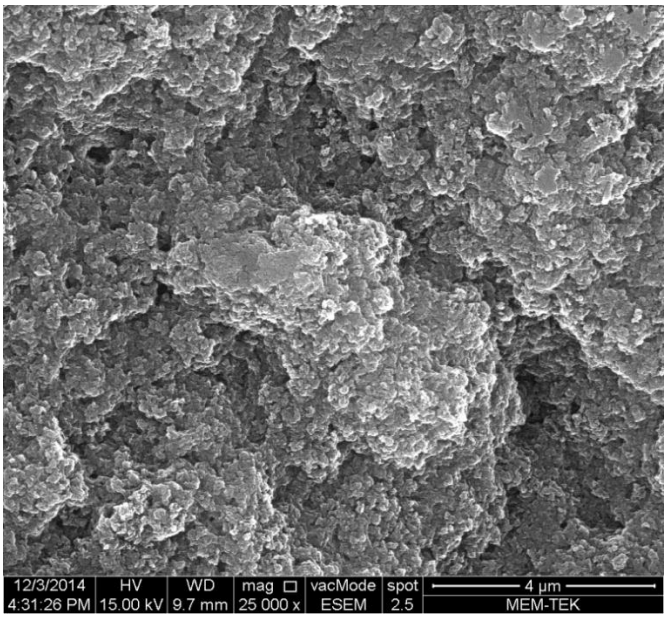


Figure 4.1: SEM image of P(AN-co-IA) nanoparticles.

Figure 4.1 shows the SEM image of matrix polymer, P(AN-co-IA). It mentiones that there are plates in the structure of copolymer and the surface is not so rough. Nanoparticles can be clearly seen in the figure.

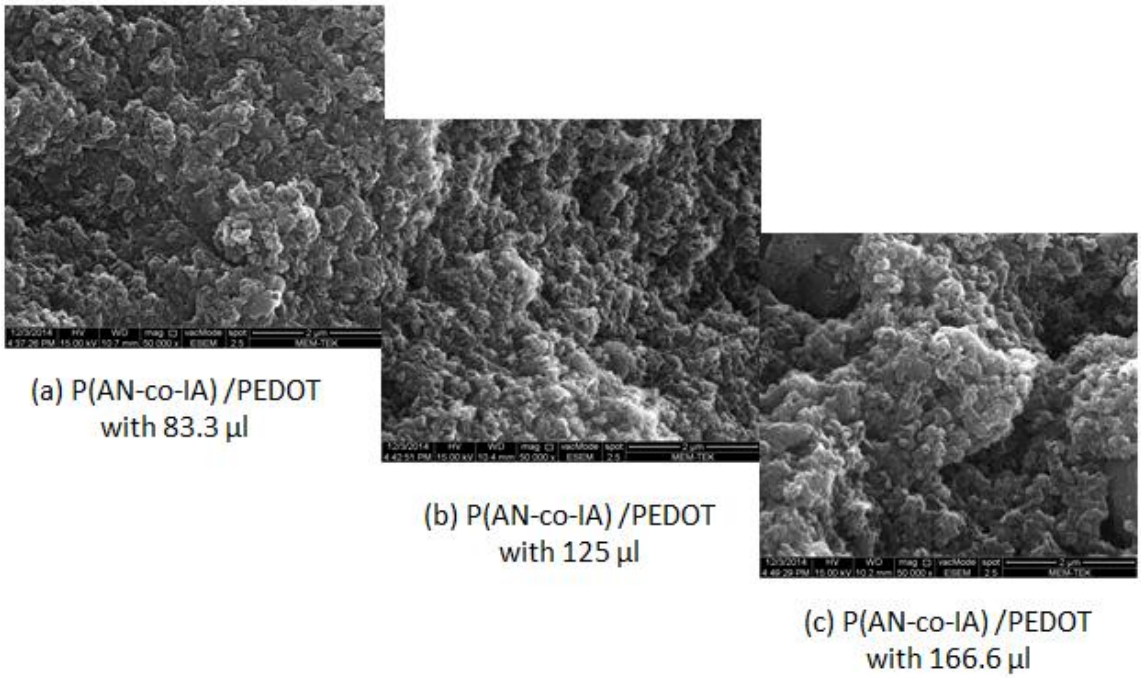


Figure 4.2: The SEM images of (a) P(AN-co-IA)/PEDOT with 83.3 µl; (b) P(AN-co-IA)/PEDOT with 125 µl; (c)) P(AN-co-IA)/PEDOT with 166.6 µl

From the Figure 4.2 it can be clearly seen that the porosity of the structures are different from the structures in the Figure 4.1. The porosity of the structures are obviously higher when compared to the matrix polymer and this situation mainly depends on the electroactive polymers exist in the copolymer. In the literature the strutures are defined as cauliflower.

Above, it was said that the structures change when electroactive polymers are incorporated into the matrix polymer. Therefore, it can be mentioned that core-shell structure was obtained as expected. The nanoparticles are embedded into the matrix polymer and forms two polymers in one composition.

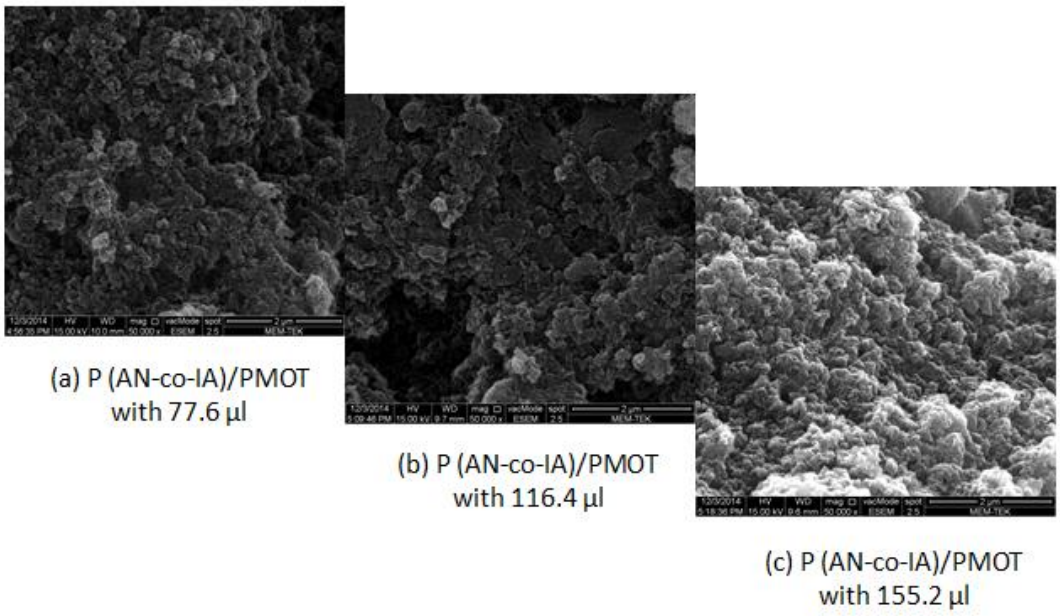


Figure 4.3: The SEM images of (a) P(AN-co-IA)/PMOT with 77.6 µl; (b) P(AN-co-IA)/PMOT with 116.4 µl; (c) P(AN-co-IA)/ PMOT with 155.2 µl

As in the Figure 4.2, Figure 4.3 also shows porous structures belonging to P(AN-co-IA)/PMOT. In addition, roughness of the surfaces incerases with the increasing amounts of electroactive monomer 3 methoxythiophene. Again core-shell structure can be seen due to the difference between SEM images of P(AN-co-IA) and P(AN-co-IA)/ PMOT. The cauliflower image can be seen clearly, as in the Figure 4.2.

4.1.2 UV-visible spectroscopy

The UV-Visible spectroscopy characterization was performed bu using the Perkin Elmer, Lambda 45 UV-Vis. spectrometer. The emulsion latexes were diluted with pure water and after calibration of the spectrometer with distilled water, the measurements were taken.

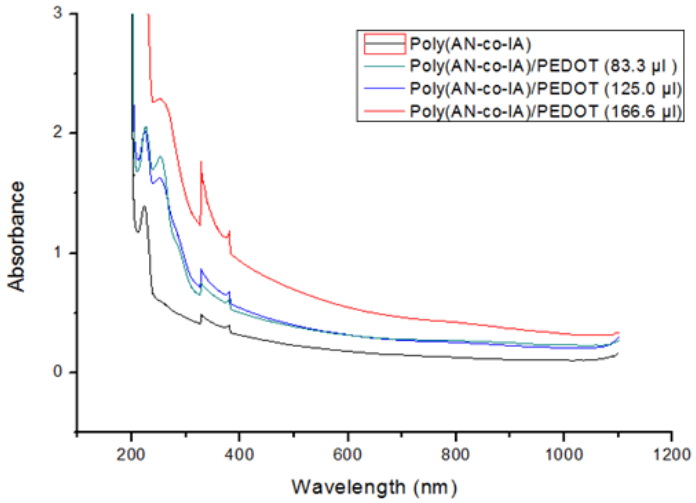


Figure 4.4: The UV-Visible spectrum of P(AN-co-IA) and increasing amounts of P(AN-co-IA)/PEDOT

The UV-Visible spectroscopy results show the absorbance increase with the relation of increase in added comonomer amounts. Figure 4.4 shows the absorbance values of P (AN-co-IA) and increasing amounts of P (AN-co-IA) /PEDOT in the range from 190 nm to 1100 nm.

In order to examine detailly, the graph can be divided into two parts as UV region (between 190 and 380 nm) and visible region (between 380 nm to 900 nm).

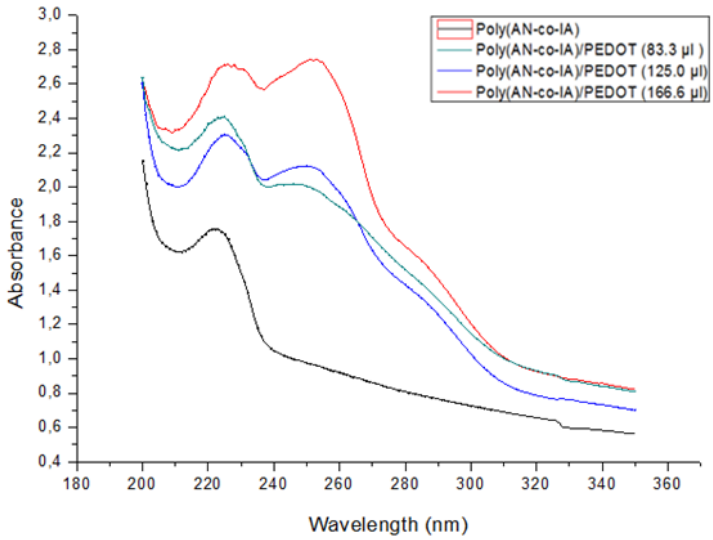


Figure 4.5: UV spectrum of P(AN-co-IA) and increasing amounts of P(AN-co-IA)/PEDOT

In the Figure 4.5 it can be clearly seen that near 250 nm there is a peak coming from the polymer PEDOT. For 3 different amounts of PEDOT addition, a broad peak was observed between the values 1,8 and 2,8.

