ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

NANOFIBERS OF POLY(ANTHRANILIC ACID)/POLYACRYLONITRILE BLENDS

M.Sc. THESIS

Diğdem GIRAY

Department of Nanoscience and Nanoengineering

Nanoscience and Nanoengineering Programme

JUNE 2012

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

POLY(ANTHRANILIC ACID)/POLYACRYLONITRILE POLİMERLERİNDEN NANOLİF ELDESİ

YÜKSEK LİSANS TEZİ

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Nano-Bilim ve Nano-Mühendislik Ana Bilim Dalı

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Diğdem GİRAY, a **M.Sc.** student of ITU **Graduate School of Science Engineering and Technology** student ID **513101002**, successfully defended the **thesis** entitled **"NANOFİBERS OF POLY(ANTHRANILIC ACID)/POLYACRYLONITRILE BLENDS"**, which she prepared after fulfilling the requirements specified in the

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To my family,

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ABBREVIATIONS

AC	**:** Alternative Current
AA	**:** Anthranilic Acid
ABS	**:** Acrylonitrile Butadiene Styrene
APS	**: A**mmonium Peroxydisulfate
CV	**:** Cyclic Voltammogram
DC	**:** Direct Current
DMA	**:** Dynamic Mechanical Analysis
DMF	**:** Dimethylformamide
EB	**:** Emeraldine Base
ECM	**:** Equivalent Circuit Modelling
EIS	**:** Electrochemical Impedance Spectroscopy
ES	**:** Emeraldine Salt
EMI	**:** Electromagnetic Interference
FTIR-ATR	**:** Fourier Transform Infrared Spectroscopy
HCl	**:** Hydrochloric Acid
ITO-PET	**:** Indium tin oxide-Polyethyene terephthalate
NSF	**:** National Science Foundation
NMP	**:** N-methylpyrolidone
PANA	**:** Poly(anthranilic acid)
PAN	**:** Polyacrylonitrile
PANI	**:** Polyaniline
PEMFCs	**:** Polymer Electrolyte Membrane Fuel Cells
PPy	: Polypyrrole
PLA	: Poly Lactic Acid
SEM	**:** Scanning Electron Microscopy
SPAN	: Sulfonated Polyaniline

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NANOFIBERS OF POLY(ANTHRANILIC ACID)/POLYACRYLONITRILE BLENDS

SUMMARY

This study can be categorized into three parts. The first part aims to obtain homogenous blends of [Poly(anthranilic acid)/Polyacrylonitrile] within dimethylformamide (DMF) solution. The obtained solutions were stirred magnetically for 3 hours at 50 °C in order to get homogeneous blends with enough viscosity for electrospinning.

The second aim was to obtain Nanofibers of [Poly(anthranilic acid)/Polyacrylonitrile] blends by electrospinning method which can be used for adhesives and coatings. The electrospinning apparatus consisted of a syringe pump (NE-500 Model, New Era Pump Systems, Inc., USA) with a feeding rate from 5.5 uL/h to 400 mL/h, a high voltage direct current (DC) power supplier generating positive DC voltage up to 50 kV DC power supply (ES 30 Model, Gamma High Voltage Inc., USA), and a grounded collector loaded into a syringe. The feeding rate of the polymer solution was controlled by a syringe pump and the solutions were electrospun horizantally on to the collector. Processing parameters effects on the morphology such as fiber diameter and its uniformity of electrospun polymer nanofibers were not changed during the process. Effects of polymer solution concentration on the electrospun nanofiber morphology were investigated. Based on the concentration depends on diffent amount of Poly(anthranilic acid) study, electrospun [Poly(anthranilic acid)/Polyacrylonitrile] nanofibers as small as 94 ± 16 nm were successfully produced. The diameters of the fibers decreased slightly as the concentration of the Poly(anthranilic acid) content is increased.

Finally, the third aim was to characterize the electrospun nanofibers of [Poly(anthranilic acid)/Polyacrylonitrile] blends. Spectroscopic, morphological and electrochemical characterization of nanofibers were performed by Fourier Transform Infrared-Attenuated Total Reflectance (FTIR-ATR), UV-Visible Spectrophotometer (UV-Vis), Scanning Electron Microscopy (SEM), Cyclic Voltammogram (CV) and Broadband Dielectric/Impedance Spectrometer (BDS). The electrochemical behaviour of nanofibers of [Poly(anthranilic acid)/Polyacrylonitrile] blends on ITO-PET electrode was tested through cyclic voltammetric measurements in an acidic electrolyte. Electrochemical measurements (EIS with supplied Power Sine software package and Cyclic Voltammograms) were performed with a Princeton Applied Research (PAR) Parstat 2263 potentiostat (Oak Ridge, USA).). The potentiostat is a self-contained unit that combines potentiostatic circuitry with phasesensitive detection. The impedance measurements were carried out by scanning in the frequency range 10 mHz–100 kHz with applied AC signal amplitude of 10 mV using Power Sine. The impedance spectrum was analyzed using AC impedance data analysis software (ZSimpWin V3.10, Michigan, USA). The electrical properties of

electrospun nanofibers were determined by electrochemical impedance measurements in monomer free solution for the first time.

POLY(ANTHRANILIC ACID)/POLYACRYLONITRILE POLİMERLERİNDEN NANOLİF ELDESİ

ÖZET

Bu çalışma üç ana bölümden oluşmaktadır. Birinci bölümde, homojen bir çözelti elde etmek amacıyla Poli(anthranilik asit) ve Poliakrilonitril polimerleri dimetilformamid (DMF) çözeltisi içerisinde hazırlanmıştır. Çözeltiler hazırlanırken Poliakrilonitril ve dimetilformamid miktarları sabit bırakılmış, Poly(anthranilik asit) miktarı değiştirilmiştir. Sonuçları kıyaslayabilmek için içerisinde hiç PANA bulundurmayan sadece Poliakrilonitril ve DMF içeren çözelti de ayrıca hazırlanmıştır. Elektrospun yöntemiyle nanolifler oluşturmak için, elde edilen [Poli(antranilik asit)/Poliakrilonitril] çözeltisi ve Poliakrilotril çözeltisi 50 °C'de 3 saat boyunca manyetik balık yardımıyla karıştırılmış, yeterli miktarda viskoziteye sahip ve homojen bir karışım elde edilmiştir.

Çalışmanın ikinci bölümünde homojen ve yeteri kadar viskoz olan [Poli(antranilik asit)/Poliakrilonitril] ve Poliakrilonitril çözeltilerinden, elektrospun yöntemiyle nanolifler üretilmiştir. Elektrospin ya da elektrospinning olarak adlandırılan teknik, polimer çözeltisinden akıtılan damla üzerine uygulanan yüksek elektrik akımı ile, polimer zincirlerinin uzamasını ve nano-ölçekte elyaflar üretilmesini sağlayan bir yöntemdir. Çözelti, polimer vizkozitesi, elektrik akımı, polimerin dielektrik dayanımı gibi birçok fiziksel değere bağlı olarak düzgün, hatta yönlendirilmiş elyaf üretimi elde edilebilir. Kullanılan elektrospun cihazı 5.5 uL/h'den 400 mL/h'ye değişen besleme hızına sahip bir şırınga pompası, 50 kV'a ulaşabilen yüksek voltajlı (direk akım) güç kaynağı ve metal toplayıcıdan oluşmaktadır. Bu çalışmada polimer besleme hızı 1 uL/h'dir. Güç kaynağı 15 kV olarak belirlenmiş, şırınga ucundan toplayıcıya kadar olan mesafe ise 15 cm olarak ayarlanmıştır. İçerisinde PANA bulunmayan çözeltiden elde dilen nanoliflerin çapları 113±23 nm iken, [Poli(antranilik asit)/Poliakrilonitril] çözelitisinden elde edilen nanoliflerin çapları 94±16 nm olarak kaydedilmiştir.

Son bölümde ise elde edilen [PANA/PAN] elektrospun nanolifleri karakterize edilmeye çalışılmıştır. Oluşan nanolifler morfolojik olarak SEM ile analiz edilmiş ve yapısal olarak FTIR-ATR, ve UV-Vis spektrofotometrik analizlerinde kullanılmıştır. Içerisinde PANA bulunmayan nanoliflerin FTIR ve UV-Vis spektrofotometrik sonuçlarına kıyasla, Poly(antranilik asit) içeren çözeltilerden elde edilen naoliflerin analizlerinde yeni bağların oluştuğu gözlenmiştir. Ayrıca PANA miktarına bağlı olarak değişiklikler incelenmiştir. Elektrokimyasal analizler için ITO-PET üzerine farklı miktarlarda PANA içeren çözeltilerden yine elektropun yöntemiyle nanolifler kaplanmış ve döngülü voltametre ile farklı tarama hızlarında akım değerleri okunmuştur. Elektrokimyasal empedans spektroskopisinden elde edilen sonuçlara göre devre modellemesi yapılmıştır.

Polimer bazlı malzemelerin kullanım alanlarında artış görülmesiyle polimer bilim teknolojisinde yapılan çalışmalar hız kazanmıştır. Son yıllarda iletken polimer teknolojisi gelişmekte olup, özellikle elektronik cihazlarda ve yarı iletken teknoloji alanlarında kullanılmaya başlanmıştır. Poliasetilen, Polipirol, Polianilin ve Politiyofen gibi polimerler yarı iletkenlik özelliği göstermekte ve yarı iletken cihaz yapımında kullanılmaktadır. Bu iletken polimerlerin içerisinde en dikkat çeken polimerlerden bir tanesi Polianilin'dir. Polianilin, mükemmel elektrokimyasal davranışa sahiptir, çevreye zararlı bir polimer değildir, kolay sentezlenebilir, kendi kendine doplanabilme özelliğine sahiptir ve sensör, batarya ve elektrot gibi bir çok alanda kullanılabilir. Ancak, diğer iletken polimerler gibi Polianilin de kırılgan ve rijit bir yapıya sahiptir. Mekanik özelliği bakımından zayıf olmasından dolayı kullanım alanları son derece kısıtlıdır. Bu problemin üstesinden gelmek amacıyla alkil, sülfonik asit veya karboksilik asit gruplarıyla güçlendirilmiş Polianilin polimerizasyonu yapılmıştır. Bu çalışmada karboksilik asit grubuna sahip Polianilin, diğer bir değişle Poli(antranilik asit) kullanılmıştır. Ayrıca, ortamın pH değeri 4'ün üzerine çıktığında Polianilin elektroaktif özelliğini kaybetmektedir. Hem mekanik özelliklerinin iyileştirilmesi, hem de pH değerinin yüksek olduğu ortamlarda da iletkenlik özelliğini kaybetmemesi için üretilen Poly(anthranilik asit) bu problemleri ortadan kaldırmaktadır. Poli(antranilik asit)'in bu olumlu özelliklerinin nedeni yapısında bulunan karboksilik asit grubuna sahip olmasıdır. Poli(anthranilik asit) kendi kendine doplanabilme özelliğine de sahiptir ve 4 farklı redoks yapısına dönüşebilir. Bunlar lökoemeraldin (tamamen redüklenmiş form), emeraldin (yarı-oksitlenmiş dorm), iletken emeraldin tuz (yarı oksitleniş ve protone edilmiş form) ve pernigranilin (tamamen oksitleniş form)'dur. Bunların içerisinde en iyi iletkenlik özelliği gösteren form, iletken emeraldin tuz formudur.

Elektrospin yöntemi ile iletken polimerlerin liflerini atmak, yeterli vizkoziteye sahip olmamalarından dolayı neredeyse imkansızdır. Bu problemi ortadan kaldırmak amacıyla, lifi atılmak istenen iletken polimerle birlikte başka bir polimerin karıştırılması öngörülmüştür. Bu çalışmada Poli(antranilik asit) iletken polimeri ile Poliakrilonitril polimeri, dimetilformamid çözücüsü içinde karıştırılmış ve elektrospin için uygun vizkoziteye sahip homojen bir çözelti elde edilmiştir. Poliakrilonitril ve kopolimerleri başta tekstil olmak üzere bir çok alanda kullanılmaktadır. Fakat literatürde Poliakrilonitril bazlı iletken polimer çalışmaları son derece kısıtlıdır. Bu açıdan yapılan bu çalışma özgün bir değere sahiptir. Poliakrilonitril iyi mekanik özelliklere sahip olmasından dolayı, Poli(anthranilik asit)'in yapısında iyileştirme yapmaktadır.

Yapılan deneysel çalışmada PAN miktarı 0,5 g olarak ayarlanmış ve her çözelti için miktarı sabit tutulmuştur. Aynı şekilde DMF miktarı 10 mL olarak belirlenmiş ve sbait tutulmuştur. Hazırlanan çözeltilerde değiştirilen tek şey Poli(anthranilik asit)'in miktarı olmuştur. İçerisinde hiç Poli(antranilik asit) bulundurmayan çözelti PO, 0,005 g PANA bulunan çözeltiye P10, 0,075 g PANA bulunan çözeltiye P15 ve son olarak içerisinde 0,100 g bulunan çözeltiye P20 kodları kullanışmıştır. Hazırlanan tüm çözeltiler 50 °C'de 3 saat boyunca manyetik balık yardımıyla karıştırılmış, yeterli miktarda viskoziteye sahip ve homojen bir karışım elde edilmiştir. Elde edilen fiberler morfolojik taramalı elektron mikroskobunda incelenmiştir. Spektroskopik inceleme için FTIR-ATR ve UV-Vis Spektroskopi cihazları kullanılmıştır. UV-Vis sonuçlarına göre spektrumda Poli(anthranilik asit)'e ait olan 340-380 nm arasında benzen halkalarına π-π^* transizyon oluşumu gözlenmiştir. Görünür bölgede ise yine Poli(antranilik asit)'e ait olan 480-650 nm arasında poloron bağları görülmüştür. Bu

piklerin oluşumu Poli(antranilik asit)'in yapıya girdiğini kanıtlamaktadır. Pikler arasında oluşan hipokromik kayma yapıdaki PANA miktarı arttıkça azalmaktadır. Hipokromik kayma, PANA'nın yapısında bulunan karboksilik grupların sterik etkisini ve buna bağlı olarak zincirler arasında yük transfer sağlanmasını ve iletkenliğin azalmasını göstermektedir. Bu çalışmada PANA miktarı arttıkça hipokromik etki azalmakta dolayısıyla iletkenliğin artmaktadır. FTIR-ATR sonuçlarına göre, Poli(antranilik asit)'e ait karakterstik pikler görülmektedir. Bu pikler 1693 cm^{-1}'de C=O, 1579 ve 1518 cm^{-1}'de C=C, 3230 cm^{-1}'de karboksilik asit OH gerilme bağlarıdır. Elektrokimyasal ölçümler için döngülü voltametre kullnışmıştır ve Poli(antranilik asit)'in ailesi olan Polianilin'e ait pikler görülmüştür. 0,2 Voltta lökoemeraldin/emeraldin ve 0,7 Voltta emeraldin/pernigranilin pikleri görülmüştür. Bu pikler de yine PANA'ya ait olan karboksilik asit gruplarından kaynaklanmaktadır. Elektrokimyasal empedans ölçümleri yapılmış, ölçülen ve hesaplanan değerler birbiriyle çok iyi fit etmiştir. Uygun devre modellemesi (R(Q(R(CR))) olarak seçilmiştir. Elektrokimyasal olarak yapılan ölçümlerde kullanılanhücrede çalışma elektrotu olarak elde edilen nanofiber kullanılmıştır. Referans elektrot olarak gümüş elektrot, karşıt elektrot olarak ise platin tel kullanılmıştır. Çalışma elektrodu olarak kullanılan nanofiber hücre içerisnde bulunan 5 mL Son olarak Broadband Diliektrik Spektrometresinde elde edilen nanoliflerin elektrik iletkenliklerinin ölçümü yapılmıştır. Çıkan sonuçlar elektrokimyasal yöntemle elde edilen iletkenlikle kıyaslanmış, benzer zonuçlar çıktığı gözrülmüştür.