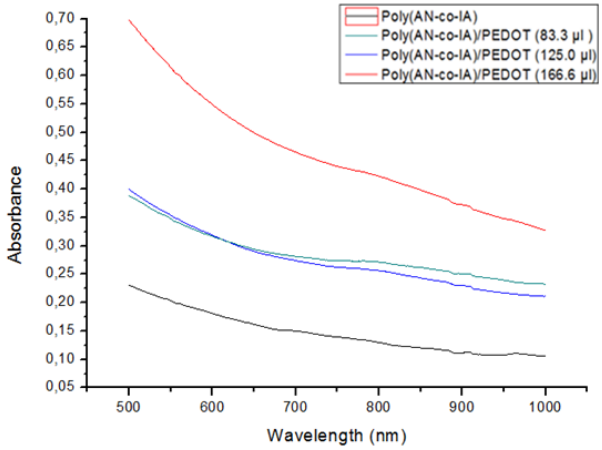


Figure 4.6: Visible spectrum of P(AN-co-IA) and increasing amounts of P(AN-co-IA)/PEDOT

For the visible spectrum, 380- 900 nm wavelength is observed. In Figure 4.6 the arising peaks related to the PEDOT addition are seen at 800 nm. The broadening of the copolymers can also be seen clearly.

Below, Figure 4.7 shows the absorbance values of the copolymers P(AN-co-IA) and P(AN-co-IA) / PMOT with three different amounts versus wavelength in the range of 190-1100 nm. As seen in the Figure 4.8 and Figure 4.9 the UV-Visible spectrum is divided into two parts as UV spectrum and visible spectrum.

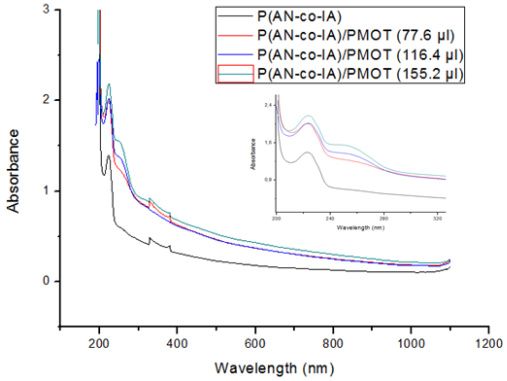


Figure 4.7: The UV-Visible spectrum of P(AN-co-IA) and increasing amounts o P(AN-co-IA)/PMOT with UV spectrum of the graph

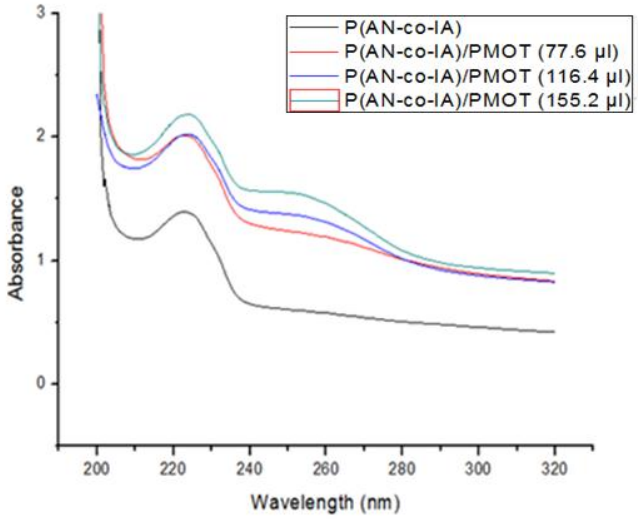


Figure 4.8: UV spectrum of P(AN-co-IA) and increasing amounts of P(AN-co-IA)/PMOT

As seen in Figure 4.8, in the UV region, approximately at 255 nm there is a clear peak, which cannot be seen for P(AN-co-IA), belonging to the polymer P(AN-co-IA) /PMOT and broadening band was seen with the increase in the amount of 3 methoxythiophene.

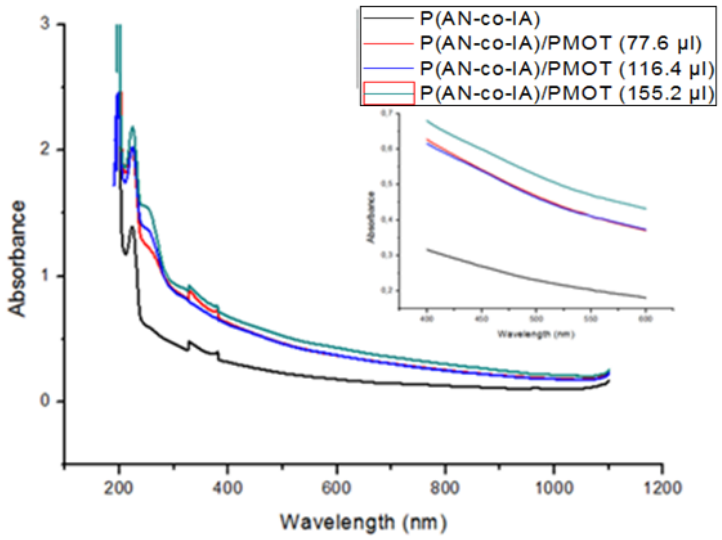


Figure 4.9: The UV-Visible spectrum of P(AN-co-IA) and increasing amounts of P(AN-co-IA)/PMOT with visible spectrum of the graph

Figure 4.9 shows the UV-Visible spectrum of P(AN-co-IA) and P(AN-co-IA)/PMOT with three different amounts. As seen in the figure, the absorbance values are different for the copolymers.

To sum up, considering the UV-Visible spectrum results of copolymers, it can be said that the copolymerization of P(AN-co-IA) with thiophene derivatives is successfully achieved. Having different absorbance values for the copolymers proves that the amounts of the EDOT and 3 methoxythiophene fed during the polymerization increases for each polymerization.

4.1.3 FTIR-ATR spectroscopy

Figure 4.10 shows the FTIR-ATR spectroscopy results belonging to the matrix polymer, P(AN-co-IA) and P(AN-co-IA)/PEDOT composites.

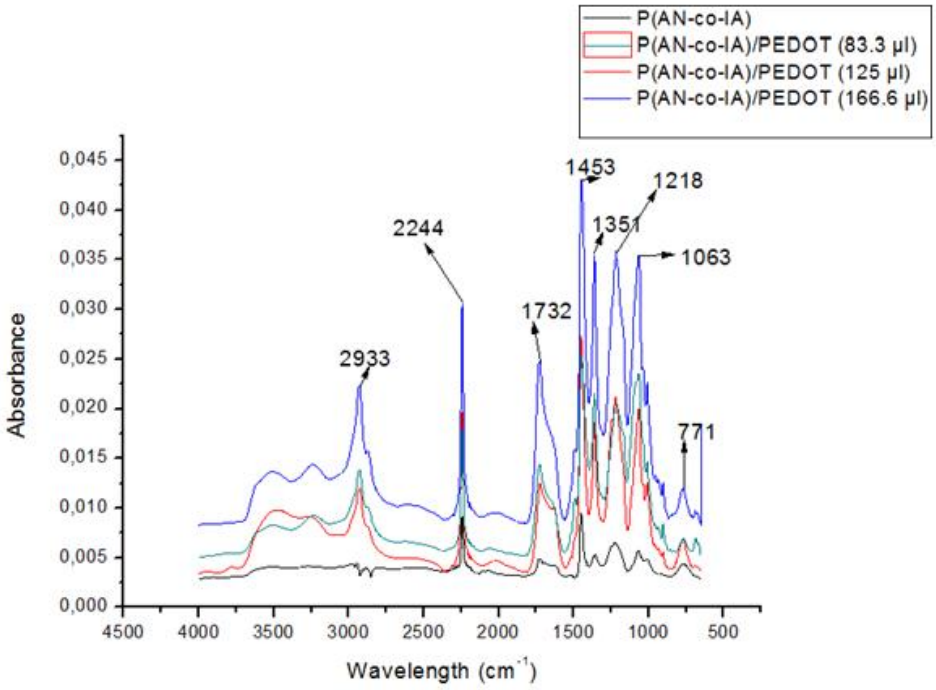


Figure 4.10: FTIR-ATR spectroscopy of P(AN-co-IA) and P(AN-co-IA) composites

The peak 2244 cm^{-1} belongs to the C≡N stretching, 2933 cm^{-1} aliphatic CH_2 strecthing, 1732 cm^{-1} carbonyl stretching vibration of the carboxylic acid,1453 cm^{-1} bending vibration of –CH, 1218, 1063, 1008 and 771 cm^{-1} ehytlenedioxy ring from the C-S bond.

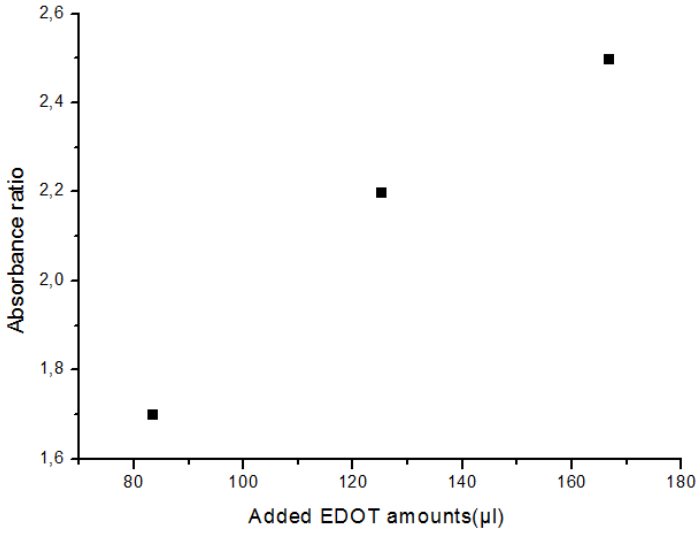


Figure 4.11: The absorbance ratio of (2244/2933) peaks

Figure 4.11 belongs to the absorbance value ratio of C≡N stretching and aliphatic CH_2 stretching. The absorbance ratio increases as in the increase of added EDOT amounts (µl) in polymerization step.