1. INTRODUCTION

Conjugated polymers [1] such as polyacetylene [2], polypyrrole [3], polyaniline [4], and polythiophene [5] can illustratre considerable levels of electrical conductivity applicable for use in electronic devices, batteries, antistatic coatings, electromagnetic interference (EMI) shielding, electrochromic devices, optical switching devices, sensors, textiles [6]. Among the conductive polymers, Polyaniline (PANI) and its derivatives are one of the most promising class of organic-conducting polymers owing to their well-behaved electrochemistry [7], good environmental durability [8], electrochromism [9], easy doping [10], and easy synthesis. But, the low processability due to its low solubility is a problem [11]. to get rid of this problem, aniline derivatives with alkyl, sulfonic acid group, or carboxyl group [12] have been used. Poly(anthranilic acid) is a very promising polymer due to the solubility of the Poly(anthranilic acid) (PANA) in aqueous and nonaqueous solvents [13]. PANA shows solubility in a variety of solvents, including basic aqueous solution [14] alcohols, and other polar solvents [15]. PANA's other feautures related with the carboxylic acid group including the presence of a redox-active substituent, and the ability to self-doping maintain PANA as the promising material. Moreover, pH dependence of polyaniline is the another drawback of its conductivity, especially in the applications used for electrochemistry [16–22]. At pH > 4,0, polyaniline becomes electrochemically inactive [20]. Anthranilic acid (2-amino benzoic acid) is a monomer which was used for the synthesis of carboxylic acid group substituted PANI. Poly(anthranilic acid) has electrochemical activity with a wide range of pH in aqueous solutions due to the substitution of carboxylic acid group [23]. In this study, nanofibers were obtained from very homogeneous blend of Poly(anthranilic acid) and Polyacrylonitrile by using electrospinning. The nanofibers were characterized by a number of techniques including Fourier Transform Infrared Spectroscopy–Attenuated Total Reflectance (FTIR-ATR), Ultraviolet Visible Spectrophotometry (UV-Vis), Scanning Electron Microscopy (SEM) and Broadband Dielectric/Impedance Spectrometer (BDS). New absorption bands were observed corresponding to the conjugated polymeric units by FTIR-ATR and UV-Vis

spectrophotometric analysis. The influence of concentration of Poly(anthranilic acid) on the composite electrospun nanofibers was studied by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) and equivalent circuit modelling (ECM). Morphologies of electrospun nanofibers were also investigated by SEM.

2. THEORITICAL PART

2.1. Polyanilines

Polyaniline (PANI) has been known for over a century since the synthesis of the so-called aniline blacks that enjoyed early use as cotton dyes in the 1860s. Systematic studies of its properties before World War I led to the proposal by Green and Woodhead of an aniline octamer structure and the existence of several oxidation states [24, 25]. The first work describing the synthesis of what is now recognized as a conducting polymer was "Aniline black" published in 1862 [26]. "Aniline black" was prepared from the anodic oxidation of aniline and accompanied a color change upon switching potential, which latterly was called as electrochromism [27]. Only sporadic studies of PANI's were undertaken over the following 70 years until investigations by MacDiarmid and coworkers in the mid-1980s. In 1985, MacDiarmid, for the first time, found that aniline monomer in an acid aqueous solution (e.g.1.0 mol/L HCl) can be chemically oxidized by ammonium peroxydisulfate (APS) to obtain green powder of PANI with a conductivity of as high as 3 S/cm, as measured by four-probe method, which results were published in 1986 [28].This was the first sample of the conducting polymers doped by proton, which latterly was called "proton doping". Compared with other conducting polymers, PANI is advantageous of easy synthesis, low-cost, structure complex and special proton doping mechanism, as well as physical properties controlled by both oxidation and protonation state. These unique properties result in PANI holding an important position in the field of conducting polymers. PANI's are most commonly prepared through the chemical or electrochemical oxidative polymerization of the respective aniline monomers in acidic solution. However, a range of polymerization techniques has now been developed, including:

1. Electrochemical polymerization

2. Chemical polymerization

3. Photochemically initiated polymerization

4. Enzyme-catalyzed polymerization

5. Polymerization employing electron acceptors

2.2. Molecular Structure of Polyanilines

PANI is now accepted to have the general polymeric structure shown as Figure 2.1. It differs from most other conducting electroactive polymers, such as polypyrroles and polythiophenes, in that it possesses three readily accessible oxidation states. These range from the fully reduced (y = 1) *leucoemeraldine* state to the half-oxidized (y = 0.5) *emeraldine* form to the fully oxidized (y = 0) *pernigraniline* state. PANI was the first sample of a doping conjugated polymer to a highly conducting regime by a proton doping [28]. Proton doping means that the emeraldine base form (EB, y = 0.5) is doped with a protonic acid (e.g. 1.0 mol/L HCl) to produce a protonated emeraldine base form with a high conductivity (~ 3 S/cm), which is called as the *emeraldine salt* form (ES) [28, 29]. As shown in Figure 2.1, the proton doping dose not involve a change of the number of electrons associated with the polymer backbone during the proton doping [28, 29]. This significantly differs from redox doping (e.g. oxidation or deduction) where involves the partial addition (reduction) or removal (oxidation) of electrons to or from the polymer backbone [30]. Thus proton doping is major characteristics of PANI differing from other conducting polymers. The emeraldine salt (ES) form Figure 2.1 (d) is the state with the highest conductivity.

PANI also differs from PPy's and polythiophenes in that the N heteroatom participates directly in the polymerization process (PANI is a ladder polymer that polymerizes head to tail) and participates in the conjugation of the conducting form of the polymer to a greater extent than the N and S heteroatoms in PPy and polythiophene.

In addition, PANI is unique among the conducting electroactive polymers in that it can be rapidly converted between base and salt forms by treatment with acid or base. These reversible redox and pH-switching properties, together with the electrical conductivity of its ES form Figure 2.1 (d), its ease and cheapness of synthesis, and its good environmental stability have led to PANI becoming the most extensively studied conducting organic polymer over the past decade, and a wide range of potential applications are currently being developed.

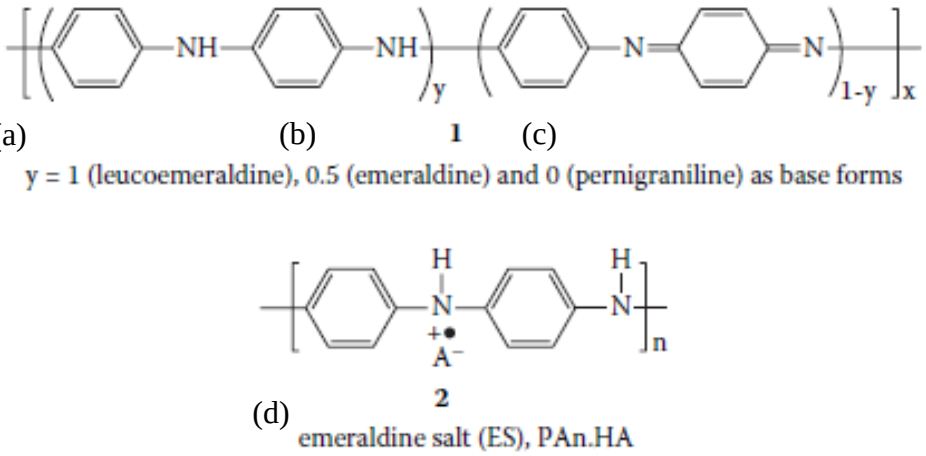


Figure 2.1: Generalized composition of PANI indicating the reduced and oxidized repeat units; (a) completely reduced polymer; (b) half-oxidized polymer; (c) fully oxidized polymer; (d) emaraldin salt form (ES), PANI, HA [31].

2.3. Solubility and Processability

As above described, PANI is very popular conductive polymer and has great scientific and industrial interest because of its high conductivity, environmental stability, simple and cheap synthesis method as well as technological applications in electrical devices [32]. PANI has also great interest as an organic magnet due to the potentially strong exchange interactions occurring through the conjugated backbone [33]. However, for such applications, PANI must be processability including soluble in common solvents or melt process below the glass transition temperature [34]. The EB form of PANI is soluble in NMP, which can be used to fabricate a freestanding film of the EB form. However its doped form (i.e. ES form) is insoluble in organic solvent or aqueous solution. Therefore, to synthesize soluble conducting PANI (i.e. the protonated state, ES form) is a key for realizing commissural application of PANI in technology. To solve solubility and processability of PANI therefore is not only necessary for commercial application, but also fundamental research (e.g. structural characterizations). Great effort for improving solubility in solvent and processability of PANI has been reported [35]. For instance, sulfonation or incorporation of *N*-alkyl-sulfonic acid pendant groups [36], dopant-inducted [37], self-doping polymer [38], micro-emulsion polymerization [39], and controlled relative molecular mass [40], have been reported for improvement of solubility and processability of PANI.

2.4. Substitution onto Backbone

In contrast to intrinsically conducting PANI, its self-doped derivatives contain an ionizable, negatively charged functional group in their structure which acts as an inner dopant anion, bound to the polymer backbone. Thus, there is no anion exchange between the polymer and solution during oxidation or reduction process [41]. These novel materials exhibit many properties that are different from those of the parent PANI and show promising applications in various fields. For instance, self-doped PANI is highly soluble in alkaline aqueous solutions and many non-aqueous media unlike PANI. Good solubility is essential for a polymer in order to facilitate postsynthetic processing. The solubility of PANI is greatly improved by the presence of the substituted acidic group.

2.4.1. Sulfonated polyaniline (SPAN)

Sulfonic acid group has been substituted to hydrogen on the benzene ring of PANI, resulting in a self-doped PANI [42]. A post-sulfonation of PANI makes the resulting polymer soluble. Also, polymerization of 2-amino benzene sulfonic acid (metanilic acid) in acidic aqueous solutions produces soluble poly(metanilic acid) [43]. Thus, preparation of a solid polymer of this type is not possible in aqueous acidic solutions, but it may be possible in a neutral solution of aqueous–organic mixed medium [44]. However, in order to exhibit the electrical and electrochemical properties, protonation of the imine nitrogen of PANI backbone in poly(metanilic acid) is essential, which requires an acidic solution [45]. Thus, the insolubility of PANI on one hand and the solubility of acid group substituted PANI on the other make the polymer system complex. An acid group substituted, self-doped PANI is expected to possess better electrical and electrochemical properties over wider pH range if it is available in solid form than the unsubstituted PANI. Thus, the synthesis of an acid group substituted solid PANI from the corresponding monomer in acidic solutions is a challenging problem.

2.4.2. Poly(anthranilic acid) (PANA)

Anthranilic acid is the organic compound with the formula $C_6H_4(NH_2)COOH$ and its structure was illustrated in Figure 2.2. Anthranilic acid (2-amino benzoic acid) is an important monomer for the synthesis of carboxylic acid group substituted PANI.

Studies on the synthesis of Poly(anthranilic acid) from aqueous acidic solution are scarcely reported in literature, probably because of difficulty in synthesis, poor yield, and brittle nature of the film due to presence of an electron withdrawing carboxylic group. Poly(anthranilic acid) reveals high solubility in an aqueous solution of NaOH or NMP [46]. Similar to the poly(metanillic acid) [47], it is expected that Poly(anthranilic acid), PANA, possesses electrochemical activity over a wide pH range in aqueous solutions owing to the substitution of carboxylic acid group.

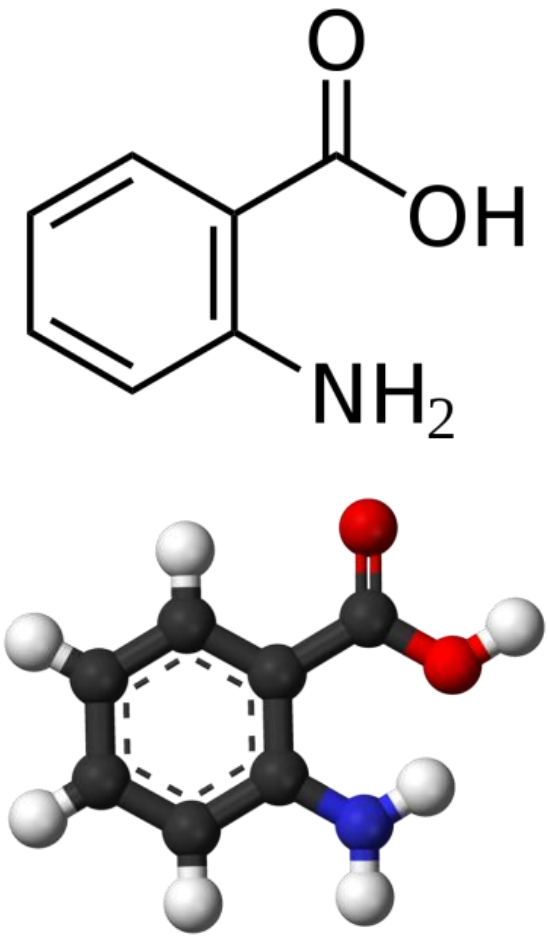


Figure 2.2: Structure of Anthranilic acid.

Poly(anthranilic acid) (PANA) seemed to be a promising material due to its high processibility, the presence of a redox-active substituent, and the ability to self-dope, all these characteristics attributable to the carboxylic acid group. PANA is much more soluble than its parent polymer. PANA exhibits solubility in a range of solvents, including basic aqueous solution [48], alcohols, and other polar solvents [49]. The carboxylic acid group can be reduced and oxidized; this may provide an additional mode of charge storage (pseudo capacitance) for the super capacitor. Self-

doping has the advantage of being a faster doping process than the one seen in externally doped polyanilines, where the dopant ion must move in and out of the polymer chain [50]. The four oxidation states of PANA are presented in Figure 2.3 [51].

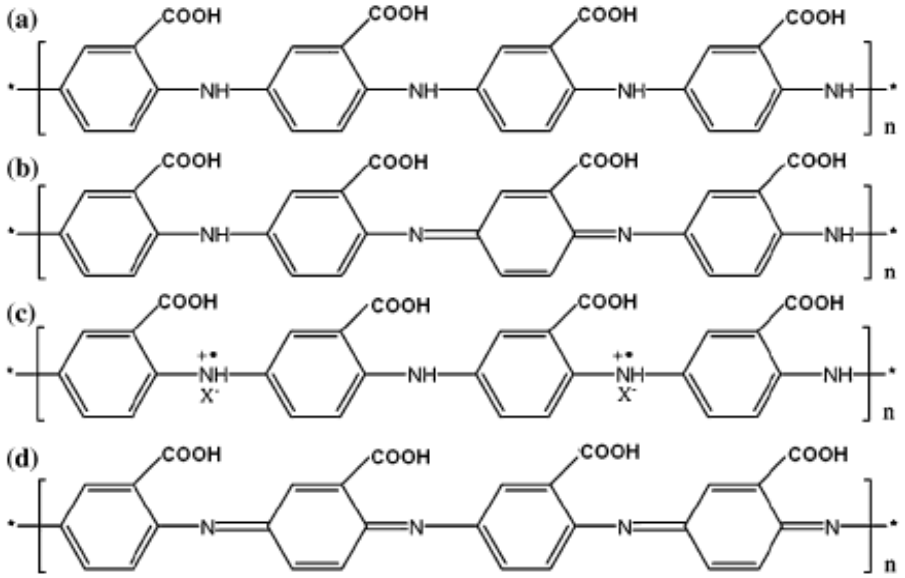


Figure 2.3: Four different redox forms of PANA: (a) leucoemeraldine base (fully reduced form), (b) emeraldine base (half-oxidized form), (c) conducting emeraldine salt (half-oxidized and protonated form), and (d) pernigraniline base (fully oxidized form).

In addition, self-doped PANI (Figure 2.4) has an extended pH range of electrical conductivity and electrochemical activity, covering that of many biocatalysts and sensors [52-56].

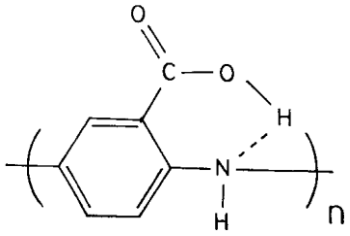


Figure 2.4: Proposed self-doped structure of the PANA.

The limits of polyaniline applications in electrochemistry arise from the pH dependence of its conductivity [57]. At pH > 4.0, polyaniline becomes electrochemically inactive. Incorporation of the acidic groups like carboxylic [58] and sulfonic acids [59 – 61] as ring substituents, influences the microenvironment of the amine groups and namely shifts the local pH and then the conductivity does not

fall off dramatically with increasing the pH as in the case of polyaniline. Hence, the pH dependence of the electrochemical activity of the self doped polyanilines was improved markedly, compared with the parent polyaniline that has a little electrochemical activity at pH > 4.0 [60]. On the other hand, because carboxylic acid is an electronwithdrawing group and also since of intramolecular proton exchange between acidic group and amine moiety, the oxidation potential of AA is higher than the aniline which thereby the rate of oxidation and it's polymer formation is largely lower than that of aniline monomer [62 – 64].

2.5. Acrylic Fibers

The first reported synthesis of acrylonitrile and polyacrylonitrile (PAN) was by the French chemist Moreau [65]. In 1893, Moreau reported two methods for synthesizing acrylonitrile and a year later, he reported the polymerization of acrylonitrile. The polymer received little attention for a number of years because there were no known solvents and because the polymer decomposes before reaching its melting point. This made processing of the polymer nearly impossible.

Already in 1931 *Rein* [66] found the first solvents for PAN calcium rhodanide, 1942 dimethylformamide (DMF) and N-methylpyrolidone [66]. Only a few months later in the USA the solvents DMF and Tetramethylsulfon [67, 68] were patented. In Japan [69] PAN was solved in potassium or sodium rhodanide, and the solution was coagulated in ethanol or propane [69]. Already in 1944 DuPont started the production of PAN filaments that were later known as "Fiber A" [70]. 1952 the company Casella (later acquired by Bayer) followed. Since 1985 the Orion capacities are being reduced and since 1995 stopped, while Dralon capacities are slowly increased. Courtelle [71] and Beslon [72] are both polymerized and spun in salt solutions, and today are used as good precursors for carbon fibers.

Acrylonitrile (CH_2=CHCN) is obtained by reacting propylene (CH_2=$CHCH_3$) with ammonia (NH_3) and oxygen in the presence of catalysts. It is a flammable liquid that is highly toxic if ingested and is a known carcinogen; strictly regulated procedures are required for its handling and disposal. Acrylonitrile monomers (single-unit molecules) are suspended, almost always in combination with other monomers, as fine droplets in water and are induced to polymerize to PAN through

the action of free-radical initiators. The acrylonitrile repeating unit of the polymer has the following structure:

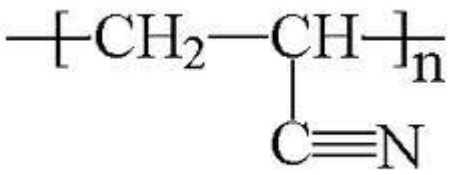


Figure 2.5: Polymeric Structure of Polyacrylonitrile (PAN)

Fibers from both polyacrylonitrile and copolymers derived from acrylonitrile are classified jointly as acrylic fibers. The Textile Fiber Products Identification Act divides these fibers into two categories: Acrylic fibers are those containing at least 85% by weight of acrylonitrile, and modacrylic fibers contain less than 85% but at least 35% acrylonitrile. These fibers are long-lasting, dry rapidly, and resist fading, wrinkling, and mildew. They are used in making carpets, sportswear, sweaters, and blankets as well as many other products [73].

2.5.1. Polyacrylonitrile (PAN)

Polyacrylonitrile (PAN) is one of the most important fiber-forming polymers and has been widely used because of its high strength, high abrasion resistance, and good insect resistance.

However, the PAN based conducting blends has not been explored, and it is expected to be a competitive system for making conductive fiber. In this study, Polyacrylonitrile and Poly(anthranilic acid) blends were prepared and the electrospun nano fibers of this blend were produced for the first time.

PAN, a synthetic resin prepared by the polymerization of acrylonitrile relatively insoluble, and high-melting materials produced by the polymerization of acrylonitrile, as shown in the Figure 2.6.

A member of the important family of acrylic resins, it is a hard, rigid thermoplastic material that is resistant to most solvents and chemicals, slow to burn, and of low permeability to gases. Most polyacrylonitrile is produced as acrylic and modacrylic fiber, a common substitute for wool in clothing and home furnishings.

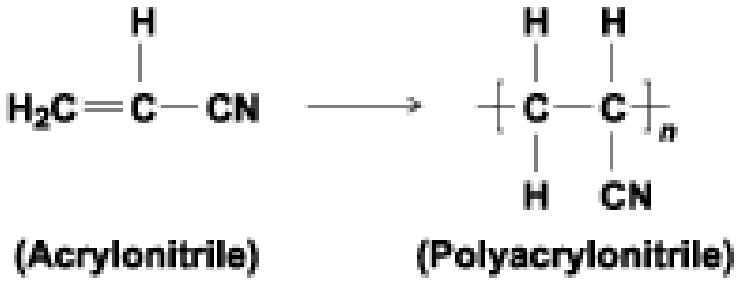


Figure 2.6: Polymerization of Acrylonitrile.

The morphology of PAN is unique [74]. Due to strong repellent dipole–dipole interactions between intramolecular neighboring nitrile groups in parallel position, the polymer backbone is forced into an irregular helical conformation. Strong attractive dipole–dipole interactions between antiparallel nitrile groups of different chains cause parallel orientation of the individual irregular helices. Nearly two-thirds of the AN production is consumed by the synthesis of PAN fibers; the rest is used for acrylic rubbers, ABS-type polymers, and the production of acrylamide [74].

PAN has none of the hazardous properties of the monomer. Owing to the formation of strong chemical bonds between the nitrile (CN) groups, the polymer molecules resist most organic solvents and do not melt without decomposing. In most cases the polymer is dissolved in special solvents and spun into acrylic fibers, which are defined as fibers that contain 85 percent or more of PAN. Because PAN is difficult to dissolve and is highly resistant to dyeing, very little fiber is produced containing PAN alone.

2.6. Nanofibers

Nanofiber technology is a branch of nanotechnology whose primary objective is to create materials in the form of nanoscale fibers in order to achieve superior functions. The unique combination of high specific surface area, flexibility, and superior directional strength makes such fibers a preferred material form for many applications ranging from clothing to reinforcements for aerospace structures [75].

The National Science Foundation (NSF) defines nanofibers as having at least one dimension of 100 nanometer (nm) or less. The name derives from the nanometer, a scientific measurement unit representing a billionth of a meter, or three to four atoms wide. Nanofibers can be produced from a wide range of polymers and they have an elongated structure as illustrated in the Figure 2.7.These fibers have extremely high

specific surface area due to their small diameters, and nanofiber mats can be highly porous with excellent pore interconnection [76].Special properties of nanofibers such as low density, high surface area to volume ratio make them suitable for a wide range of applications from medical to consumer products and industrial to high-tech applications for aerospace, capacitors, transistors, drug delivery systems, battery separators, energy storage, fuel cells, and information technology.

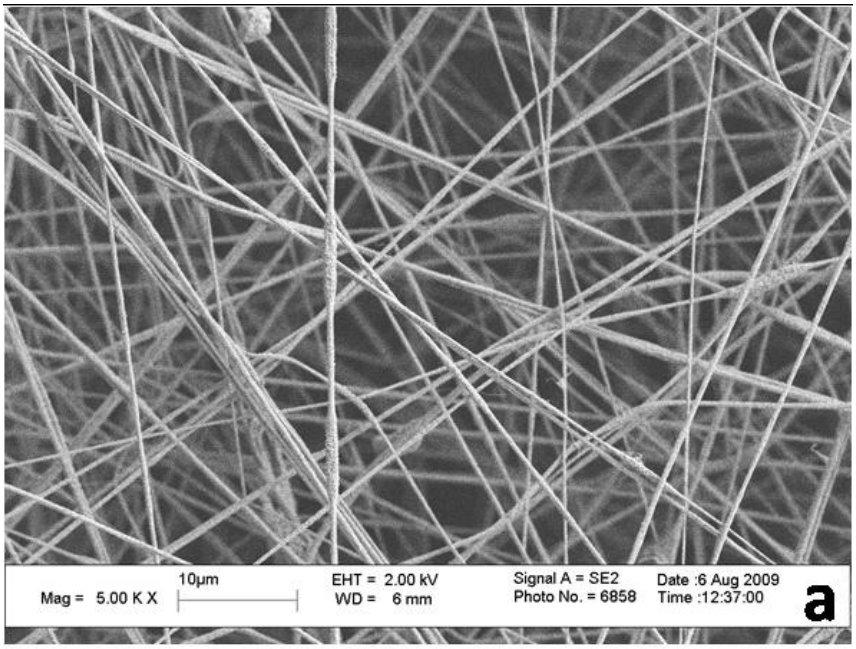


Figure 2.7: SEM image of a nanofiber [77].

Several methods have been developed to fabricate nanofibers, such as template, self-assembly, phase separation, melt-blown and electrospinning [77]. However, their usefulness is limited by combinations of restricted material ranges, possible fiber assembly, cost, and production rate [78]. Electrospinning is currently the most promising technique to produce continuous nanofibers on a large scale and the fiber diameter can be adjusted from nanometers to microns. As electrospinning is a relatively easy and fast process to produce nanofibers, in this thesis study, electrospinning was used for fabrication of non-woven fibers. Moreover, electrospinning process will be given in detail in the next section [75].

2.7. Electrospinning

With the emergence of nanotechnology, researchers become more interested in studying the unique properties of nanoscale materials. Electrospinning, an electrostatic fiber fabrication technique has evinced more interest and attention in

recent years due to its versatility and potential for applications in diverse fields. The notable applications include in tissue engineering, biosensors, filtration, wound dressings, drug delivery, and enzyme immobilization. The nanoscale fibers are generated by the application of strong electric field on polymer solution or melt. The non-wovens nanofibrous mats produced by this technique mimics extracellular matrix components much closely as compared to the conventional techniques. The sub-micron range spun fibers produced by this process, offer various advantages like high surface area to volume ratio, tunable porosity and the ability to manipulate nanofiber composition in order to get desired properties and function. Over the years, more than 200 polymers have been electropun for various applications and the number is still increasing gradually with time [79].

Electrospinning, also known as electrostatic spinning, has its basis in early studies. In 1745, Bose described aerosols generated by the application of high electric potentials to drops of fluids [80]. In 1882, Lord Rayleigh investigated the question of how many charges are needed to overcome the surface tension of a drop [81]. Later, the first devices to spray liquids through the application of an electrical charge were patented by Cooley and Morton, in 1902 and 1903 [82–84]. In 1929, Hagiwaba et al. described the fabrication of artificial silk through the use of electrical charge [85]. The crucial patent, in which the electrospinning of plastics was described for the first time, appeared in 1934 with Anton Formhals from Mainz as the author (and can be traced back to a German patent filing in 1929) [86]. Despite these early discoveries, the procedure was not utilized commercially. In the 1970s, Simm et al. patented the production of fibers with diameters of less than 1 mm [87]. However, this work, which was followed by other patents, also remained unnoticed. Electrospun fibers were first commercialized for filter applications, as part of the nonwovens industry [88]. Electrospinning gained substantial academic attention in the 1990s, which was partially initiated by the activities of the Reneker group [89]. One reason for the fascination with the subject is the combination of both fundamental and application oriented research from different science and engineering disciplines. These research efforts usually target complex and highly functional systems, which could certainly be applied on a commercial level. Fiber systems in which the macroscopic properties (that is, specific chemical, physical or biological combinations of properties) can be targeted through modifications on the molecular level are of particular interest. The

scope of possibilities presented by electrospinning encompasses a multitude of new and interesting concepts, which are developing at breakneck speed. Several expressions are used to describe the electrospinning technique. Among them, the terms “electrostatic spinning” and “electrospinning” are both frequently used. For consistency, we use “electrospinning” as the noun and “electrospin” as the verb [90].

Electrospinning is a highly versatile method to process solutions or melts, mainly of polymers, into continuous fibers with diameters ranging from a few micrometers to a few nanometers. Electrospinning appears to be straightforward, but is a rather intricate process that depends on a multitude of molecular, process, and technical parameters. The method provides access to entirely new materials, which may have complex chemical structures. Electrospinning is not only a focus of intense academic investigation; the technique is already being applied in many technological areas [90].

2.7.1 Electrospinnin process

Electrospinning, a spinning technique, is a unique approach using electrostatic forces to produce fine fibers from polymer solutions or melts and the fibers thus produced have a thinner diameter (from nanometer to micrometer) and a larger surface area than those obtained from conventional spinning processes. Furthermore, a DC voltage in the range of several tens of kVs is necessary to generate the electrospinning. Currently, there are two standard electrospinning setups, vertical and horizontal. With the expansion of this technology, several research groups have developed more sophisticated systems that can fabricate more complex nanofibrous structures in a more controlled and efficient manner [91]. Electrospinning is conducted at room temperature with atmosphere conditions. The typical set up of electrospinning apparatus is shown in the Figure 2.8. Basically, an electrospinning system consists of three major components: a high voltage power supply, a spinneret (e.g., a pipette tip) and a grounded collecting plate (usually a metal screen, plate, or rotating mandrel) and utilizes a high voltage source to inject charge of a certain polarity into a polymer solution or melt, which is then accelerated towards a collector of opposite polarity [92]. Most of the polymers are dissolved in some solvents before electrospinning, and when it completely dissolves, forms polymer solution. The polymer fluid is then introduced into the capillary tube for electrospinning [93]. In

the electrospinning process, a polymer solution held by its surface tension at the end of a capillary tube is subjected to an electric field and an electric charge is induced on the liquid surface due to this electric field. When the electric field applied reaches a critical value, the repulsive electrical forces overcome the surface tension forces. Eventually, a charged jet of the solution is ejected from the tip of the Taylor cone and an unstable and a rapid whipping of the jet occurs in the space between the capillary tip and collector which leads to evaporation of the solvent, leaving a polymer behind [94-96]. The jet is only stable at the tip of the spinneret and after that instability starts. Thus, the electrospinning process offers a simplified technique for fiber formation.

Almost any soluble polymer can be electrospun if its molecular weight is high enough. However, the creation of fine nanofibers requires the careful consideration of many operating parameters (such as polymer molecular weight, applied voltage, solution feed rate and spinning distance), environmental parameters (such as temperature, humidity and air velocity in the chamber) and solution properties (such as conductivity, viscosity and surface tension).

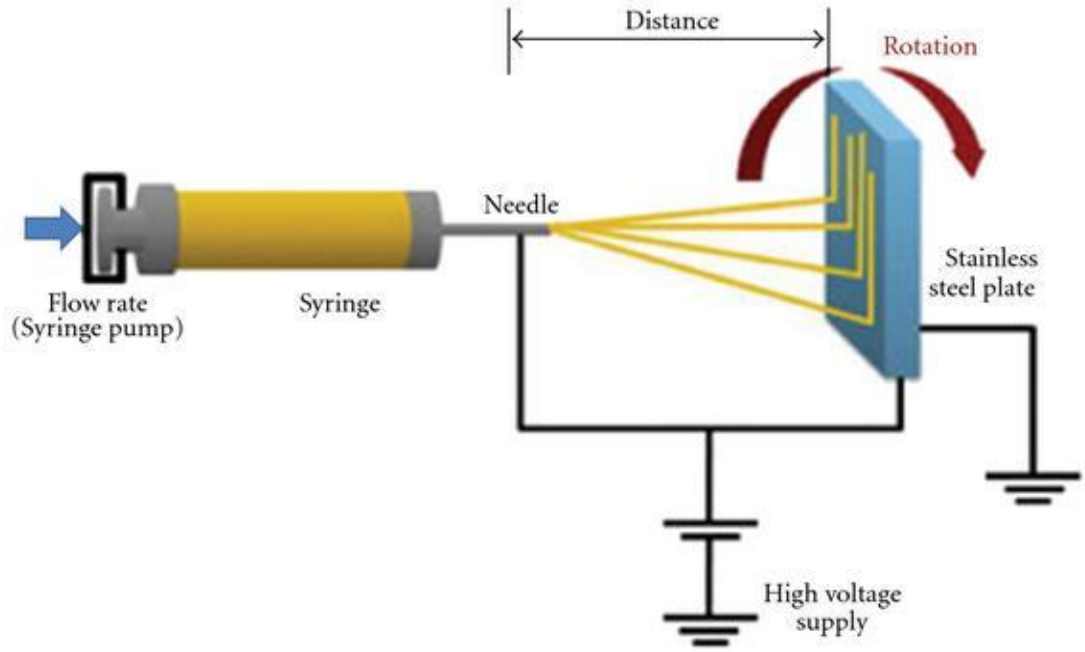


Figure 2.8: Schematic diagram of an electrospinning apparatus.