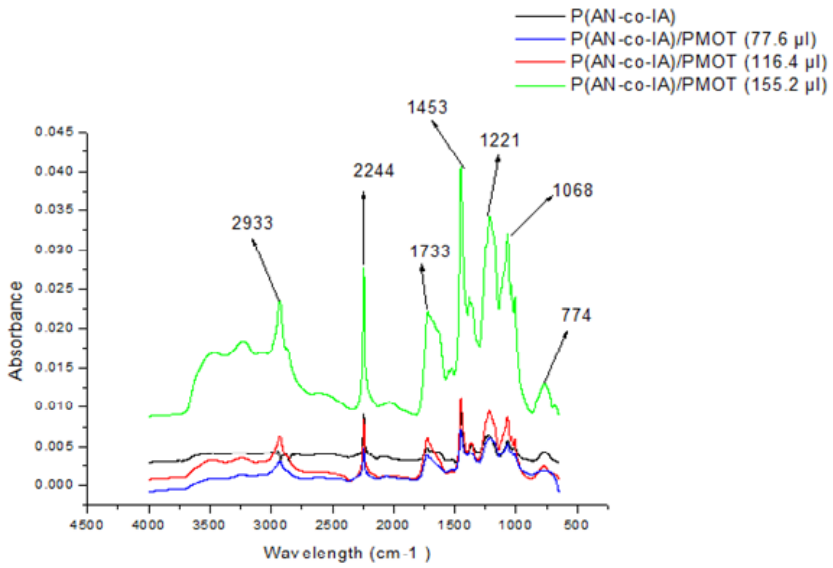


Figure 4.12: FTIR-ATR Spectroscopy of P(AN-co-IA) and P(AN-co-IA)/PMOT composites

Figure 4.12 shows the FTIR-ATR spectroscopy results belonging to the matrix polymer, P(AN-co-IA) and P(AN-co-IA)/PMOT composites.

The peak 2933 cm^{-1} relates to the aliphatic CH_2 strecthing, 2244 cm^{-1} C≡N stretching, 1733 cm^{-1} carbonyl stretching vibration of the carboxylic acid, 1453 cm^{-1}

bending vibration of –CH, 1221 cm^{-1} PMOT stretching vibration of C-C bond, 1068, 774 cm^{-1} α-α coupling in PMOT.

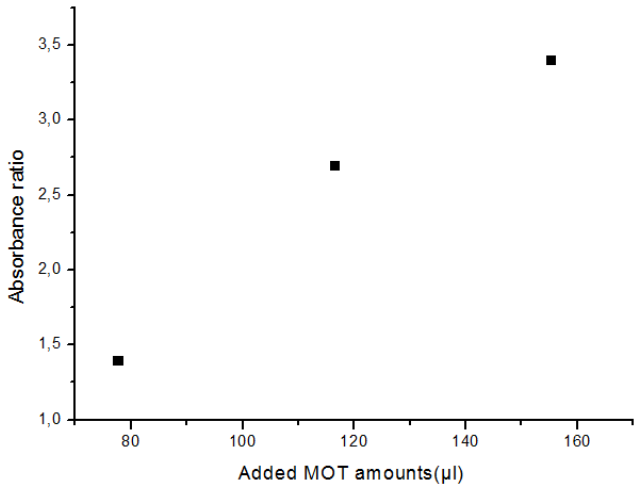


Figure 4.13: The absorbance ratio of (2244/2933) peaks

Figure 4.13 belongs to the absorbance value ratio of C≡N stretching and aliphatic CH_2 stretching. The absorbance ratio increases as in the increase of added MOT amounts (µl) in polymerization step.

4.1.4 Atomic force microscopy (AFM)

Atomic Force Microscopy (AFM), uses a tip to evaluate the surface features by scanning the sample and gives information about the surface morphology.

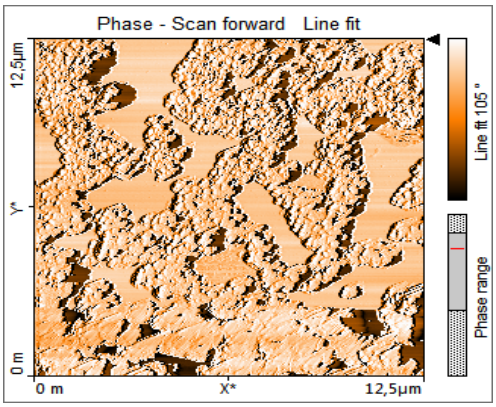


Figure 4.14: AFM image of smooth glass

Figure 4.14 belongs to the AFM image of smooth glass. Surface roughness value of the smooth glass is 6.05 nm.

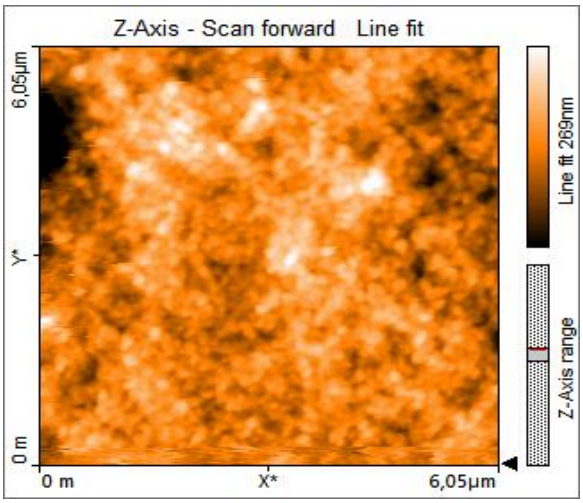


Figure 4.15: AFM image of P(AN-co-IA)

Figure 4.15 shows the AFM image of P(AN-co-IA) film, which was spin-coated onto the smooth glass. Surface roughness value of the P(AN-co-IA) film is 15.58 nm,that is higher than the surface roughness value of smooth glass. When the film is examined in detail, it can be seen that approximately 100 nm particles exist and they are homogeneously distributed over the film.

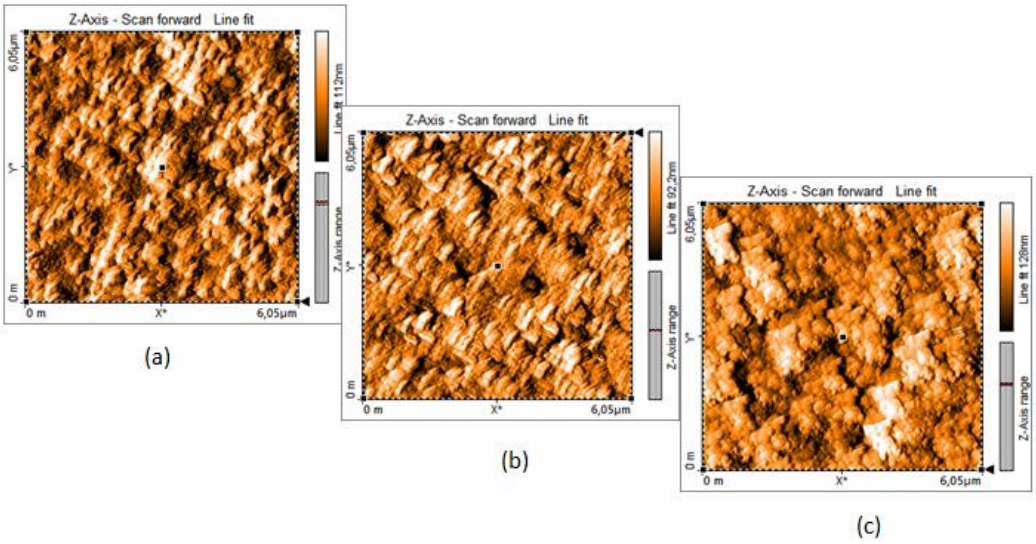


Figure 4.16: AFM images of (a)P(AN-co-IA) /PEDOT with 83.3 µl; (b) P(AN- co-IA)/PEDOT with 125 µl; (c)P(AN-co-IA)/PEDOT with 166.6 µl

As mentioned in the Figure 4.16, the AFM images reveal that there are some particles in the solution prepared for spin coating and the particles' size increases with the increasing EDOT amounts added during the polymerization. In addition the

surface roughness values increases respectively as 15.58,16.08,17.39 nm for P(AN-co-IA) /PEDOT with 83.3 µl, P(AN- co-IA)/PEDOT with 125 µl, P(AN-co-IA)/PEDOT with 166.6 µl.

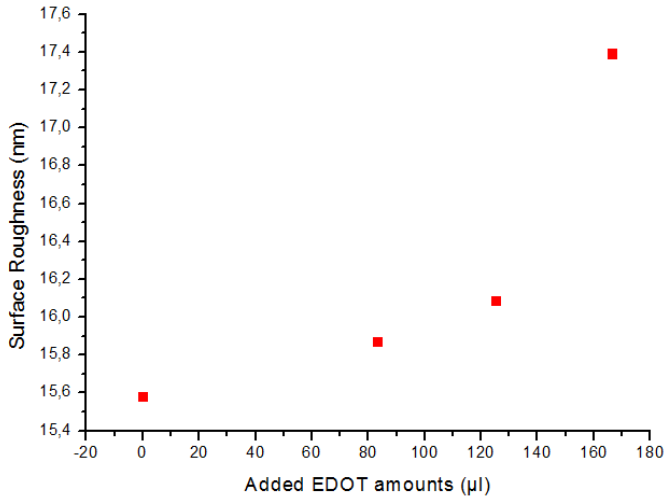


Figure 4.17: The relationship between added EDOT amounts and surface roughness of the films

Figure 4.17 demonstrates the relationship between the added EDOT amounts (in µl)and surface roughness of the films. It can be clearly seen that as the amount of EDOT (in µl) increases the surface roughness also increases from the value of 15.87 to 17.39 nm.

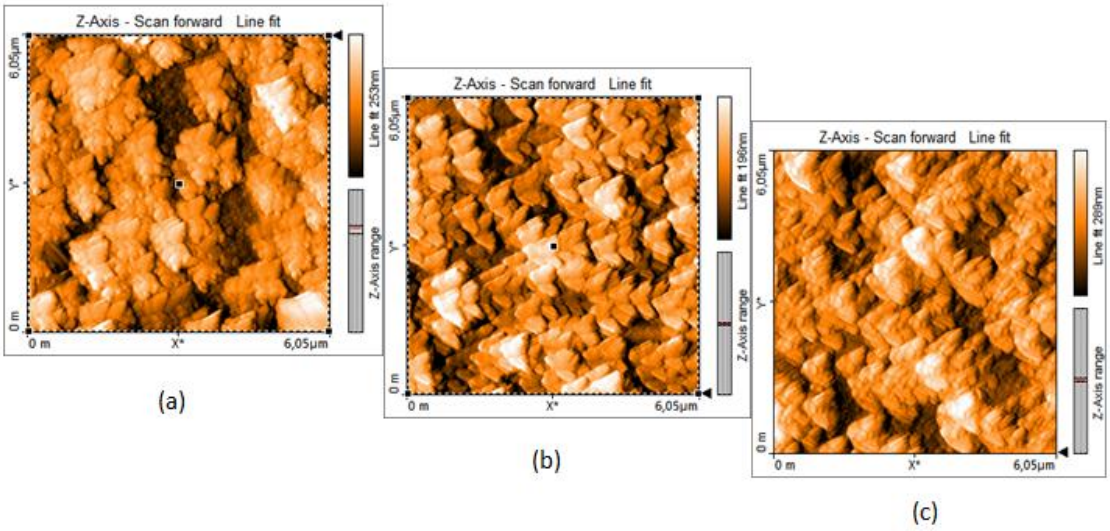


Figure 4.18: AFM images of (a) P(AN-co-IA)/PMOT with 77.6 µl; (b) P(AN-co-IA)/PMOT with 116.4 µl; (c)) P(AN-co-IA)/ PMOT with 155.2 µl

Figure 4.18, shows AFM images of with increasing 3 methoxythiophene amounts. The common point for all AFM images belonging to P(AN-co-IA)/PMOT films is the regularly aligned interesting triangular shapes. The scene of the triangular shapes becomes clear as the amount of 3 methoxythiophene increases in the solution added during polymerization process. The existence of the shapes may depend on the structure of 3 methoxythiophene.