2.7.2 Effects of parameters on electrospinning

The electrospinning process is solely governed by many parameters, classified broadly into solution parameters, process parameters, and ambient parameters. Solution parameters include viscosity, conductivity, molecular weight, and surface tension and process parameters include applied electric field, tip to collector distance and feeding or flow rate. Each of these parameters significantly affect the fibers morphology obtained as a result of electrospinning, and by proper manipulation of these parameters we can get nanofibers of desired morphology and diameters [97]. In addition to these variables, ambient parameters encompass the humidity and temperature of the surroundings which play a significant role in determining the morphology and diameter of electrospun nanofibers [98]. In the Table 1, various parameters and their effects on fiber morphology were discussed.

2.7.2.1. Solution parameters

Concentration

In the electrospinning process, for fiber formation to occur, a minimum solution concentration is required. It has been found that at low solution concentration, a mixture of beads and fibers is obtained and as the solution concentration increases, the shape of the beads changes from spherical to spindle-like and finally uniform fibers with increased diameters are formed because of the higher viscosity resistance [99].

There should be an optimum solution concentration for the electrospinning process, as at low concentrations beads are formed instead of fibers and at high concentrations the formation of continuous fibers are prohibited because of the inability to maintain the flow of the solution at the tip of the needle resulting in the formation of larger fibers [100].

Researchers have attempted to find a relationship between solution concentration and fiber diameter and they found a power law relationship, that increasing the concentration of solution, increases the fiber diameter with gelatin electrospinning. Solution surface tension and viscosity also play important roles in determining the range of concentrations from which continuous fibers can be obtained in electrospinning [101].

Molecular Weight

Molecular weight of the polymer has a significant effect on rheological and electrical properties such as viscosity, surface tension, conductivity and dielectric strength. This is the other important solution parameter that affects the morphology of electrospun fiber and generally high molecular weight polymer solutions have been used in electrospinning as they provide the desired viscosity for the fiber generation. It has been observed that too low a molecular weight solution tends to form beads rather than fibers and a high molecular weight solution gives fibers with larger average diameters. Molecular weight of the polymer reflects the number of entanglements of polymer chains in a solution, thus solution viscosity. Chain entanglement plays an important role in the processing of electrospinning. It has been observed that high molecular weights are not always essential for the electrospinning process if sufficient intermolecular interactions can provide a substitute for the interchain connectivity obtained through chain entanglements, and using this principle, researchers have prepared oligomer-sized phospholipids from lecithin solutions into nonwoven membranes through electrospinning [102].

Viscosity

Solution viscosity plays an important role in determining the fiber size and morphology during spinning of polymeric fibers. It has been found that with very low viscosity there is no continuous fiber formation and with very high viscosity there is difficulty in the ejection of jets from polymer solution, thus there is a requirement of optimal viscosity for electrospinning. Sukigara et al. [103] have shown the significant effects of viscosity on silk nanofibers. Earlier, Larrondo and Manley [104] also showed that viscosity was important when they electrospun fibers from the melt. The viscosity range of a different polymer solution at which spinning is done is different. Viscosity, polymer concentration and molecular weight of polymer are correlated to each other. The solution viscosity has been strongly related to the concentration of the solution and the relationship between the polymer viscosity and/or concentration and fibers obtained from electrospinning has been studied in a number of systems. At very high viscosity polymer solutions usually exhibit longer stress relaxation times, which could prevent the fracturing of the ejected jets during electrospinning. An increase in solution viscosity or concentration

gives rise to a larger and more uniform fiber diameter [105]. In electrospinning, viscosity of solution plays an important role in determining the range of concentrations from which continuous fibers can be obtained. For solution of low viscosities, surface tension is the dominant factor and just beads or beaded fibers are formed while above a critical concentration, a continuous fibrous structure is obtained and its morphology is affected by the concentration of the solution [106]. Taken together, these studies indicate that there exist polymer-specific, optimal viscosity values for electrospinning and this property has a remarkable influence on the morphology of fibers.

Surface Tension

Surface tension, more likely to be a function of solvent compositions of the solution plays a critical role in the electrospinning process and by reducing the surface tension of a nanofiber solution; fibers can be obtained without beads. Different solvents may contribute different surface tensions. Generally, the high surface tension of a solution inhibits the electrospinning process because of instability of the jets and the generation of sprayed droplets [107]. The formation of droplets, bead and fibers depends on the surface tension of solution and a lower surface tension of the spinning solution helps electrospinning to occur at a lower electric field [108]. However, not necessarily a lower surface tension of a solvent will always be more suitable for electrospinning. Basically, surface tension determines the upper and lower boundaries of the electrospinning window if all other variables are held constant [109].

Conductivity/Surface Charge Density

Polymers are mostly conductive, with a few exceptions of dielectric materials, and the charged ions in the polymer solution are highly influential in jet formation. Solution conductivity is mainly determined by the polymer type, solvent used, and the availability of ionisable salts. It has been found that with the increase of electrical conductivity of the solution, there is a significant decrease in the diameter of the electrospun nanofibers whereas with low conductivity of the solution, there results insufficient elongation of a jet by electrical force to produce uniform fiber, and beads may also be observed. Hayati et al. [110] have showed that highly conductive

solutions are extremely unstable in the presence of strong electric fields, which results in a dramatic bending instability as well as a broad diameter distribution. Generally, electrospun nanofibers with the smallest fiber diameter can be obtained with the highest electrical conductivity and it has been found that the there is drop in the size of the fibers is due to the increased electrical conductivity.

2.7.2.2. Processing parameters

Applied Voltage

In the electrospinning process a crucial element is the applied voltage to the solution. Only after attainment of threshold voltage, fiber formation occurs, this induces the necessary charges on the solution along with electric field and initiates the electrospinning process. It has been already proved experimentally that the shape of the initiating drop changes with spinning conditions (voltage, viscosity, and feed rate) [111]. There is a little dispute about the behaviour of applied voltage in the electrospinning process.

Reneker and Chun [112] have showed that there is not much effect of electric field on the fiber diameter with electrospinning of polyethylene oxide. Researchers have suggested that when higher voltages are applied, there is more polymer ejection and this facilitates the formation of a larger diameter fiber [113]. Other authors have reported that an increase in the applied voltage (i.e., by increasing the electric field strength), increases the electrostatic repulsive force on the fluid jet which ultimately favours the narrowing of fiber diameter.

In most cases, a higher voltage causes greater stretching of the solution due to the greater columbic forces in the jet as well as a stronger electric field and these effects lead to reduction in the fiber diameter and also rapid evaporation of solvent from the fibers results.

At a higher voltage there is also greater probability of beads formation [114–122]. Similar behaviour of applied voltage on fiber diameter is also observed by Larrondo and Manley [123-125]. They have showed the decrease of fiber diameter by roughly half by doubling the applied electric field. Thus, voltage influences fiber diameter, but the level of significance varies with the polymer solution concentration and on the distance between the tip and the collector [126].

Feed Rate/Flow Rate

The flow rate of the polymer from the syringe is an important process parameter as it influences the jet velocity and the material transfer rate. A lower feed rate is more desirable as the solvent will get enough time for evaporation [127]. There should always be a minimum flow rate of the spinning solution. Few studies have systematically investigated the relationship between solution feed or flow rate on fiber morphology and size [128–129]. High flow rates result in beaded fibers due to unavailability of proper drying time prior to reaching the collector.

Types of Collectors

One important aspect of the electrospinning process is the type of collector used. In this process, a collector serves as a conductive substrate where the nanofibers are collected. Generally, aluminium foil is used as a collector but due to difficulty in transferring of collected fibers and with the need for aligned fibers for various applications, other collectors such as, conductive paper, conductive cloth, wire mesh [130], pin [131], parallel or grided bar [132], rotating rod, rotating wheel [133], liquid non solvent such as methanol coagulation bath and others are also common types of collectors nowadays. The fiber alignment is determined by the type of the target/collector and its rotation speed. The generated nanofibers are deposited on the collector as a random mass due to the bending instability of the highly charged jet. Several research groups have demonstrated the use of a rotating drum or a rotating wheel-like bobbin or metal frame as the collector, for getting aligned electrospun fibers more or less parallel to each other [134]. Several types of split electrodes have been used for getting aligned nanofibers and typically such collectors consist of two conductive substrates separated by a void gap where aligned nanofibers are deposited [132–134].

Tip to Collector Distance

The distance between the tip and the collector has been examined as another approach to control the fiber diameters and morphology. It has been found that a minimum distance is required to give the fibers sufficient time to dry before reaching the collector, otherwise with distances that are either too close or too far, beads have been observed [132–135]. One important physical aspect of the electrospinning

nanofibers is their dryness from the solvent used to dissolve the polymer [136]. Thus, there should be optimum distance between the tip and collector which favours the evaporation of solvent from the nanofibers.

2.7.2.3. Ambient parameters

Apart from solution and processing parameters, there are also ambient parameters that include humidity, temperature etc. Studies have been conducted to examine the effects of ambient parameters (i.e., temperature and humidity) on the electrospinning process.

There is an inverse relationship between viscosity and temperature. The variation in humidity while spinning polystyrene solutions has been studied and shows that by increasing humidity there is an appearance of small circular pores on the surface of the fibers; further increasing the humidity leads to the pores coalescing [137]. It has been found that at very low humidity, a volatile solvent may dry rapidly as the evaporation of the solvent is faster. Sometimes the evaporation rate is so fast than compared to the removal of the solvent from the tip of the needle and this would create a problem with electrospinning. As a result, the electrospinning process may only be carried out for a few minutes before the needle tip is clogged [138]. It has also been suggested that the high humidity can help the discharge of the electrospun fibers. Hence, apart from solution and processing parameters, ambient parameters also affect the electrospinning process.

Table 1: Parameters and their effects on fiber morphology [79].

Parameters	**Effect on fiber morphology**
Solution parameters	
Viscosity	Low-beads generation, high-in fiber diameter, disappearance of beads.
Polymer concentration **Molecular weight of polymer**	Increase in fiber fiber diameter with increase of concentration.
Conductivity	Decrease in fiber diameter with increase in conductivity.
Surface Tension	No conclusive link with fiber morphology, high surface tension results in instability of jets.
Processing parameters	
Applied voltage	Decrease in fiber diameter with increase in voltage.

Distance between tip and collector	Generation of beads with too small and too large distance, minimum distance required for uniform fibers.
Feed rate/Flow rate	Decrease in fiber diameter with decrease in flow rate, generation of beads with too high flow rate.
Ambient parameters	
Humidity	High humidity results in circular pores on the fibers.
Temperature	Increase in temperature results in decrease in fiber diameters.

2.7.3. Applications of electrospun nanofibers

Polymeric nanofiber non-woven materials produced by electrospinning have extremely high surface-to-mass (or volume) ratio and a porous structure with excellent pore-interconnectivity. These characteristics plus the functionalities and surface chemistry of the polymer itself impart the nanofibers with desirable properties for a range of advanced applications [76].

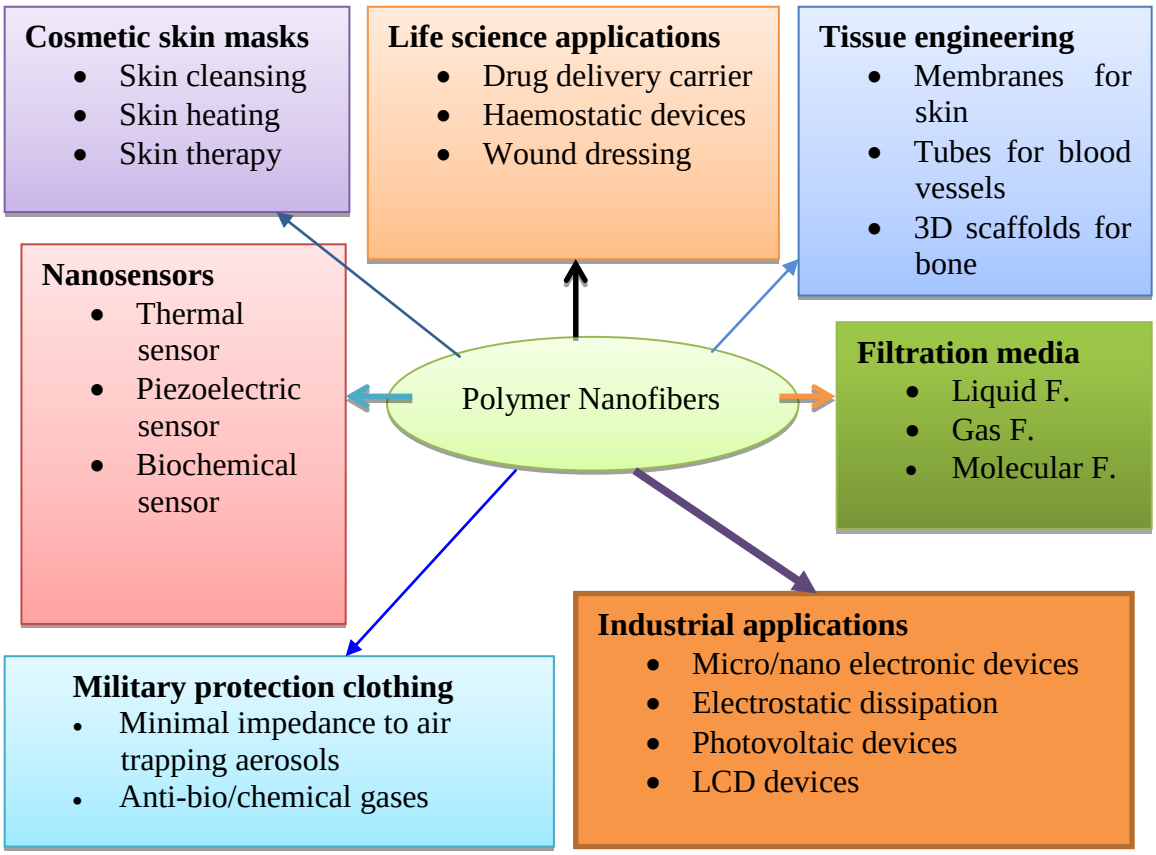


Figure 2.9: Potential applications of nanofibers.

Electrospinning has the unique ability to produce nanofibers of different materials in various fibrous assemblies. The relatively high production rate and simplicity of the setup makes electrospinning highly attractive to both academia and industry. A variety of nanofibers can be made for applications in energy storage, healthcare, biotechnology, environmental engineering, and defense and security [78]. The potential applications of nanofibers have been reviewed, as shown schematically in Figure 2.9 [139].

2.7.3.1. Healthcare applications

Current medical practice is based almost entirely on treatment regimes. However, it is envisaged that medicine in the future will be based heavily on early detection and prevention before disease manifestation. Together with nanotechnology, new treatment modalities will emerge that will significantly reduce medical costs. With recent developments in electrospinning, both synthetic and natural polymers can be produced as nanofibers with diameters ranging from tens to hundreds of nanometers with controlled morphology and function. The potential of these electrospun nanofibers in human healthcare applications is promising, for example in tissue/organ repair and regeneration, as vectors to deliver drugs and therapeutics, as biocompatible and biodegradable medical implant devices, in medical diagnostics and instrumentation, as protective fabrics against environmental and infectious agents in hospitals and general surroundings, and in cosmetic and dental applications.

2.7.3.2. Biotechnology and environmental engineering applications

High porosity, interconnectivity, microscale interstitial space, and a large surface-to-volume ratio mean that nonwoven electrospun nanofiber meshes are an excellent material for membrane preparation, especially in biotechnology and environmental engineering applications. Ligand molecules, biomacromolecules, or even cells can be attached or hybridized with the nanofiber membrane for applications in protein purification and waste water treatment (affinity membranes), enzymatic catalysis or synthesis (membrane bioreactors), and, in the future, chemical analysis and diagnostics (biosensors).