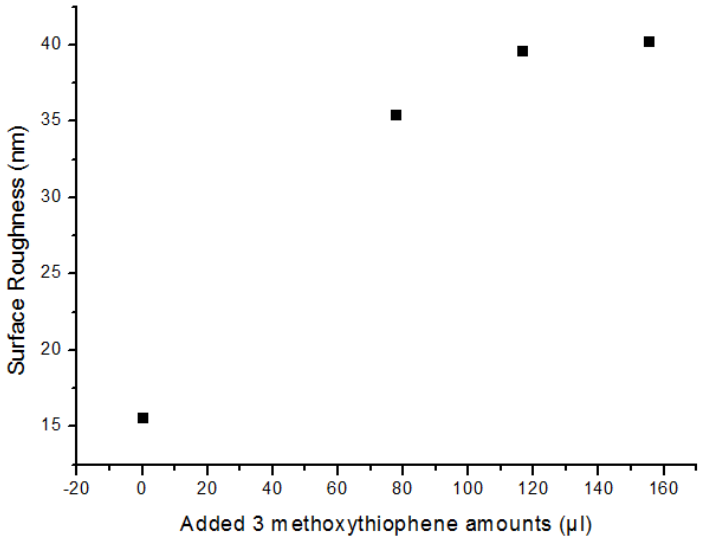


Figure 4.19: The relationship between added 3 methoxythiophene amounts and surface roughness of the films

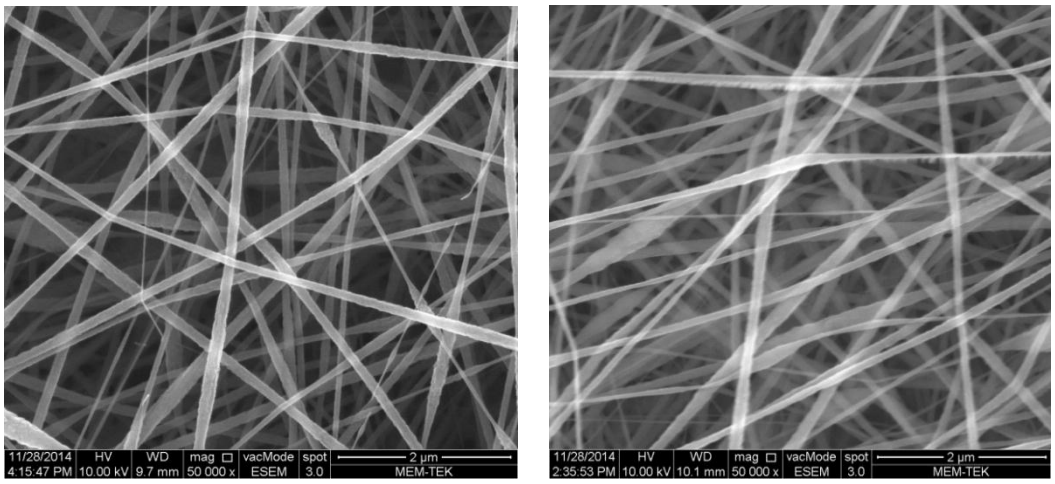
Figure 4.19 correlates the 3 methoxthiophene amounts added during copolymerization with P(AN-co-IA) and surface roughness of the spin-coated films. As the amount of comonomer fed during polymerization increases the surface roughness of the films also increases. This can be due to the solution prepared for spin coating in which P (AN-co-IA)/PMOT did not dissolve completely. The roughness values are 35.42, 39.64 and 40.22 for 77.6, 116.4, 155.2 µl 3 methoxythiophene.

4.2 Nanofiber Characterization

4.2.1 SEM analysis of nanofibers

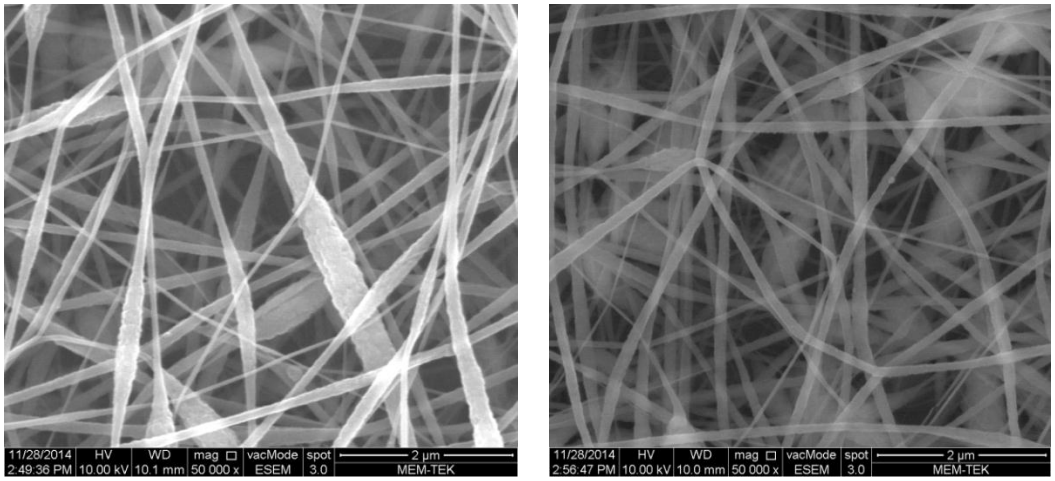
The obtained nanofibers were characterized by Scanning Electron Microscope (FEI Quanta FEC 250). Before the measurement, the samples were coated with gold (Ion Sputter Metal Coating Device, Quorum).

Figure 4.20 shows the SEM images of PAN and PAN-P(AN-co-IA). From the figure it can be seen that the morphology of the fibers differs when two images are compared.



(a) (b)

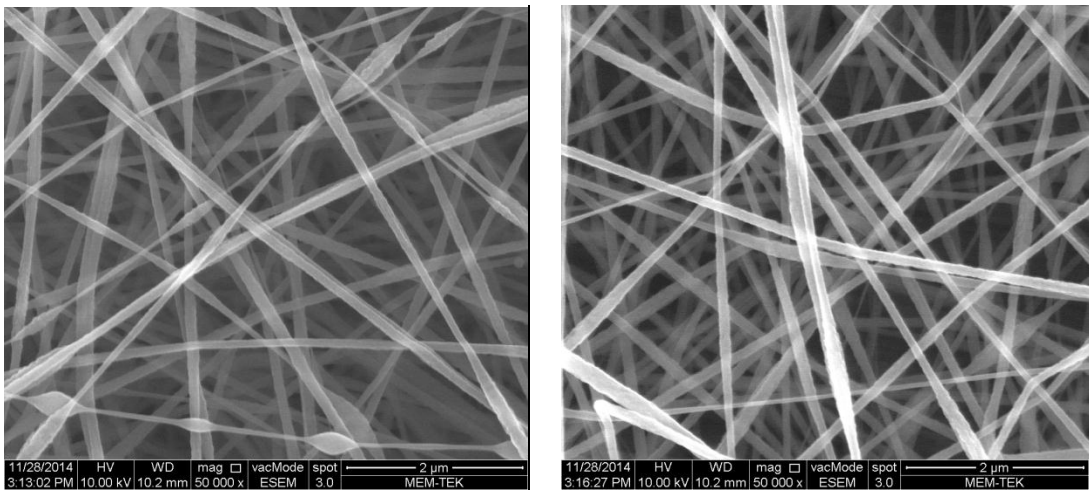
Figure 4.20: SEM images of (a) PAN and (b) PAN-P(AN-co-IA).



(a) (b)

Figure 4.21: SEM images of PAN-P(AN-co-IA)/PEDOT with (a)83.3 and (b)125 µl.

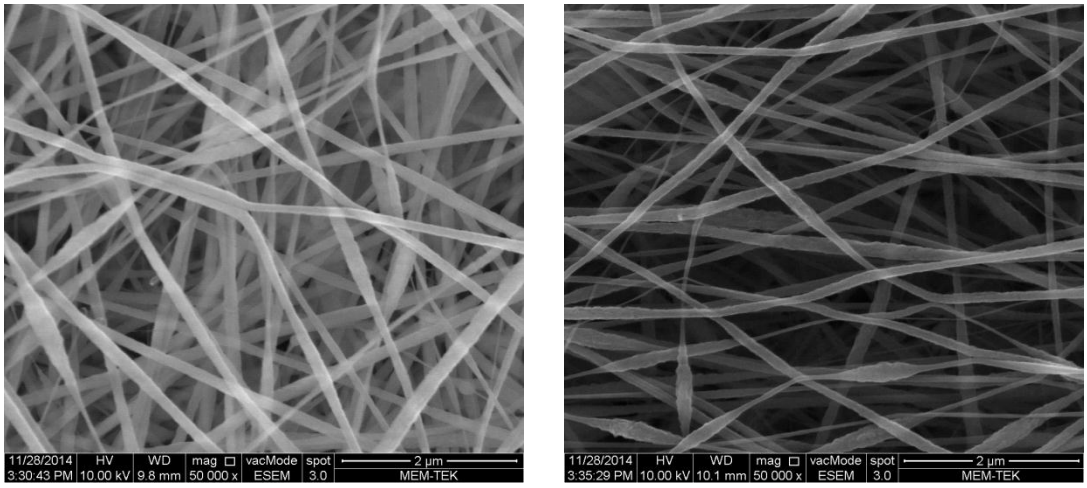
Figure 4.21 belongs to the SEM images of PAN-P(AN-co-IA)/PEDOT with 83.3 and 125 µl. From the figures it can be understood that the diameters of the nanofibers decreased as in the increase in PEDOT amount.



(a) (b)

Figure 4.22: SEM images of (a)PAN-P(AN-co-IA)/PEDOT with 166.6 µl and PAN-P(AN-co-IA)/PMOT 77.6 µl.

From the Figure 4.22, it can be concluded that the nanofibers are obviously smooth and fine and also the morphology of them resembles very much.



(a) (b)

Figure 4.23: SEM images of PAN-P(AN-co-IA)/PMOT with (a)116.4 and (b)155.2 µl.

As seen Figure 4.23 there is a clear difference between the morphology and diameters of the images of (a) and (b). Increase in the PMOT amount in the blends let decrease in the diameter of the nanofibers.

When the images are concluded, it can be mentioned that obtained fibers have small fiber diameters in the range of 100-200 nm. The nanofibers are both fine and smooth, also homogeneously distributed over the collector.

For the comparison, it should be said that the nanofibers obtained from PAN-P(AN-co-IA)/PMOT blends are more straigth than the nanofibers obtained from PAN-P(AN-co-IA)/PEDOT blends.

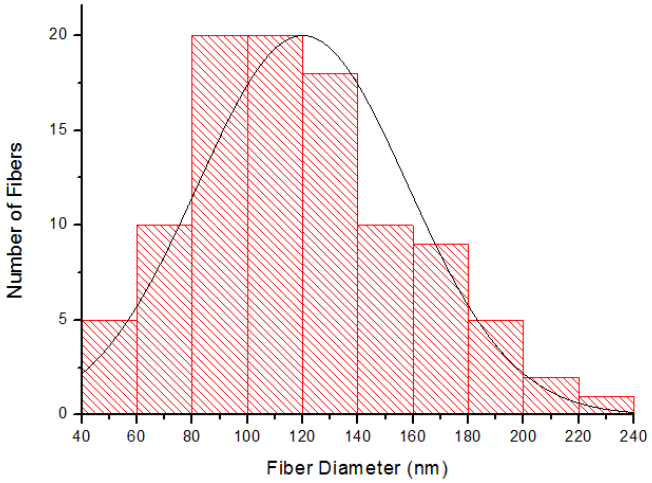


Figure 4.24: Diameter distribution of PAN nanofibers

The diameter distribution of electrospun PAN fiber is shown in the Figure 4.24. From the figure, it can be understood that the fiber diameter differentiates in the scale of 40-240 nm, however, average fiber diameter is 120 nm.

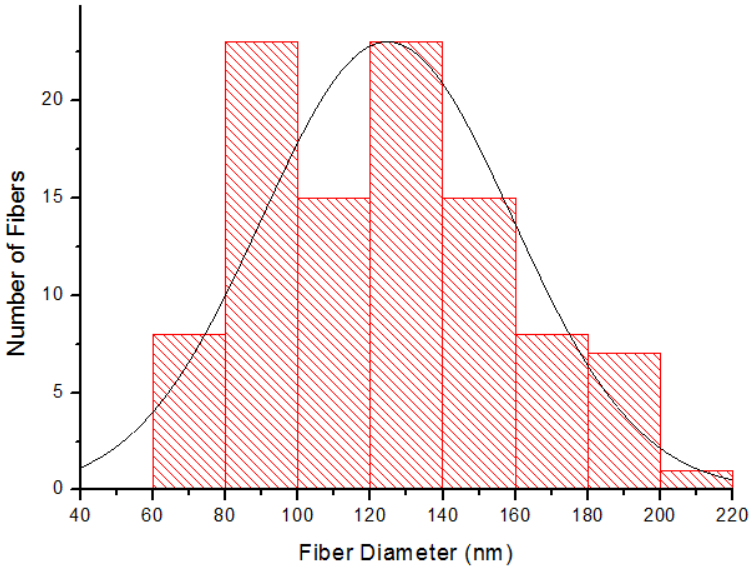


Figure 4.25: Diameter distribution of the nanofibers of PAN-P(AN-co-IA) blend

The diameter distribution of electrospun nanofibers of PAN-P(AN-co-IA) blend is shown in the Figure 4.25. As seen in the figure, the average fiber diameter is 124 nm.The value is nearly same as the fiber diameter of PAN.

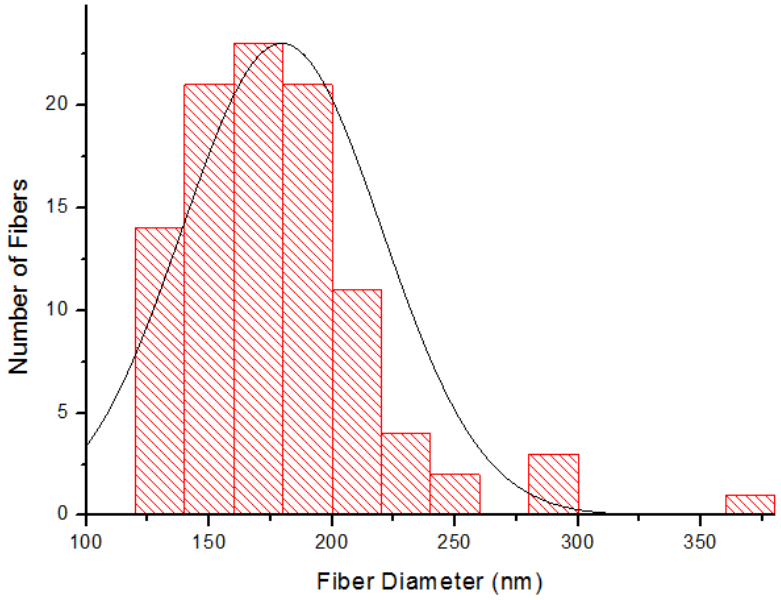


Figure 4.26: Diameter distribution of the nanofibers of PAN-P(AN-co-IA)/PEDOT (83.3µl) blend

Figure 4.26 belongs to the diameter distribution of electrospun nanofibers of PAN-P(AN-co-IA)/PEDOT (83.3µl) blend. As seen in the figure, the average fiber diameter is 180 nm. Incorporating PEDOT to the P(AN-co-IA) copolymers increased the fiber diameter.However, the fibers are even fine and well distributed as the other composites.

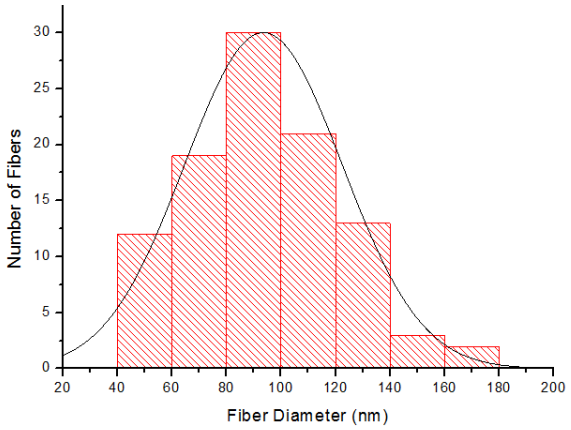


Figure 4.27: Diameter distribution of the nanofibers of PAN-P(AN-co-IA)/PEDOT (125 µl) blend

Figure 4.27 belongs to the diameter distribution of electrospun nanofibers of PAN-P(AN-co-IA)/PEDOT (125µl) blend. As seen in the figure, the average fiber diameter is 94 nm.As distinct from the previous sample, here the average fiber diameter is finer.

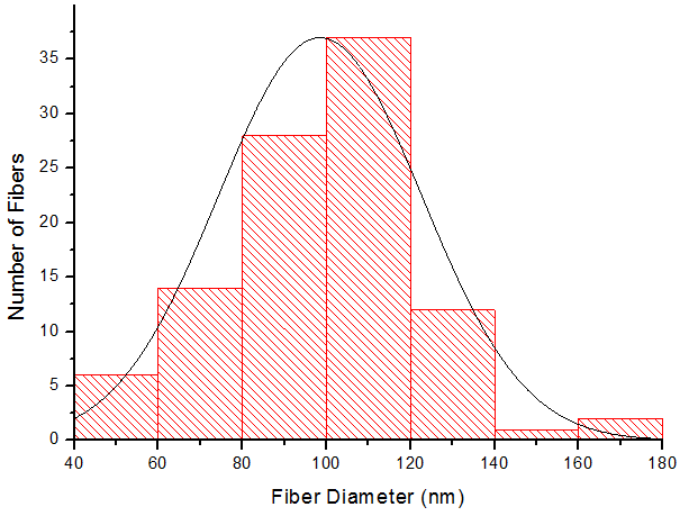


Figure 4.28: Diameter distribution of the nanofibers of PAN-P(AN-co-IA)/PEDOT (166.6 µl) blend

Figure 4.28 shows the diameter distribution of electrospun nanofibers of PAN-P(AN-co-IA)/PEDOT (166.6 µl) blend. As seen in the figure, the average fiber diameter is 99 nm. The average fiber diameter is nearly same as the PAN-P(AN-co-IA)/PEDOT (125 µl) blend.

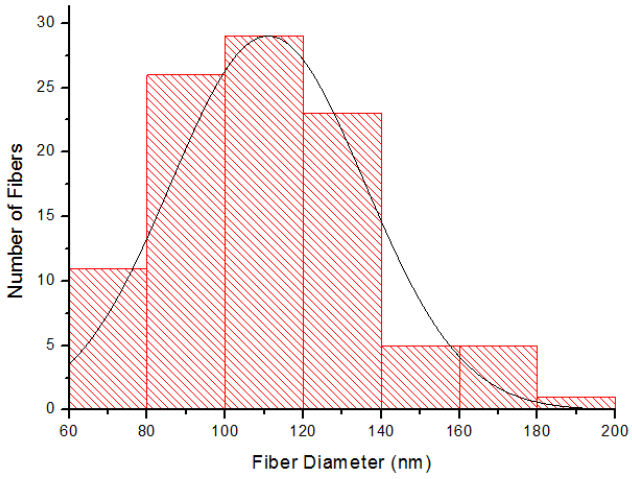


Figure 4.29: Diameter distribution of the nanofibers of PAN-P(AN-co-IA)/ (77.6 µl) blend

Figure 4.29 demonstrates the diameter distribution of electrospun nanofibers of PAN-P(AN-co-IA)/PMOT (77.6 µl) blend. As seen in the figure, the average fiber diameter is 110 nm.

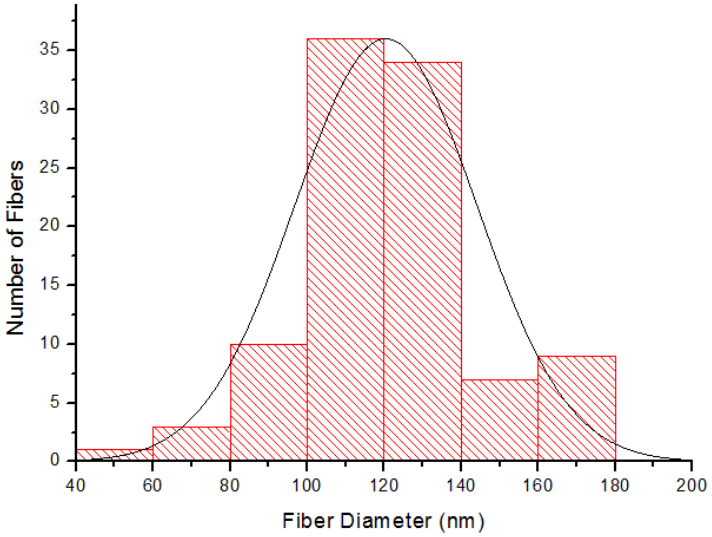


Figure 4.30: Diameter distribution of the nanofibers of PAN-P(AN-co-IA)/PMOT (116.4 µl) blend

Figure 4.30 displays the diameter distribution of electrospun nanofibers of PAN-P(AN-co-IA)/PMOT (116.4 µl) blend. As seen in the figure, the average fiber diameter is 120 nm, with fine and straight nanofibers.