2.7.3.3. Defense and security applications

Military, firefighter, law enforcement, and medical personnel require high-level protection when dealing with chemical and biological threats (which include chemicals like nerve agents, mustard gas, blood agents such as cyanides, and biological toxins such as bacterial spores, viruses, and rickettsiae) in many environments ranging from combat to urban, agricultural, and industrial. Current protective clothing is based on full barrier protection such as hazardous materials suits, or permeable adsorptive protective overgarments such as those used by the US military. The obvious limitations of these suits are weight and moisture retention, which prevent the user from donning them for long periods. There are many avenues for future research in nanofibers from the defense perspective. As well as serving protection and decontamination functions, nanofiber membranes will also have to provide the durability, washability, resistance to intrusion of all liquids, and tear strength required of battle dress fabrics.

2.7.3.4. Energy generation applications

Natural energy resources such as crude oil, coal, natural gas, and uranium are a necessity for everyday life. Rapid economic growth in Asia and the subsequent increase in demand for energy mean that the rate of oil production is no longer adequate. Large volumes of carbon dioxide emitted by the burning of fossil fuels is also the main culprit in climate change. Thus, there is an urgent need to identify new sources of energy that are environmentally friendly and able to replace current supplies. Polymer batteries, fuel cells, photovoltaic cells, wind power generators, and geothermal power generators are some possible alternatives. Given their high porosity and inherent large total surface area, electrospun nanofiber membranes are being considered for polymer batteries, photovoltaic cells, and polymer electrolyte membrane fuel cells (PEMFCs).

3. EXPERIMENTAL PART

3.1 Materials

Hydrochloric acid (37 %) and dimethylformamide (73.09 g/mol) were purchased from Sigma Aldrich. Polyacrylonitrile with a density of 1.84 g/cm^3 was obtained from Sigma Aldrich and Poly(anthranilic acid) was synthesized by Potsdam University, Germany. All of these chemicals were analytical and used as received.

3.2 Preparation of Poly(anthranilic acid)/Polyacrylonitrile Blends

Different amounts of Poly(anthranilic acid) was dissolved in 10 ml DMF containing 0.5 g Polyacrylonitrile. Polyacrylonitrile solutions [(without any Poly(anthranilic acid)] were prepared and characterized to indicate the differences between [PANA/PAN] blends prepared by changing amounts of PANA (0.05 g, 0.075 g and 0.1 g). The obtained solutions were stirred magnetically for 3 hours at 50 °C in order to get homogeneous blends with enough viscosity for electrospinning.

3.3 Electrospinning Setup

The electrospinning apparatus consisted of a syringe pump (NE-500 Model, New Era Pump Systems, Inc., USA) with a feeding rate from 5.5 uL/h to 400 mL/h, a high voltage direct current (DC) power supplier generating positive DC voltage up to 50 kV DC power supply (ES 30 Model, Gamma High Voltage Inc., USA), and a grounded collector loaded into a syringe.

A positive electrode was clipped onto the syringe needle, having an outer diameter of 0.7 mm. The feeding rate of the polymer solution was controlled by a syringe pump and the solutions were electrospun horizantally on to the collector (Figure 3.1). The polymer blends were electrospun to obtain nano fibers at room temperature at 15 kV driving voltages. The feeding rate was 1ml/h and the distance between the capilary tip and the collector was constant, 15 cm.

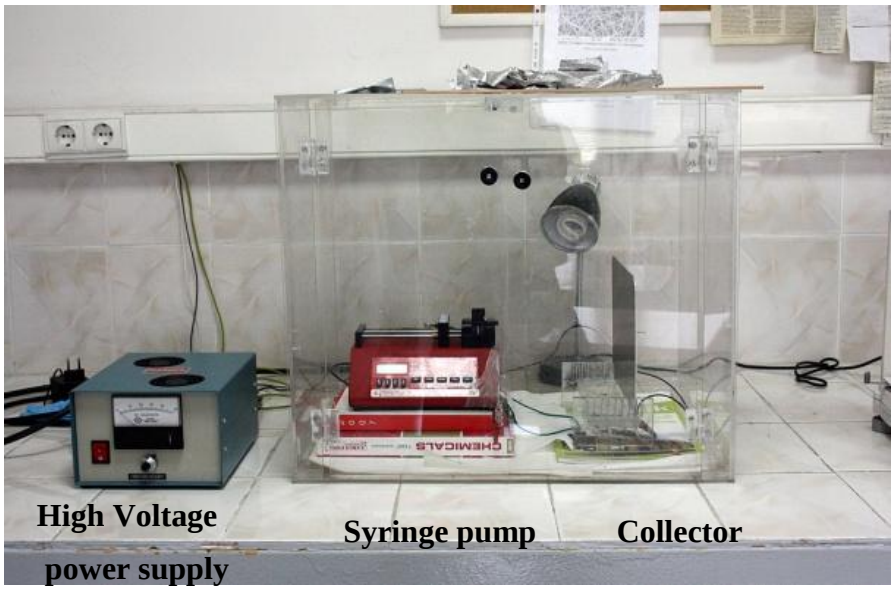


Figure 3.1: A representative picture captured during electrospinning.

3.4 Characterization of Poly(anthranilic acid)/Polyacrylonitrile Blends

Fourier transform infrared – attenuated total reflectance (FTIR-ATR) analysis of the nanofibers was carried out by a FTIR reflectance spectrophotometer (Perkin Elmer, Spectrum One, with a universal ATR attachment with a diamond and ZnSe crystal). The effect of the PANA on the resulting nanofibers were also characterized by UV-Visible (Perkin Elmer, Lmabda 45) spectrophotometric analysis. The morphology of the electrospun nanofibers were observed with a Leo Supra 35 VP Scanning Electron Microscope after the mats were coated by gold. Conductivity measurements were investigated using by Broadband Dielectric/Impedance Spectrometer (BDS-40). Electrochemical measurements (EIS with supplied Power Sine software package and Cyclic Voltammograms) were performed with a Princeton Applied Research (PAR) Parstat 2263 potentiostat (Oak Ridge, USA). The potentiostat is a self-contained unit that combines potentiostatic circuitry with phasesensitive detection. The impedance measurements were carried out by scanning in the frequency range 10 mHz–100 kHz with applied AC signal amplitude of 10 mV using Power Sine. The impedance spectrum was analyzed using AC impedance data analysis software (ZSimpWin V3.10, Michigan, USA). For cyclic voltammetric measurements, Poly(anthranilic acid)/Polyacrylonitrile electrospun nano fibers were covered onto ITO-PET (NV Innovative Sputtering Technology, Zulte, Belgium, PET 175 µm,Coating ITO-60) in the potential range from –0.3 to 1.2 V at a scan rate of 20, 50 and 100 mV/s in 0.1M HCl/H_20.

4. RESULTS AND DISCUSSION

4.1. UV-Vis Spectrophotometer

Electrically conducting composite containing different amounts of PANA was followed by UV-Visible spectroscopy in dimethylformamide solution of nanofibers of [PANA/PAN] blends. The spectra consists of bands with the maxima located at about 536 and 370 nm. These peaks are characteristic for PANA absorption and confirms the formation of PANA in the nanofiber.

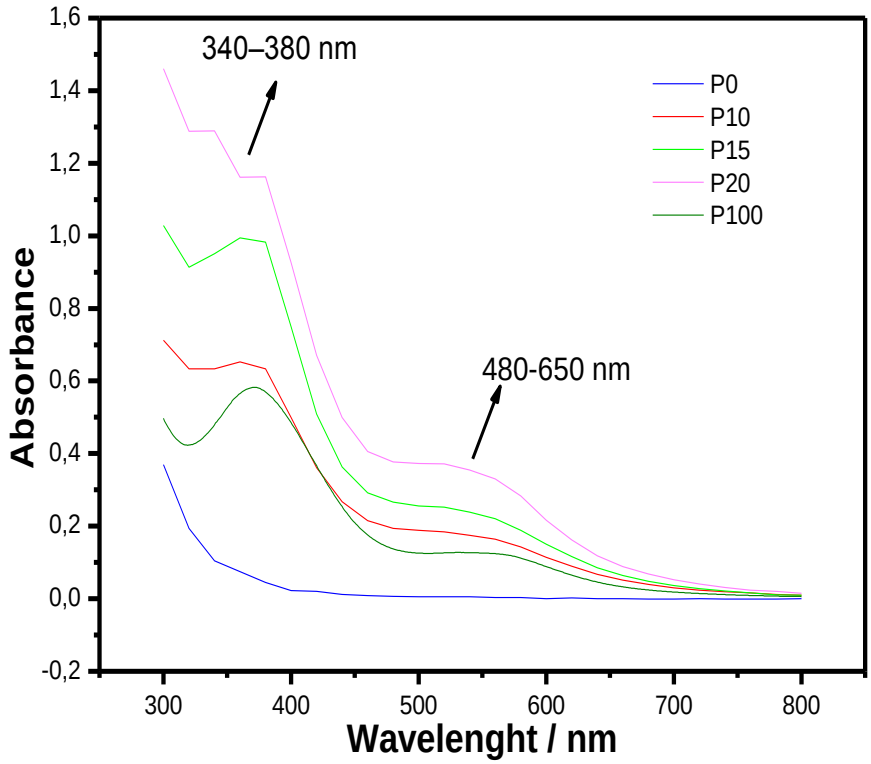


Figure 4.1: UV-Vis Spectrum of the [PANA/PAN] Nanofibers including different amount of PANA, P0 and P100 indicate that dissolved nanofiber mats contain no PANA, dissolved nanofiber mats contain no PAN, respectively.

0.1 g [PANA/PAN] electrospun nanofibers with different initial mass ratios (including 0.05 g, 0.075 g and 0.1 g PANA, respectively) were dissolved in DMF (20 ml) and peaks were exhibited between 340-380 nm, corresponding to π- π* transition in benzene ring of Poly(anthranilic acid). The broad absorption band extended from 480 nm to 650 nm due to the existence of polaron bands [140–142]. These bands have been found to dependent on the overall oxidation state of the polymer (Figure 4.1). As the amount of the PANA increases, hyposchromic shift also rises (from 380 nm to 312 nm and from 650 nm to 480 nm) [142–144]. The hyphochromic shifts illustrate that carboxylate groups' steric effect in the polymer chain leads perturbation of the coplanarity of the π system; thus, it decreases the level of conjugation and prevents the charge transfer among the chains [145]. Spectrum of PAN nanofibers dissolved in DMF (20 ml) was also investigate by UV-Vis. Spectrophotometer for comparison. Any peak was not observed from PAN nanofibers between 300-800 nm.

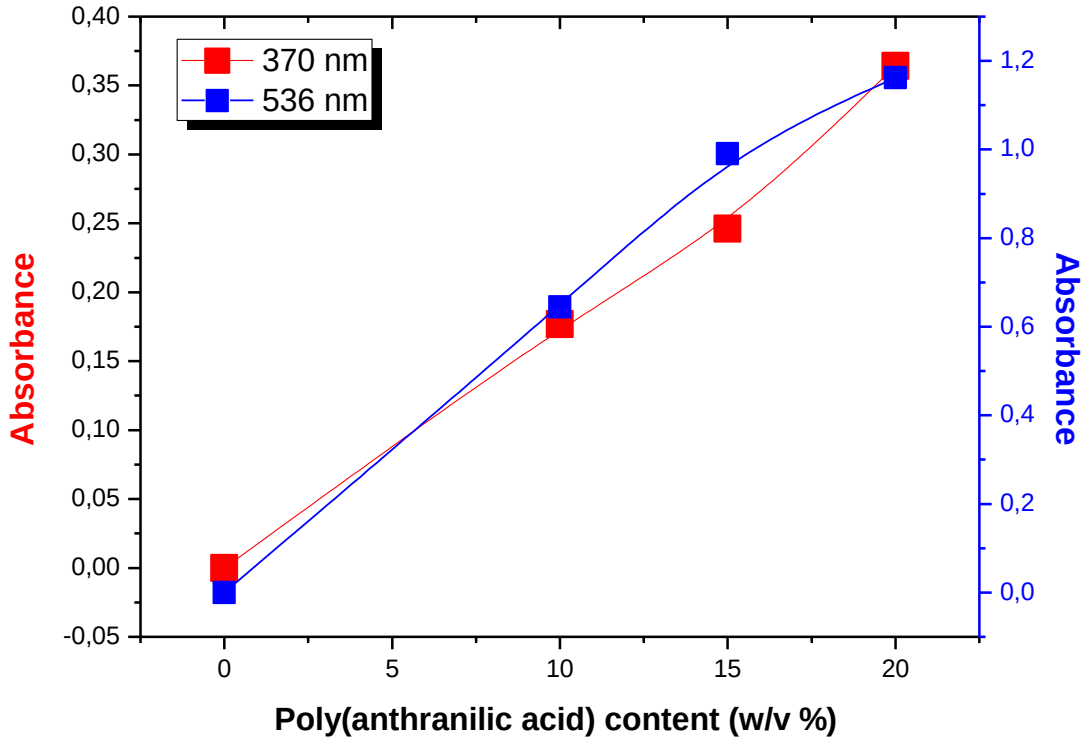


Figure 4.2: Absorbance values of dissolved electrospun nanofiber mats (P0, P10, P15, P20) within the DMF, red line shows the values occured in UV Region (370 nm) and blue one shows the values occured in Visible Region (536 nm).

Several parameters including chain length, the overall oxidation state of the polymer, interchain or interchain charge-transfer, the extent of conjugation amoung adjacent phenyl rings, the steric effect of the carboxylate groups in the polymer chain indicate the real band positions of the spectra (Figure 4.2) and the changes in these band positions are probably the cause of the changes in these parameters [146].

Self-doping gives the benefit of being a faster doping process than the one illustrated in externally doped polyanilines in which the dopant ion has to be in motion in and out of the polymer chain. The Polyanthranilic acid/Polyacrylonitrile interaction was presented in the Figure 4.3 [141].

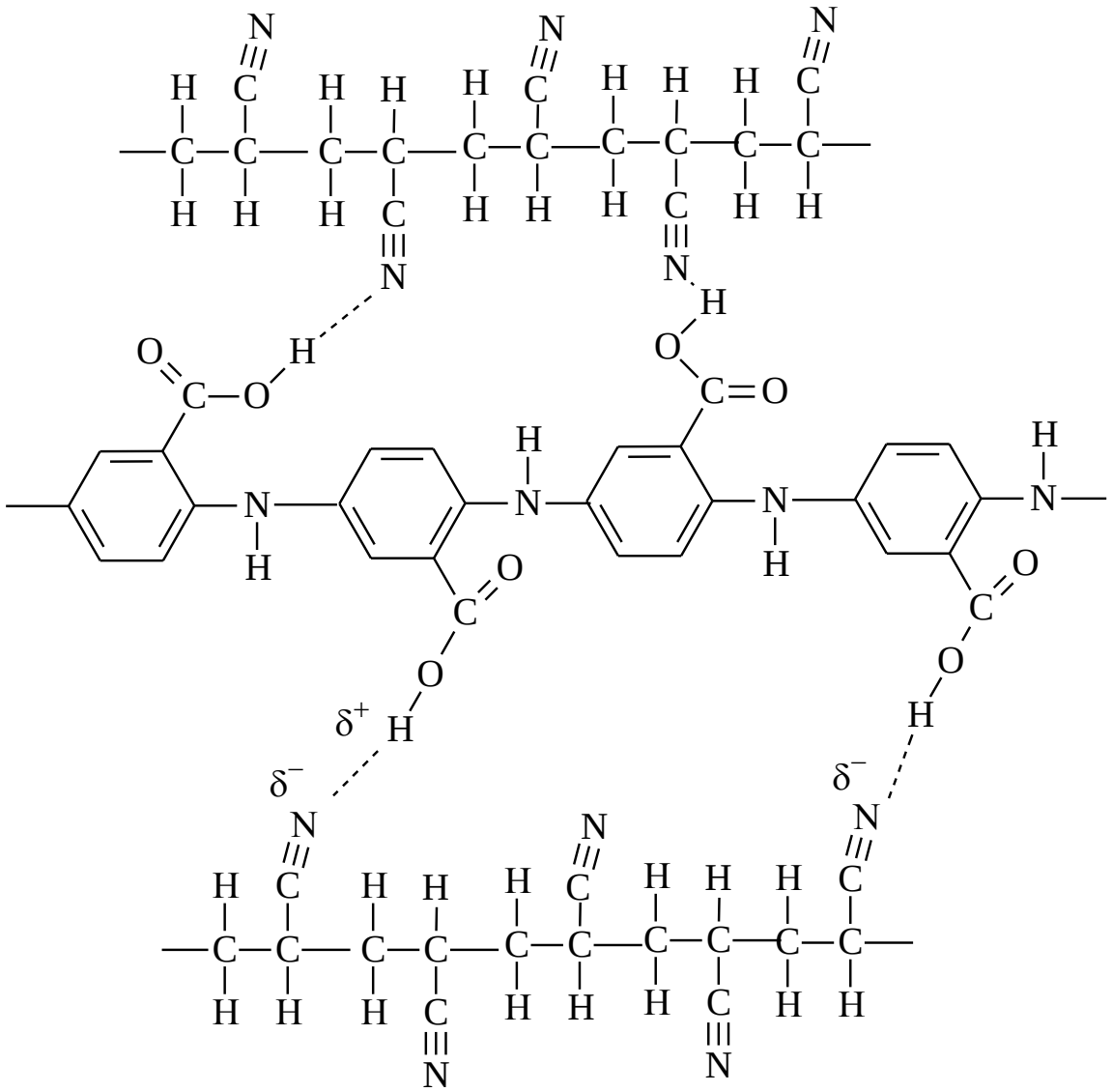


Figure 4.3: [PANA/PAN] interaction.