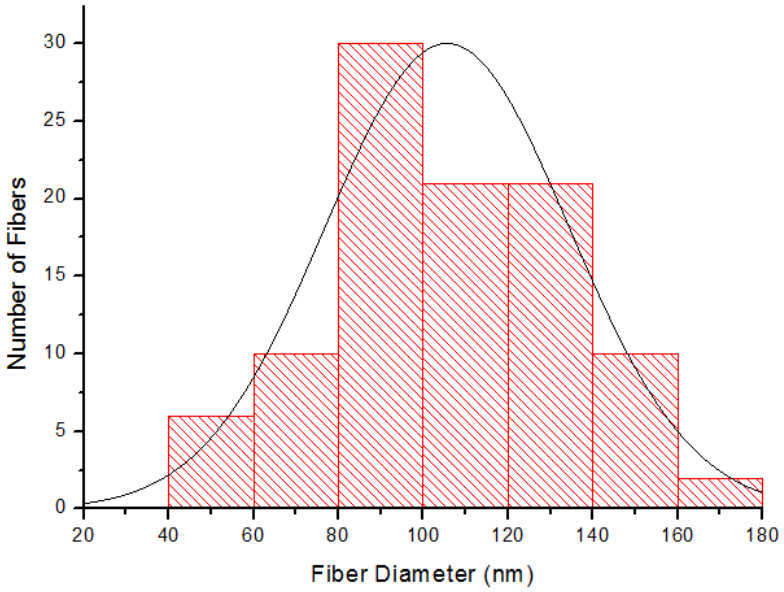


Figure 4.31: Diameter distribution of the nanofibers PAN-P(AN-co-IA)/PMOT (155.2 µl) blend

Finally, Figure 4.31 indicates the diameter distribution of electrospun fibers of PAN-P(AN-co-IA)/PMOT (155.2 µl) blend. The average fiber diameter is 105 nm.

Table 4.1: Standard deviation of the fiber diameters.

Blend	Average Fiber Diameter (nm)	Standard Deviation (%)
PAN	120	38.00
PAN-P(AN-co-IA)	124	36.39
PAN-P(AN-co-IA)/PEDOT (83.3 µl)	180	40.62
PAN-P(AN-co-IA)/PEDOT (125 µl)	94	28.94
PAN-P(AN-co-IA)/PEDOT (166.6 µl)	99	24.24
PAN-P(AN-co-IA)/PMOT (77.6 µl)	110	24.85
PAN-P(AN-co-IA)/PMOT (116.4 µl)	120	23.64
PAN-P(AN-co-IA)/PMOT (155.2 µl)	105	28.71

As mentioned in the Table 4.1 the standard deviation of the nanofibers are in the reasonable scale as in the literature. To make a conclusion, it is clear that all obtained electrospun fibers are fine and the results are close to each other that means there is no abnormality.

4.2.2 Viscosity measurements

Before the electrospinning process, the solutions had been prepared and blend of PAN with produced P(AN-co-IA)/PEDOT and P(AN-co-IA)/PMOT had been applied. The aim of this blend was optimizing the viscosity of the solutions. Table 4.2 shows the viscosity values of the PAN, solutions prepared with produced nanoparticles and final blend.

Table 4.2: Viscosity values of the solutions.

Solution	Viscosity Value (mPa.s)	Temperature (ºC)
PAN	48.8	22.7
P(AN-co-IA)/PEDOT and P(AN-co-IA)/PMOT	2.09	23.3
Blend	39.1	23.3

4.2.3 Energy dispersive spectroscopy (EDS)

Energy Dispersive Spectroscopy (EDS) uses X-Ray spectrum bombarded with a focused beam of electrons for observing chemical analysis of produced samples. All elements can be examined by using EDS, which can easily measures the intensity of the elements in the sample.

Table 4.3: EDS results of the blends.

	C (At %)	N (At %)	O (At %)	S (At %)
PAN-P(AN-co-IA)	69.52	19.88	10.60	0
PAN-P(AN-co-IA)/PEDOT (83.3 µl)	58.78	27.48	13.51	0.23
PAN-P(AN-co-IA)/PEDOT (125 µl)	55.92	32.24	11.55	0.30
PAN-P(AN-co-IA)/PEDOT (166.6 µl)	59.97	29.77	09.92	0.34
PAN-P(AN-co-IA)/PMOT (77.6 µl)	61.55	29.17	08.91	0.37

PAN-P(AN-co-IA)/PMOT (116.4 µl)	52.09	27.78	19.76	0.38
PAN-P(AN-co-IA)/PMOT (155.2 µl)	76.27	18.97	04.15	0.61

As seen in the Table 4.3, atomic percentages are given according to EDS analysis. It shows that blending of PAN with P(AN-co-IA), P(AN-co-IA)/PEDOT and P(AN-co-IA)/PMOT is successfully achieved. It is understood from the existence of S in the blend and also increase in atomic percentage of S depending on the added amount of EDOT and 3 methoxythiophene. The atomic percentages C, N and O belongs to the PAN and IA.

4.2.4 Electrochemical measurements

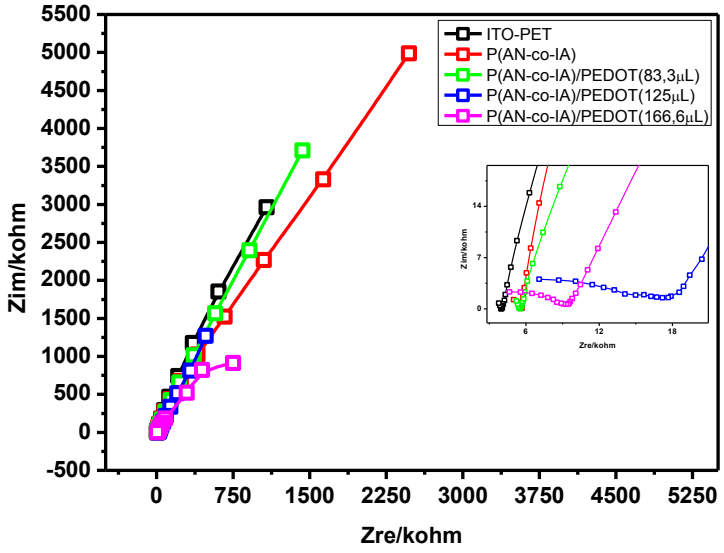


Figure 4.32: Nyquist graphic of the nanofibers of PEDOT consisting nanoparticles blended with PAN

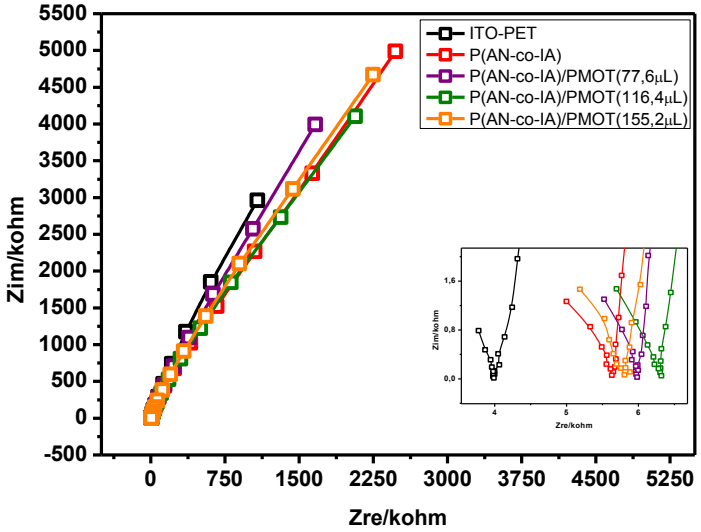


Figure 4.33: Nyquist graphic of the nanofibers of PMOT consisting nanoparticle blended with PAN

The Nyquist plots of the PEDOT and PMOT consisting fibers were tested in the frequency range of 0.001 Hz-100 kHz. Nyquist plots give information about the capacitance behaviour of the nanofibers. When Figure 4.32 and Figure 4.33 are detailly examined it can be seen that PEDOT and PMOT consisting nanofibers are more capacitif compared to the ITO-PET and matrix polymer P(AN-co-IA). The nanofibers are also more resistant when the plots are closer to the imajiner part with another name y axis of the graphic.

5. CONCLUSIONS AND RECOMMENDATIONS

In this thesis, the copolymerization of AN and IA was achieved by emulsion polymerization and emulsion latex was obtained. After that, without any initiator addition,production of composites of P(AN-co-IA) with EDOT and 3 methoxythiophene was performed by EDOT and 3 methoxythiophene addition into the reaction medium as three different amounts for each comonomer. Therefore,P(AN-co-IA)/polythiophene composite nanoparticles were achieved. Samples taken from the emulsion latexes were characterized by UV-Visible Spectroscopy, while the powder of the nanoparticles were analyzed by FTIR-ATR Spectroscopy and Scanning Electron Microscopy.According to the these analysis results, it was observed that thiophene derivatives had successively polymerized in the structure. Beyond these characterizations, AFM characterization was also used for the spin-coated films gained by treating the nanoparticles with DMF. By the help of this characterization, it can clearly be understood that the morphology of the obtained particles are different from each other, and the morphology changes when the amount of electroactive monomers(EDOT and MOT) change. After nanoparticle characterization,electrospinning method was applied to nanoparticles which had been treated with DMF and blended with PAN.Blending was applied in order to get optimum viscosity for the electrospinning. The obtained fibers were analyzed both by SEM and EDS and it was seen that the fiber diameters are so fine and standard deviation of the fibers are small enough. EDS results helped to prove that blending nanoparticle with PAN had accomplished. In addition electrochemical measurements were carried out to compare the capacitance behaviour of the nanofibers with ITO-PET.

In the light of these informations,it can be said that the obtained copolymers and nanofibers can be used in many applications nanocoatings for textile industry, gas sensors, biosensors etc. where the electroactivity is requested.

REFERENCES

[1] **Gibson, R.F.** (2010). A review of recent research on mechanics of multifunctional composite materials and structures. *Compos. Struct.*,Vol.92, Issue 12, pp 2793-2810.

[2] **Cochrane, C., Koncar, V., Lewandowski, M., Dufour, C.** (2007). Design and Development of a Flexible Strain Sensor for Textile Structures Based on a Conductive Polymer Composite. *Sensors*, Vol.7, Issue 4, pp. 473–492.

[3] **Skotheim, T. A.** (1986). *Handbook of conducting polymers*, Vol.2

[4] **Kuhn, H. H., Child, A. D., Kimbrell, W. C.** (1995). Toward real applications of conductive polymers. *Synth. Met.* Vol.71, Issue 1-3, pp. 2139–2142.

[5] *Sensors and Actuators B: Chemical*. , (n.d.) Date retrieved 11.12. 2014, adress: http://www.sciencedirect.com/science/journal/09254005

[6] *Handbook of Advanced Electronic and Photonic Materials and Devices*. Academic Press.

[7] Core shell nanostructures., (n.d.) Date retrieved 11.12. 2014, adress: http://www.slideshare.net/Shashank180391/core-shell-nanostructures

[8] **Bajaj, P., Paliwal, D. K., Gupta, A. K.** (1993). Acrylonitrile–acrylic acids copolymers. I. Synthesis and characterization. *J. Appl. Polym. Sci.* Vol.49, Issue 5, pp. 823-833.

[9] **Han, N., Zhang, X., Wang, X., Wang, N.** (2010). Fabrication, structures and properties of Acrylonitrile/Vinyl acetate copolymers and copolymers containing microencapsulated phase change materials. *Macromol. Res.*, Vol.18, Issue 2, pp. 144-152.

[10] **Bhanu, V. A., Rangarajan, P. , Wiles, K., Bortner, M., Sankarpandian, M., Godshall, D., Glass T. E., Banthia, A. K., Yang, J., Wilkes, G.** (2002). Synthesis and characterization of acrylonitrile methyl acrylate statistical copolymers as melt processable carbon fiber precursors. *Polymer*, Vol. 43, Issue 18, pp. 4841–4850.

[11] **Jamil, S. N. A. M., Daik, R., Ahmad, I.** (2014). Synthesis and Thermal Properties of Acrylonitrile/Butyl Acrylate/Fumaronitrile and Acrylonitrile/Ethyl Hexyl Acrylate/Fumaronitrile Terpolymers as a Potential Precursor for Carbon Fiber. *Materials*, Vol. 7, Issue 9, pp. 6207–6223

[12] **Cetiner, S., Sen, S., Arman, B., Sarac, A. S.** (2013). Acrylonitrile/vinyl acetate copolymer nanofibers with different vinylacetate content. *J. Appl. Polym. Sci.*, Vol. 127, Issue 5, pp. 3830–3838.

[13] **Yerlikaya, Y., Unsal, C., Sarac, A. S.** (2014). Nanofibers of Poly(Acrylonitrile-co-Methylacrylate)/Polypyrrole Core–Shell Nanoparticles. *Adv. Sci. Eng. Med.,* Vol. 6, Issue 3, pp. 301–310.

[14] **Unsal, C., Kalaoğlu F., Karakas, H., Sarac, A. S.** (2013). Polypyrrole/Poly(acrylonitrile-co-butyl acrylate) Composite. *Adv. Polym. Technol.,* Vol. 32, Issue S1, pp. E784–E792.

[15] **Miao, J., Cheng, Z., Zhou, M., Pan, D.** (2012). Kinetic Studies on the Copolymerization of Acrylonitrile and Itaconic Acid in Dimethylsulfoxide. *J. Macromol. Sci. Part A.* Vol. 49, Issue 10, pp. 869–875.

[16] **Cao,Y., Smith, P., Heeger, A. J.** (1992). Counter-ion induced processibility of conducting polyaniline and of conducting polyblends of polyaniline in bulk polymers. *Synth. Met.*, Vol. 48, Issue 1, pp. 91–97.

[17] **Chern, C. S.** (2006). Emulsion polymerization mechanisms and kinetics. *Prog. Polym. Sci.,* Vol. 31, Issue 5, pp. 443–486.

[18] **Eliseeva, V. I., Ivanchev, S. S., Kuchanov, S. I., Lebedev, A. V.** (1981). Emulsion Polymerization of Nonpolar Monomers. *Springer US*, pp.3-45.

[19] **Odian, G.** (2004). Principles of Polymerization. *John Wiley & Sons, Inc.*, pp. 350-371.

[20] **Berber, H.** (2013). Emulsion Polymerization: Effects of Polymerization Variables on the Properties of Vinyl Acetate Based Emulsion Polymers. *Polymer Science*, pp. 35-72.

[21] **Dinsmore R.P** (1929) U.S. Patent. 1,732,975 (to Goodyear Tire & Rubber Co.)

[22] **Bovey, F.A, Kolthoff, I.M, Medalia, A.I, Meehan, E.J.** (1965). Emulsion Polymerization. High Polymer Series Vol. IX. New York: Interscience Publishers Inc.

[23] **Eliseeva, V.I, Ivanchev, S.S, Kuchanov, S.I, Lebedev A.V.** (1981).Emulsion Polymerization and Its Applications in Industry. New York: Plenum Publishing Corporation.

[24] **Blackley, D.C.** (1975). Emulsion Polymerization, Theory and Practice. London: Applied Science Publishers.

[25] **Piirma, I.** (1982) Emulsion Polymerization. New York:Academic Press.

[26] **Erbil, H.Y.** (2000). Vinyl Acetate Emulsion Polymerization and Copolymerization with Acrylic Monomers. Florida: CRC Pres.

[27] **Chern, C.S.** (2006). Emulsion Polymerization Mechanisms and Kinetics. Prog. *Polym. Sci*., Vol.31, pp. 443-486.

[28] **Chern, C.S., Lin, S.Y., Chang, S.C., Lin, J.Y., Lin, Y.F.** (1998). Effect of Initiator on Styrene Emulsion Polymerisation Stabilised by Mixed SDS/NP-40 Surfactants. *Polymer*. Vol. 39, pp. 2281-2289.

[29] **Guyot, A., Tauer, K., Asua, J.M., Van, S., Gauthier, C., Hellgren, A.C., Sherrington, D.C., Goni, A.M., Sjoberg, M., Sindt, O., Vidal, F., Unzue, M., Schoonbroad, H., Shipper, E., Desmazes, P.L.** (1999). Reactive Surfactants in Heterophase Polymerization. *Acta Polym*. Vol.50, pp. 57-66.

[30] **Gardon, J. L.** (1968). Emulsion Polymerization I. Recalculation and Extension of Smith- Ewart Theory. *J. Polym. Sci. A*. Vol. 6, pp. 623-641.

[31] Emulsion Polymerization., (n.d). Date retrieved 11.12.2014, adress:: en.wikipedia.org/wiki/Emulsion_polymerization

[32] **Suadiye, D. (2014).** Synthesis and Characterization of poly(acrylonitrle-co-vinylacetate-co-itaconic) acid terpolymer as carbon fiber precursor. Master Thesis.

[33] **Rahaman, M. S. A., Ismail, A. F., & Mustafa, A.** (2007). A review of heat treatment on polyacrylonitrile fiber. *Polymer Degradation and Stability*.Vol. 92. Issue 8, pp. 1421–1432.

[34] **Bai, Y.-J., Wang, C.-G., Lun, N., Wang, Y.-X., Yu, M.-J., & Zhu, B.** (2006). HRTEM microstructures of PAN precursor fibers. *Carbon.*, Vol. 44. Issue 9, pp.1773–1778.

[35] **Han, N., Zhang, X.-X., & Wang, X.-C.** (2010). Various comonomers in acrylonitrile based copolymers: effects on thermal behaviour. Iranian Polymer Journal. Vol.19. Issue 4, pp. 243–253.

[36] **Mahdavian, A., Abdollahi, M.** (2007). Kinetic study of radical polymerization. VII. Investigation into solution copolymerization of acrylonitrile and itaconic acid by real-time H NMR spectroscopy, *Journal of Applied Polymer Science*. Vol.103, pp. 3253-3260.

[37] **Wangxi, Z., Jie, L., & Gang, W.** (2003). Evolution of structure and properties of PAN precursors during their conversion to carbon fibers. *Carbon*. Vol.41. Issue 14, pp. 2805–2812.

[38**] Sen, K., Hajir Bahrami, S., Bajaj, P.** (1996). High-Performance Acrylic Fibers. *JMS Rev Macromol Chem Phys.*,Vol. 36. Issue 1, p. 1.

[39] **Mohammady, S. Z., Elkholy, S. S., and Elsabee, M. Z.** (2006) Investigation of the relaxation behavior of novel terpolymers of acrylonitrile, methyl methacylate and indene, *Polym Int*, pp. 0959–8103.

[40] **Devasia, C. P., Nair, R., Sadhana, N. S., Babu, Ninan, K. N.** (2006). Fourier Transform Infrared and Wide-Angle X-Ray Diffraction Studies of the Thermal Cyclization Reactions of High-Molar-Mass Poly (acrylonitrile-co-itaconic acid), *J. App Poly Sci.*, Vol.,100, 3055–3062.

[41] **Ouyang, Q., Cheng, L., Wang, H., Li, K.** (2008). Mechanism and Kinetics Of the Stabilization Reactions of Itaconic acid- Modified Polyacrylonitrile. *Polymer Degradation and Stability*, Vol.93, pp. 1415–1421.

[42] **Tsai, J. S., Lin, C. H.** (1990). Polyacrylonitrile Precursors by Copolymer and Additive with Itaconic Acid, *Journal of Materıals Science Letters*, Vol. 9, Issue 8, pp. 869-871.

[43] **Zhao, Y., Wang, C., Yu, M., Cui, M., Wang, O., Zhu,B.** (2009). Study on Monomer Reactivity Ratios of Acrylonitrile/itaconic acid in Aqueous Deposited Copolymerization System Initiated by Ammonium Persulfate. *J Polym Res*, Vol.16, pp. 437–442.

[44] **Devasia, R. Nair, R. Ninan, K.N.** (2003). Copolymerization of Acrylonitrile with Itaconic Acid in Dimethylformamide: Effect of Triethylamine. *European Polymer Journal*, Vol.39, pp. 537–544.

[45] **Devasia, R., Reghunadhan Nair C. P., Ninan, K. N.** (2002). Solvent and Kinetic Penultimate Unit Effects in the Copolymerization of Acrylonitrile with Itaconic acid. *European Polymer Journal*,Vol. 38, pp. 2003–2010.

[46] **Yu, M., Chen, H., Liang, Y., Cui, H., Zhou, W., Cui, X., Li, D.** (2009). Porous Acrylonitrile/Itaconic Acid Copolymers Prepared by Suspended Emulsion Polymerization. *Journal of Applied Polymer Science*, Vol. 111, pp. 2761–2768.

[47] **Craver, C. D., & Carraher, C. E.** (2000). Preface. *Applied Polymer Science: 21st Century*

[48] **Eftekhari, A.** (2010). *Nanostructured Conductive Polymers*.

[49] *Physica E: Low-dimensional Systems and Nanostructures*.

[50] Twenty-five years of conducting polymers. (2003). *Chemical Communications*,Vol. 1, pp. 1–4.

[51] **Patil, A. O.** (2000). Electrically conducting polymers. *Applied Polymer Science: 21st Century*, pp. 325–341.

[52] **Walton, D. J.** (1990). Electrically conducting polymers. *Materials & Design*,Vol.11 .Issue 3, pp 142–152.

[53] **Bakhski, A. K., Bhalla, G.** (2004). Electrically conducting polymers: Materials of the twentyfirst century. *Journal of Scientific & Industrıal Research.* Vol. 63, pp.715-728.

[54] **Hideki Shirakawa, E. J. L.** (1977). Synthesis of electrically conducting organic polymers: halogen derivatives of polyacetylene, (CH) x. *Journal of The Chemical Society, Chemical Communications*,Vol.16.