According to the literature, the UV peak levels obtained reached to the form as the conducting emeraldine salt and thus the structure of PANA presented similarity with the one in the literature [141].

4.2 FTIR-ATR Spectrophotometric Analysis

FTIR-ATR spectrum of [PAN/PANA] nanofibers were given in Figure 4.4 (a) and (b); 3220 cm^{-1}, 1698 cm^{-1}, 1514 cm^{-1} peaks respectively refered to carboxylic acid OH streching, C=O streching and C=C streching of benzenoid rings [142, 144, 147, 148]. In addition, the band appearing at 732 cm^{-1} cm probably corresponds to the C-H out of plane bending vibration of the 1, 2, 3 trisubtituted benzene rings [141–143]. The peak at 1450 cm^{-1} refers to C-O streching vibration of the carboxylic group and its therefore proved that both –COOH and –COO groups are involved in the resulting polymer chain. These results provide the presence of an emeraldine structure for Poly(anthranilic acid) [142].

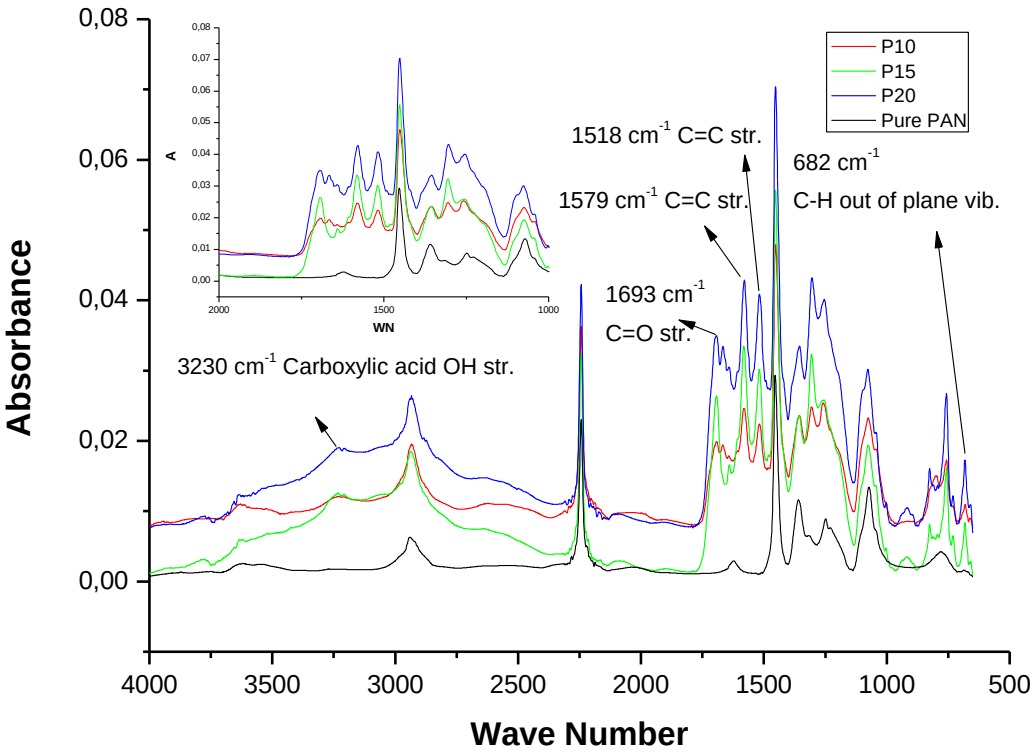


Figure 4.4: FTIR-ATR Spectrum of [PAN/PANA] nanofibers with different amount of PANA between 500 – 4000 cm-1 (a) and 1000 – 2000 cm-1 (b).

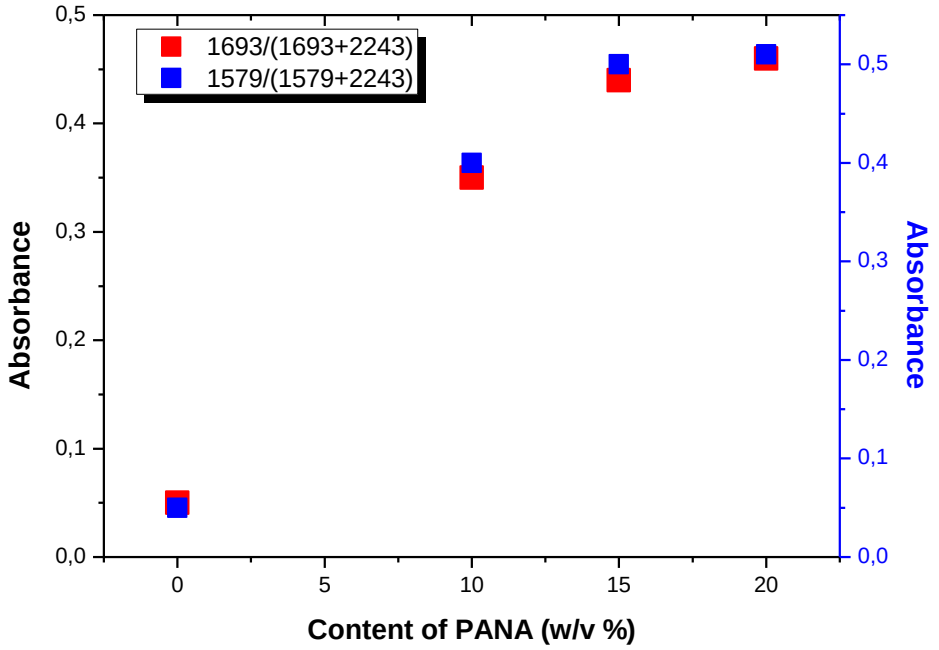


Figure 4.5: FTIR-ATR Graph shows the increasing of absorbance values with the ratio of peaks 1693 to 2243 cm-1 (red points) and 1579 to 2243 cm-1 (black points) versus PANA concentration (w/ v %), peak at 1693 and 1579 refer to C=O streching and C=C str., respectively.

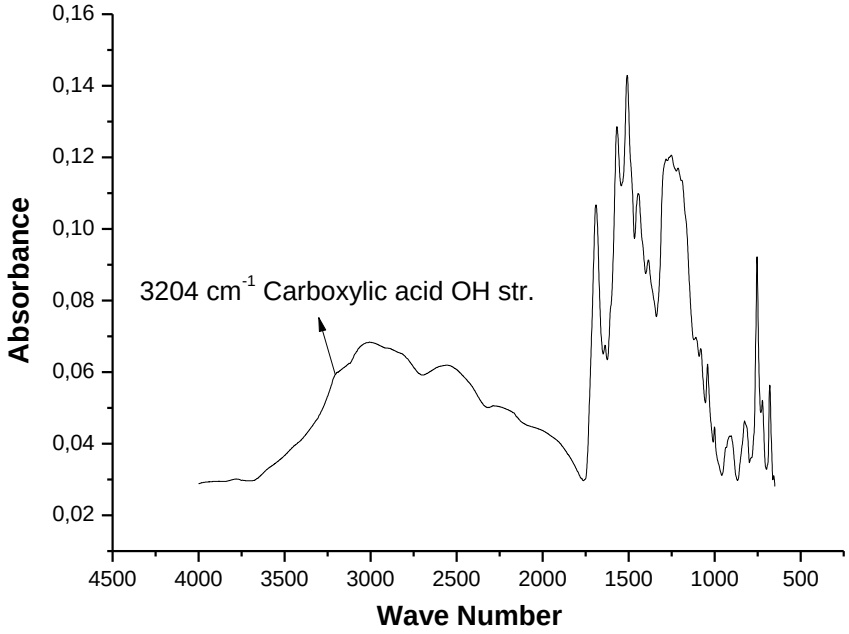


Figure 4.6: FTIR-ATR Spectrum of Poly(anthranilic acid) with its characteristic peak at 3204 cm-1

Their intensity surged by the increase of PANA displayed in the Figure 4.5. According to the literature the absorption band appearing at 1663 cm-1 is C=O stretching of DMF and it may effect on the increase of mechanical strenght of the composite nanofiber [155–157]. Figure 4.6 shows the spectrum of Poly(anthranilic acid) within the polymer form.

4.3. Morphology of Electrospun Nanofibers of PANA/PAN Blends

Morphological studies were performed via SEM observation of the cross section of nanofiber samples with a Leo Supra 35 VP scanning electron microscope. SEM images show that morphology of the nanofibers of [PANA/PAN] blends changed with different amount of [PANA] of the mixed polymers. The morphologies of electrospun nanofibers are presented in Figures 4.7 (a)-(h). According to the SEM images, the diameters of the [PANA/PAN] nanofibers are dependent on initially added PANA concentrations in the reaction mixture. The diameter of [PANA/PAN] fibers was smaller than for pure PAN fibers. The average nanofiber diameter decreased from 113 ±23 nm for pure PAN fibers to 105 ±23 nm for [PANA/PAN] (10 w/v %), 102 ± 20 nm for [PANA/PAN] (15 w/v %) and 94 ± 16 nm for [PANA/PAN] (20 w/v %) was shown in Table 2.

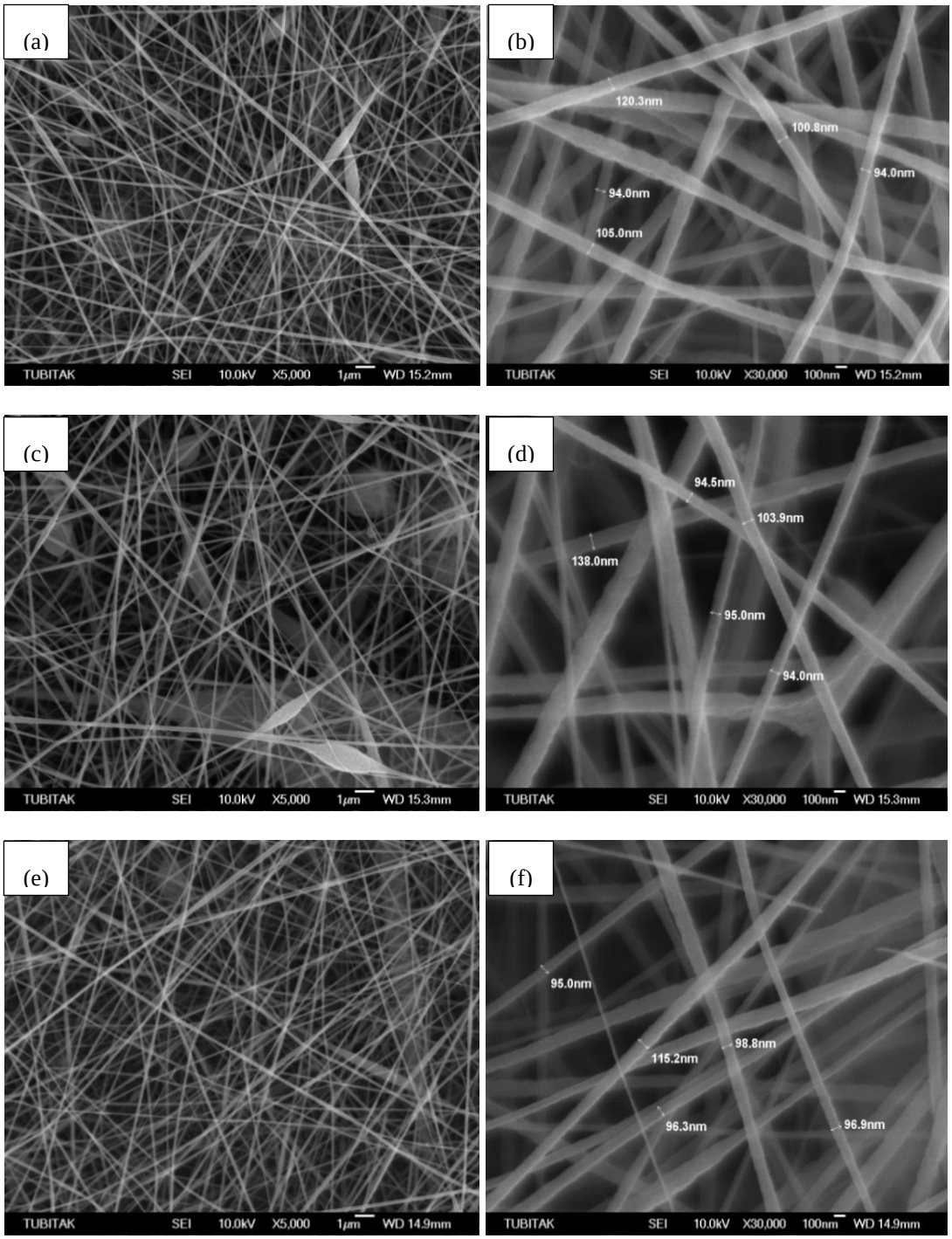
Table 2: Avg. Diameter of Electrospun Nanofibers (0, 10, 15, 20 PANA content % w/v).

Sample Name	**Avg. Diameter of NFBs (nm)**
P0	113 ±23
P10	105 ±23
P15	102 ± 20
P20	94 ± 16

Our method exhibits that PANA is homogenously distributed in the [PANA/PAN] blends. A similar trend was found by Li et al and N. Abdul Rahman et al [33] for PANI (Polyaniline) and Poly Lactic Acid (PLA) [149]. The diameter of the as spun nanofibers was in the range of 500-800 nm, and that of the treated ones was in the range of 300-500 nm. PAN/PMMA nanofibers with or without post drawing

treatment [150]. From the SEM micrographs(Figure 4.7), it is clearly seen that PANA dispersion site in PAN matrix is on nano-level.

This excellent dispersion is assigned to the interaction (hydrogen bonding) between two functional groups of PANA and PAN, namely C-OH and CN groups which is the case of low percolation threshold [151].