[55] **Ruckenstein, E., & Park, J. S.** (1991). Polythiophene and polythiophene-based conducting composites. *Synthetic Metals*, Vol. *44*.Issue 3,pp. 293–306.

[56] **Wu, J.** (2011). Morphology of Poly (3,4-Ethylene Dioxythiophene) (PEDOT) Thin Films, Crystals, Cubic Phases, Fibers and Tubes.

[57] **Kim, D., Kim, Y., Choi, K., Grunlan, J. C., & Yu, C.** (2009). Improved Thermoelectric Behavior of Nanotube-Filled Polymer Composites with Poly(3,4-ethylenedioxythiophene) Poly(styrenesulfonate). *ACS Nano*, Vol.*4*.Issue 1, pp. 513–523.

[58] **Fan, L., Zhang, N., & Sun, K.** (2014). Flexible patterned micro-electrochemical capacitors based on PEDOT. *Chemical Communications*, Vol.*50.Issue* 51, pp. 6789–6792.

[59] **Ltd, S. R.** (2007). *Polymers in Defence and Aerospace Applications*.

[60] **Bhatt, M. P., Magurudeniya, H. D., Rainbolt, E. A., Huang, P., Dissanayake, D. S., Biewer, M. C., & Stefan, M. C.** (2014). Poly(3-hexylthiophene) nanostructured materials for organic electronics applications. *Journal of Nanoscience and Nanotechnology*, Vol.14. Issue 2, pp. 1033–1050.

[61] **Kuo, C.-C., Wang, C.-T., & Chen, W.-C.** (2009). Poly(3-hexylthiophene)/Poly(methyl methacrylate) Core-Shell Electrospun Fibers for Sensory Applications. *Macromolecular Symposia*, Vol 279. Issue 1, pp. 41–47.

[62] Conjugated organic polymers. http://www.google.com/patents/US3198767

[63] **Gerard, M., Chaubey, A., & Malhotra, B. D.** (2002). Application of conducting polymers to biosensors. *Biosensors and Bioelectronics*, Vol.17. Issue 5, pp. 345–359.

[64] **Udmale, V., Mishra, D., Gadhave, R., Pinjare, D., & Yamgar, R.** (2013). Development Trends in Conductive Nano-Composites for Radiation Shielding. *Oriental Journal Of Chemistry*,Vol.29. Issue 3, pp. 927–936.

[65] **Gustafsson, G., Cao, Y., Treacy, G. M., Klavetter, F., Colaneri, N., & Heeger, A. J.** (1992). Flexible light-emitting diodes made from soluble conducting polymers. *Nature*,Vol.357 .Issue 6378, pp. 477–479.

[66] **Baughman, R. H., Shacklette, L. W., Elsenbaumer, R. L., Plichta, E., & Becht, C.** (1990). Conducting Polymer Electromechanical Actuators.*Conjugated Polymeric Materials: Opportunities in Electronics, Optoelectronics, and Molecular Electronics*, pp. 559–582.

[67] Plastics Assembly: Electrically Conductive Polymers. Date retrieved 11.12. 2014, adress: http://www.assemblymag.com/articles/88381-plastics-assembly-electrically-conductive-polymers

[68] **Skotheim, T. A., & Reynolds, J.** (2006). *Conjugated Polymers: Processing and Applications*.

[69] **Münstedt, H., Köhler, G., Möhwald, H., Naegele, D., Bitthin, R., Ely, G., & Meissner, E.** (1987). Rechargeable polypyrrole/lithium cells. *Synthetic Metals*,Vol.18. Issue 1–3, pp. 259–264.

[70] **Chen, J., Liu, Y., Minett, A. I., Lynam, C., Wang, J., & Wallace, G. G.** (2007). Flexible, Aligned Carbon Nanotube/Conducting Polymer Electrodes for a Lithium-Ion Battery. *Chemistry of Materials*, Vol.19.Issue 15, pp. 3595–3597.

[71] Elkaoutit, M. Application of Conducting Polymers in Electroanalysis.

[72] **Kumar, K. S., Kumar, V. B., & Paik, P.** (2013). Recent Advancement in Functional Core-Shell Nanoparticles of Polymers: Synthesis, Physical Properties, and Applications in Medical Biotechnology. *Journal of Nanoparticles*.

[73] **Ghosh Chaudhuri, R., & Paria, S.** (2012). Core/shell nanoparticles: classes, properties, synthesis mechanisms, characterization, and applications. *Chemical Reviews*,Vol.112. Issue 4, pp. 2373–2433.

[74] **Yerlikaya, Y.** (2012). Polypyrrole /poly (acrylonitrile-co-methylacrylate) Nanocomposites, Nanofibers and Their Characterizations. M.Sc. Thesis.

[75] **Arman, B. Sarac, A. S.** (2014). In situ Preparation of Core-Shell-Polypyrrole /Poly (acrylonitrile-co-Vinylacetate) Nanoparticles and Their Nanofibers, *Scientific Research.*

[76] **Palkovits, R., Althues, H., Rumplecker, A.** (2005). Polymerization of w/o Microemulsions for the Preparation of Transparent SiO_2 /PMMA Nanocomposites.Vol.21. Issue 13, pp. 6048-6053.

[77] **Crespilho, F. N., Borges, T. F. C. C., Zucolotto, V., Leite, E. R., Nart, F. C., & Oliveira, O. N. J.** (2006). Synthesis of core-shell Au@polypyrrole nanocomposite using a dendrimer-template approach. *Journal of Nanoscience and Nanotechnology*.Vol.6. Issue 8, pp. 2588–2590.

[78] **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*.Vol.63. Issue 15, pp. 2223–2253.

[79] **Doshi, J., & Reneker, D. H.** (1995). Electrospinning process and applications of electrospun fibers. *Journal of Electrostatics*.Vol.35. Issue 2–3, pp. 151–160.

[80] **Venugopal, J., & Ramakrishna, S.** (2005). Applications of polymer nanofibers in biomedicine and biotechnology. *Applied Biochemistry and Biotechnology*. Vol.125. Issue 3, pp. 147–158.

[81] **Silva, A. N. R. da, Furlan, R., Ramos, I., & Santiago-Avilés, J. J.** (2005). Electrostatic deposition of nanofibers for sensor application. *Materials Research*. Vol. *8.*Issue 1, pp. 105–108.

[82] **Frenot, A., & Chronakis, I. S.** (2003). Polymer nanofibers assembled by electrospinning. *Current Opinion in Colloid & Interface Science*. Vol.8. Issue 1, pp. 64–75.

[83] **Fang, R., Zhang, E., Xu, L., & Wei, S.** (2010). Electrospun PCL/PLA/HA based nanofibers as scaffold for osteoblast-like cells. *Journal of Nanoscience and Nanotechnology* .Vol.10. Issue 11, pp. 7747–7751.

[84] **Reneker, D. H., & Yarin, A. L.** (2008). Electrospinning jets and polymer nanofibers. *Polymer*. Vol.49. Issue 10, pp. 2387–2425.

[85] **Cipitria, A., Skelton, A., Dargaville, T. R., Dalton, P. D., & Hutmacher, D. W.** (2011). Design, fabrication and characterization of PCL electrospun scaffolds—a review. *Journal of Materials Chemistry*. Vol.21.Issue 26, pp. 9419–9453.

[86] **Liu, Y., He, J.-H., Yu, J., & Zeng, H.** (2008). Controlling numbers and sizes of beads in electrospun nanofibers. *Polymer International*, Vol.57 . Issue 4, pp. 632–636.

[87] **Li, Z., & Wang, C.** (2013). Effects of Working Parameters on Electrospinning. *One-Dimensional nanostructures*, pp. 15–28.

[88] **Thompson, C. J., Chase, G. G., Yarin, A. L., & Reneker, D. H.** (2007). Effects of parameters on nanofiber diameter determined from electrospinning model. *Polymer*. Vol.49. Issue 23, pp. 6913–6922.

[89] **Beachley, V., & Wen, X.** (2009). Effect of electrospinning parameters on the nanofiber diameter and length. *Materials science & engineering. C, Materials for biological applications*. Vol.29. Issue 3,pp. 663–668.

[90] **Rajput, M.** (2012). *Optimization of electrospinning parameters to fabricate aligned nanofibers for neural tissue engineering* (MTech).

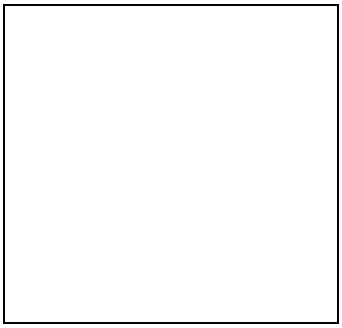
[91] **Deitzel, J. M., Kleinmeyer, J., Harris, D., & Beck Tan, N. C.** (2001). The effect of processing variables on the morphology of electrospun nanofibers and textiles. *Polymer*. Vol.42. Issue 1, pp. 261–272.

[92] **Fong, H., Chun, I., & Reneker, D. H.** (1999). Beaded nanofibers formed during electrospinning. *Polymer*.Vol.40 . Issue 16, pp. 4585–4592.

[93] **Si, Y., Tang, X., Yu, J., & Ding, B.** (2014). Electrospun Nanofibers: Solving Global Issues. *Electrospun Nanofibers for Energy and Environmental Applications*, pp. 3–38.

[94] **Fang, J., Wang, X., & Lin, T.** (2011). Functional applications of electrospun nanofibers. *Nanofibers-production, properties and functional applications*, pp. 287–326.

CURRICULUM VITAE



Name Surname: Havva BAŞKAN

Place and Date of Birth: Trabzon, 08.07.1988

E-Mail: baskan@itu.edu.tr

B.Sc.: Istanbul Technical University /Textile Engineering

Professional Experience And Rewards:

02.2013-…: Research Assistant at Istanbul Technical University in Textile Engineering

PUBLICATIONS, PRESENTATIONS AND PATENTS ON THE THESIS:

- Baskan, H., Sarac, A.S., Karakas, H., 2015: Production and Characterization of Poly (Acrylonitrile-co-Itaconic Acid)/ Polythiophene Nanocomposites. *5th International Istanbul Textile Congress 2015: Innovative Technologies 'Inspire to Innovate',* September 11-12. 2015 Istanbul, Turkey.

OTHER PUBLICATIONS, PRESENTATIONS AND PATENTS:

- Armagan, O., Baskan, H., Kayaoglu, B., Karakas, H.,2013: Durability of Leather Effect on Plasma Pre-Treated and Polyurethane Coated Denim Fabric. *International Istanbul Textile Congress 2013,* May 30-31. 2013 Istanbul , Turkey.

- Baskan, H. Sarac, A. S., Karakas, H., 2013: The Effect of Electrospinning Parameters on PCL Electrospun Nanofiber Mats. *Polymar 2013,* October 3-7. 2013 Barcelona, Spain.

- Karakas, H., Clerk, K., Sarac, A. S., Baskan, H., 2013: Electrospinning of Nanofibers for Functional Textile Applications. *International R &D Project Market, Innovative and Functional Textiles,* June 1. 2013 Istanbul, Turkey.