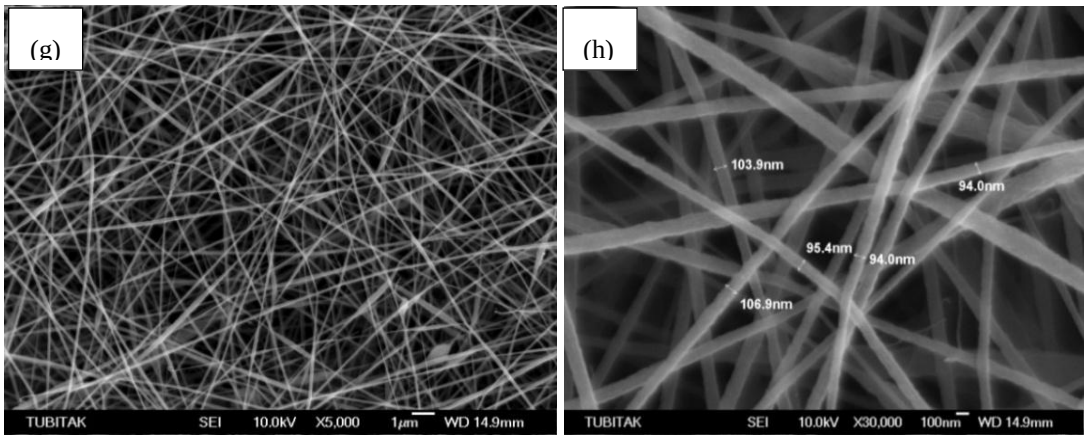
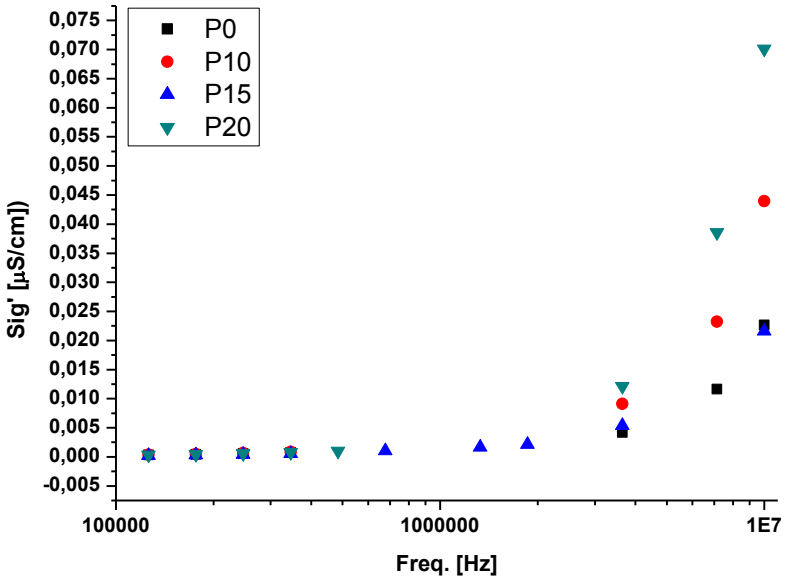


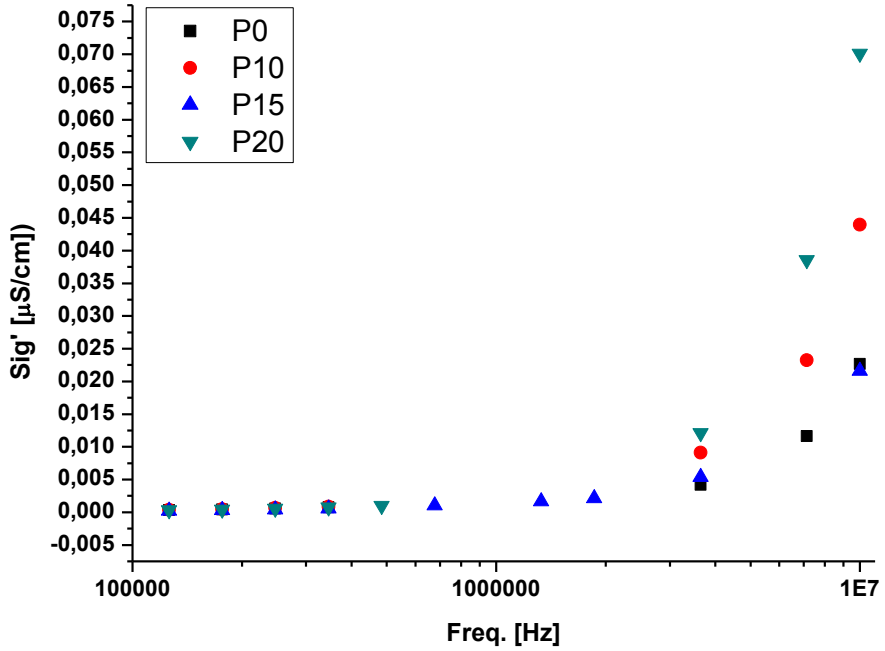
Figure 4.7: SEM Images of Nanofibers 0 w/v % [PANA/PAN] X5000 (a) and X30000 (b), 10 w/v % [PANA/PAN] X5000 (c) and X30000 (d), 15 w/v % [PANA/PAN] X5000 (e) and X30000 (f), 20 w/v % [PANA/PAN] X5000 (g) and X30000 (h).

4.4 Broadband Dielectric Spectrometer

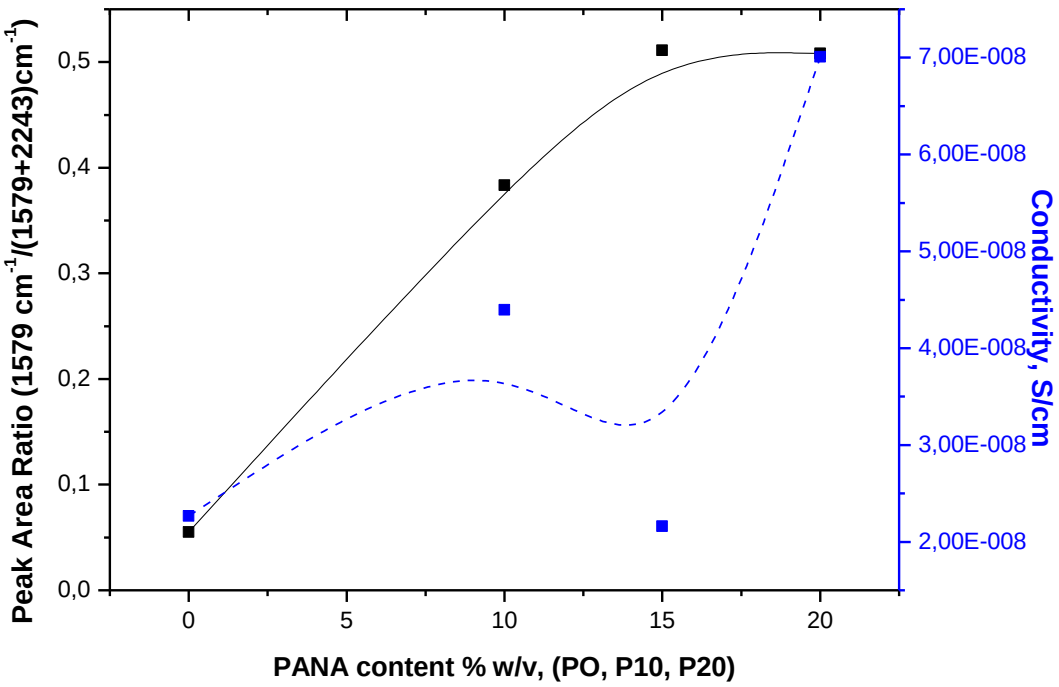
Conductivity measurements were analyzed using by Broadband Dielectric Spectrometer (BDS-40). Nanofiber mat samples were prepared with the area of 2,5 cm^2 for the measurement. As a result, conductivity values has increased with the increase of Poly(anthranilic acid) content. Figure 4.8 and 4.9 show the conductivity changes with the increase of conducting polymer in the nanofiber composite and the nyquist values of the nanofibersi, respectively.



Fgure 4.8: Conductivity values vs. content of PANA.

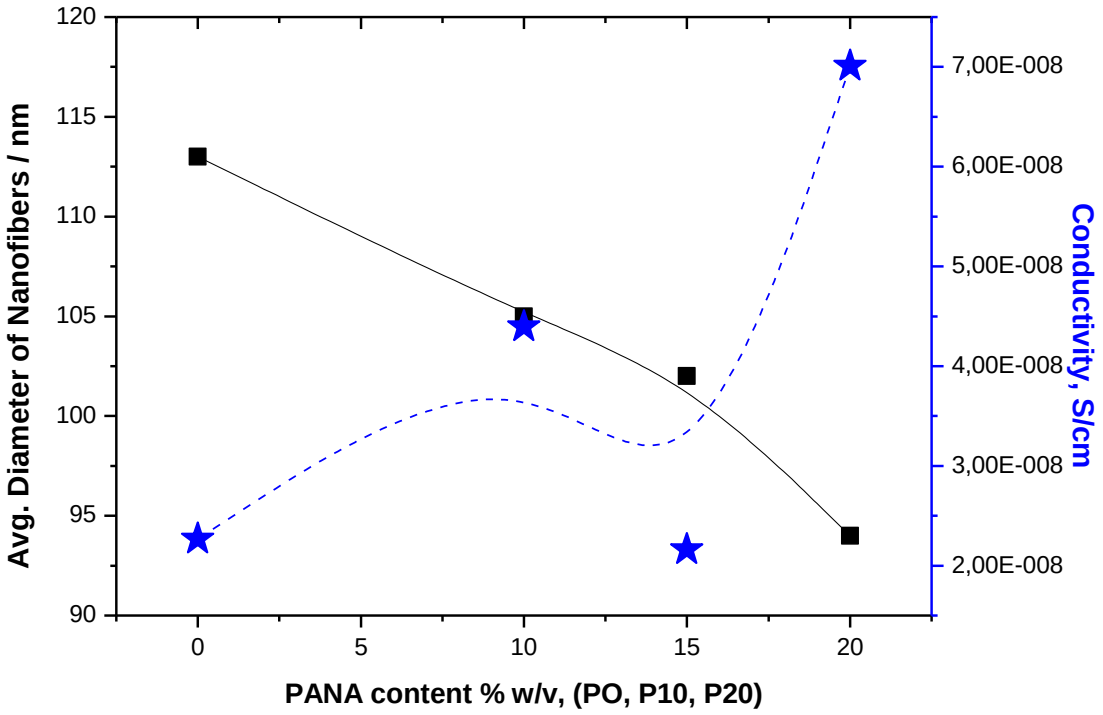


Fgure 4.9: Nyquist values of obtained from solid form of the nanofibers.



Fgure 4.10: Variations between the peak area ratio of 1579 cm^{-1}/(1579+2243)cm^{-1} and conductivity as a function of PANA content.

Figure 4.9 presents the variations between the peak are ratios of 1579 cm-1 whisc refered the C=C stretching band and 2243 cm-1 CN which indicate the stretching band. When the PANA content increased, the conductivity increased in parallel to the peak area ratio of C=C stretching. It indicates that PANA and PAN successfully well dispersed in DMF solution, and PANA formation can be followed by Fourier Transform Infrared-Attenuated Total Reflectance (FTIR-ATR) measurments. Figure 4.10 shows the relationship between average diameter of the nanofibers and the conductivity related to the amount of PANA.



Fgure 4.11: Conductivity values decreased with average diameter of the nanofibers increase.

4.5 Cyclic Voltammetry

The electrochemical behaviour of nanofibers of [PANA/PAN] blends on ITO-PET electrode was tested through cyclic voltammetric measurements in an acidic electrolyte including of 1M HCl and cyclic voltammogram were recorded at a sweep rate of 20, 50 and 100 mV/s. Figure 4.12 (a) depicts the oxidation/reduction process of [PANA/PAN] nanofibers on ITO-PET electrode.

Spectroelectrochemical cell consisting of an optically transparent indium tin oxide (ITO) coated PET (NV Innovative Sputtering Technology, Zulte, Belgium, PET 175 μm,Coating ITO-60) as working electrode, Ag/AgCl and Pt wire as reference and counter electrodes, respectively [152].

Unlike polyaniline and many of its substituted forms, [PANA/PAN] nanofibers do not show well defined redox peaks in the potential range from -0,3 to 1,2 V. Among them, a pair of current peaks at about 0,2 V corresponding to the reversible transformation of leucomeraldine/emeraldine and another pair at about 0,7 V corresponding to emeraldine/pernigraniline reversible transition are prominent [153]. The voltammogram is characterized by a pair of broad current peaks in 0,5-0,6 V range, suggesting the electrochemical activity of PANA present in the [PANA/PAN] blends. The nature of this voltammogram differs from the voltammogram of PANI films because of the presence of –COOH group on PANI backbone [154].

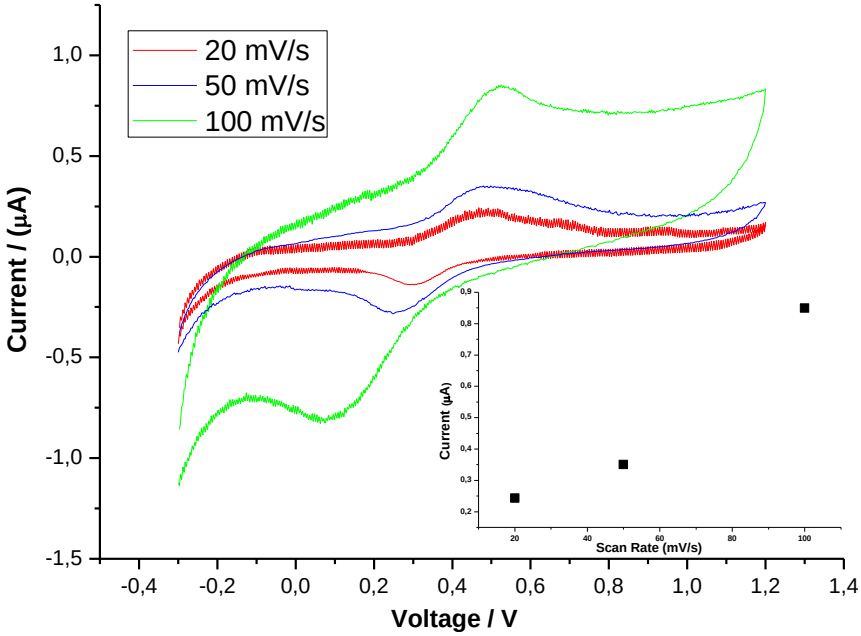


Figure 4.12: Cyclic Voltammogram of the Nanofibers of 20 w/v % [PANA/PAN] with different scan rates as 20, 50 and 100 mV/s (a) and the graph indicates that increasing of current values depending on scan rates (b).

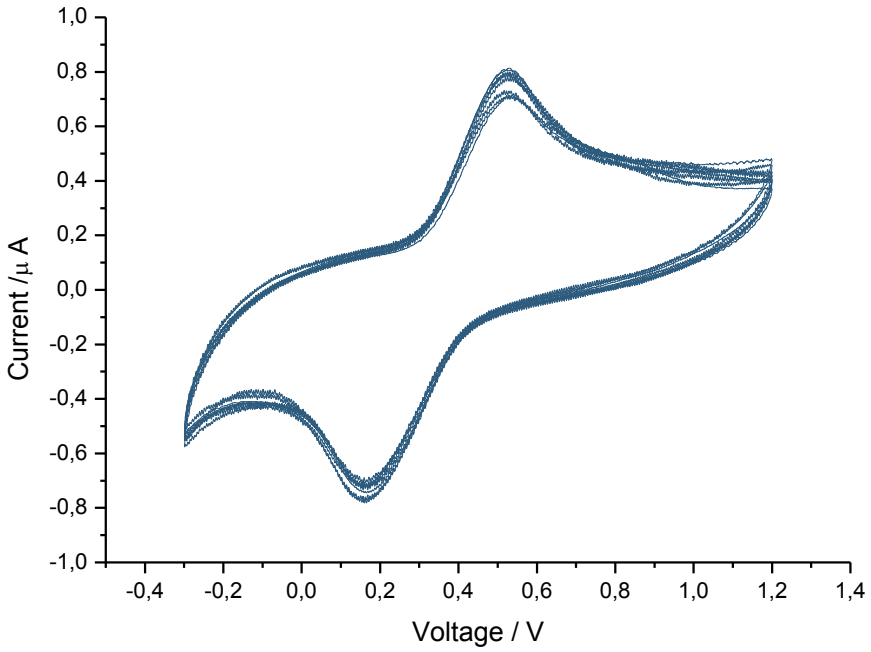


Figure 4.13: The stability of the film coating on ITO-PET with increasing the number of cycles in monomer free solution (1M HCl).

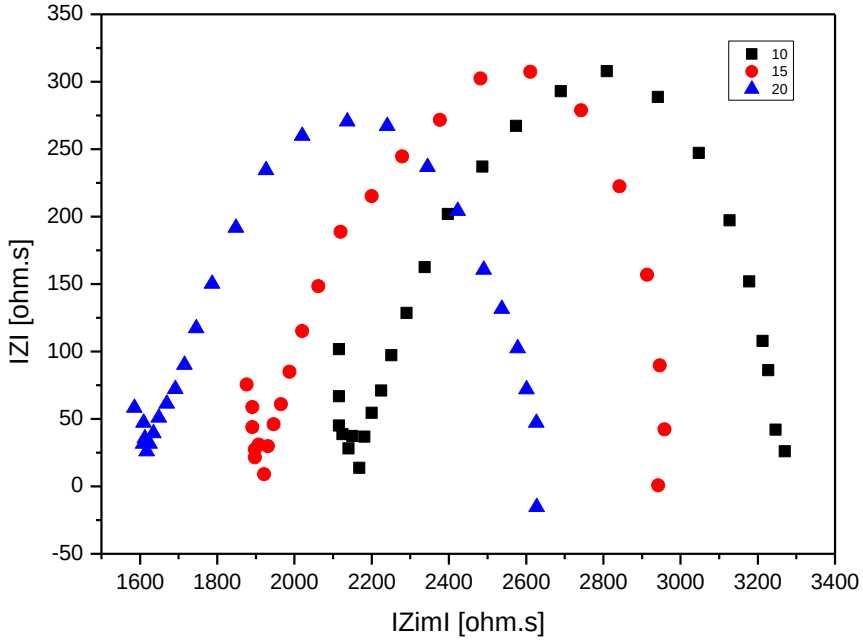
In addition to this, different scanning rates were used to examine the dynamic property of [PANA/PAN] blends during the redox process (Figure 4.12 (a)). As is shown in Figure 4.12 (b) the peak current is proportional to the scan rates, suggesting an electric charge-transfer controlled process. Exhibited a reversible behaviour indicating the radical cation formation and reduction of these sites reversibly in the electrolyte which can be used as a sensing to the ions electrolyte. High surface area and presence of carboxyl group result a high current during oxidation and reduction. Figure 4.13 shows the stability of the film coating on ITO-PET with increasing the number of cycles in monomer free solution. Further detailed electrochemical study on these fibers are in progress.

4.5. Electrochemical Impedance Spectroscopy

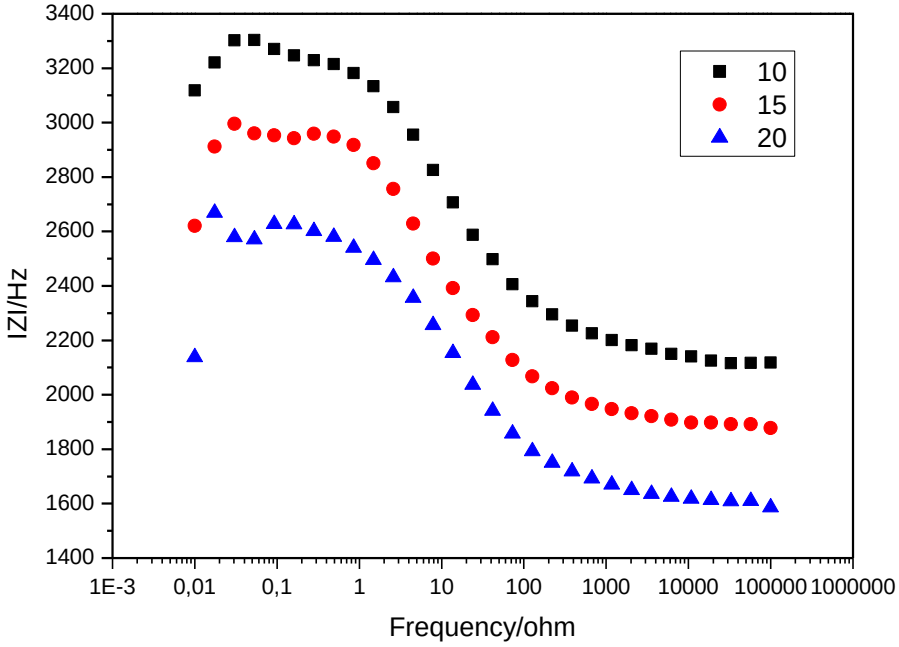
The electrical properties of these electrospun nanofibers were determined by electrochemical impedance measurements in monomer free solution for the first time. The Nyquist, Bode Magnitude and Bode Phase plots of the fibers were given in the frequency range 0.01 Hz–100 kHz (Figure 4.14 (a–c)). Bodephase angles which

approached the maximum at 15.20 Hz were ~ 6.17° for 10% w/v, ~6.58° for 15% w/v and ~7.27° for 20% w/v, respectively, (Figure 4.11 (c)).

(a)



(b)



(c)

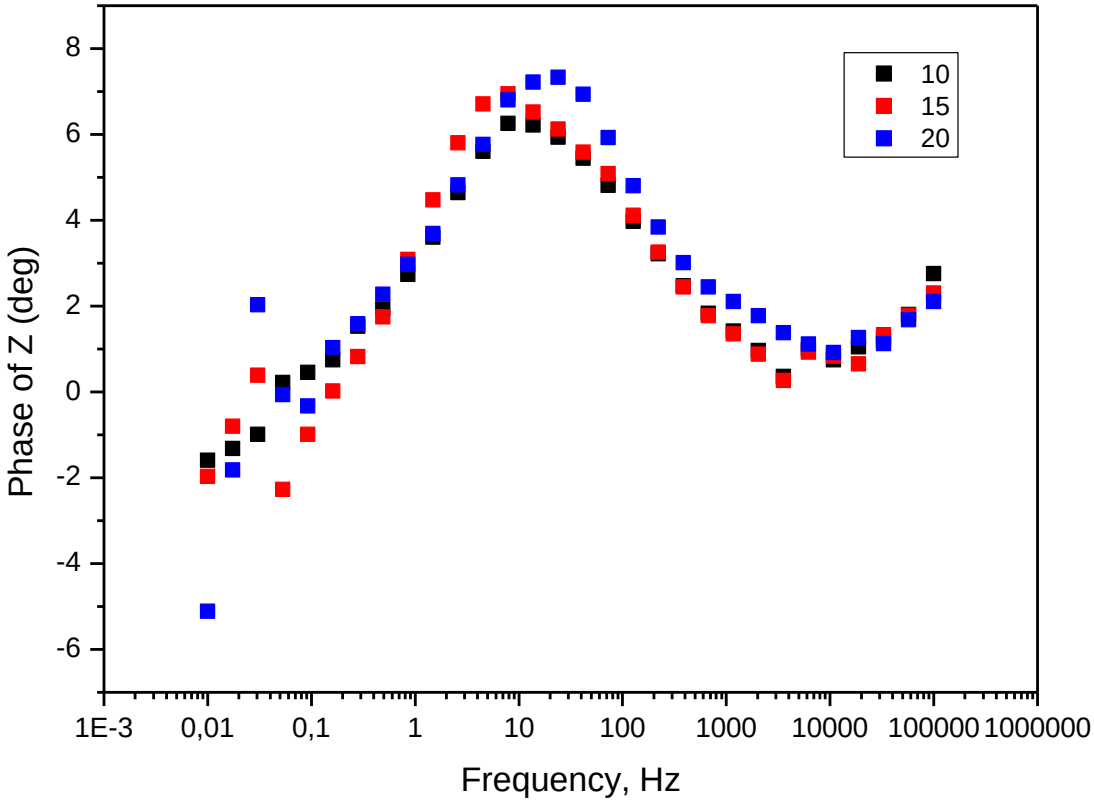
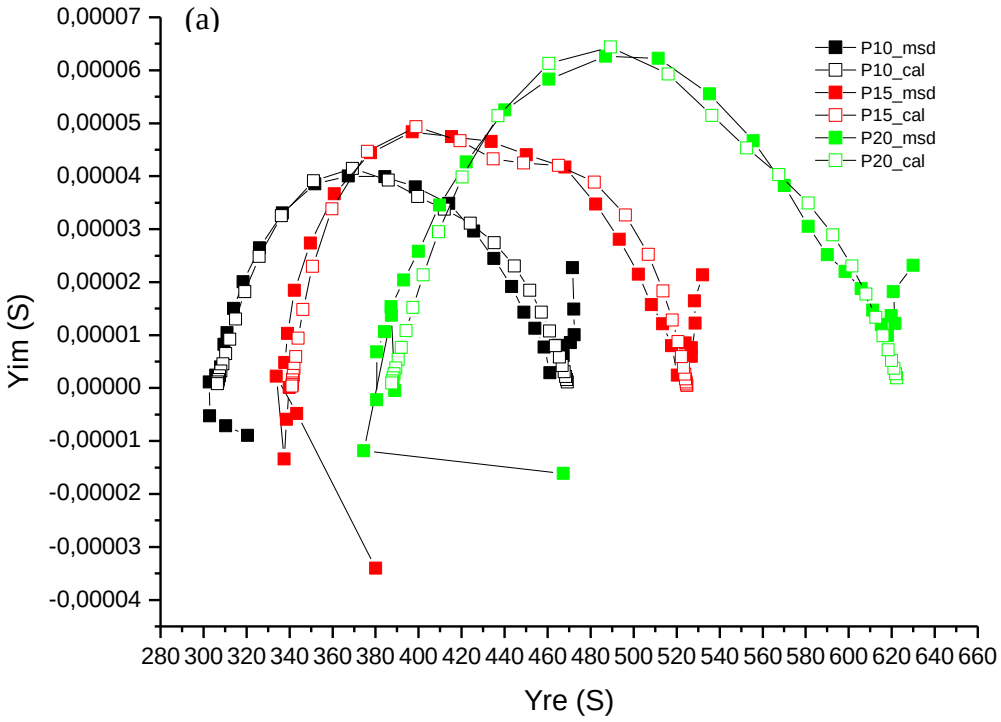


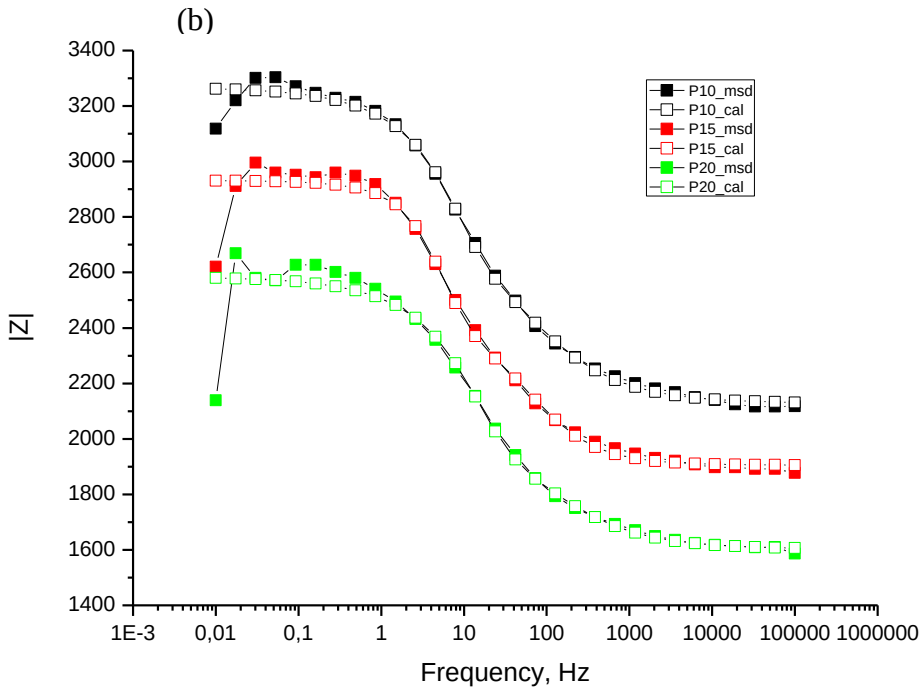
Figure 4.14: (a) Nyquist (b) Bode magnitude (c) Bode phase plots of of different mole fractions of PANA/PAN composite nanofibers; correlated with the calculated data from the equivalent circuit modelling; (R(Q(R(CR))).

That indicates the presence of PANA in the composite structure. The Bodephase peaks of the fibers in the frequency range of 10 000 Hz–100 000 Hz appeared whichindicate that nanofibers of [PANA/PAN] can not used as a capacitor. The Bode magnitude plots for copolymers were presented in Figure 4.14 (b), PANA with 20% w/v had higher conductivity compared to 10% w/v and 15% w/v.

Nyquist plots were also used to estimate the low-frequency redox capacitance (C_{LF}) of the composite fibers. It can be evaluated from the equation $C_{LF} = -1/(2\pi \cdot f \cdot Z_{IM})$, where Z_{IM} is the obtained from the slope of a plot of the imaginary component of the impedance at low frequencies versus inverse of the reciprocal frequency f (f = 0.01 Hz) and other symbols have their usual meanings. The C_{LF} of composite nanofibers slightly decreased which indicates the increase of PANA concentration in the blend

(Table 3). The Nyquist plots (complex plane plots) were semicircles and formed under ideal conditions for biosensing [155].





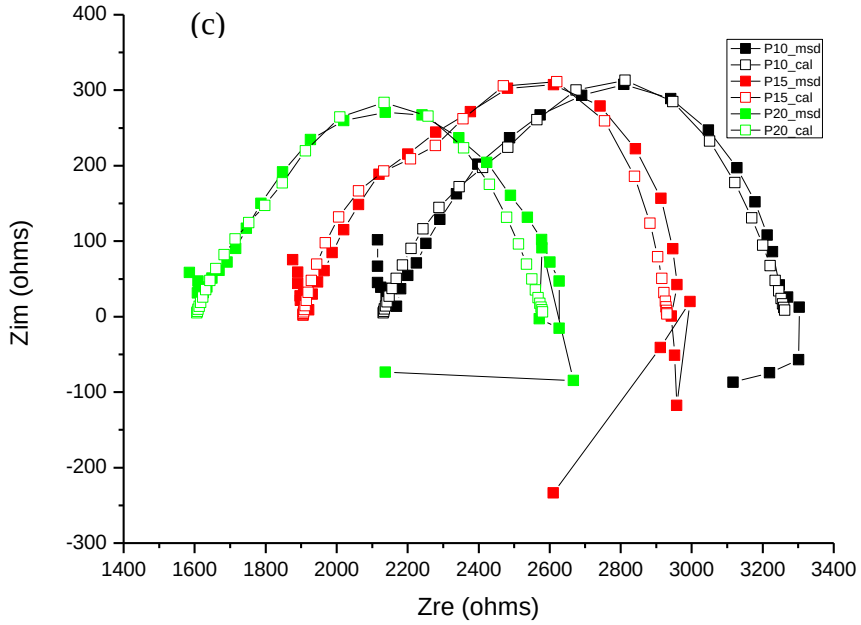


Figure 4.15: (a) Admittance, (b) Bode Magnitude, (c) Nyquist plots indicating that measured and calculated datas well fitted to each other with this model.

Figure 15 indicates that calculated datas and measured datas were well fitted with the chosen model.

Table 3: Content of PANA dependence of parameters calculated from the equivalent circuit model for the electrospun nanofibers of [PANA/PAN] blends.

	10 w/v % PANA	**15 w/v % PANA**	**20 w/v % PANA**
R_S [Ω]	2128	1905	1603
CPE [$\Omega \cdot s^{-1}$]	4,226E-5	2,147E-5	4,272E-5
n	0,6178	0,8	0,8
R_{ct} [Ω]	735,1	570,9	535,6
C_{nfb} [mF]	3,034E-5	5,351E-5	1,394E-5
R_{nfb} [Ω]	404,8	456	445,3
Chi Squred	3.991e-04	1.198e-03	1.733e-03

The diameter of the semicircle increased with an increase of PANA in the composite. It corresponds to the charge transfer resistance which included in the equivalent circuit (Figure 4.16) as the resistance of the composite fiber.

4.6. Modelling

The EIS data were fitted with an equivalent electrical circuit in order to characterize the electrochemical properties of copolymer.

The experimental results and values obtained from equivalent circuit modelling have shown that both the charge transfer resistance and the double-layer capacitance decreased with the increase of incorporated PANA ratio into composite structure.

The impedance spectra for nanofibers may be described by the equivalent circuit of Figure 4.16, (R(Q(R(CR))).

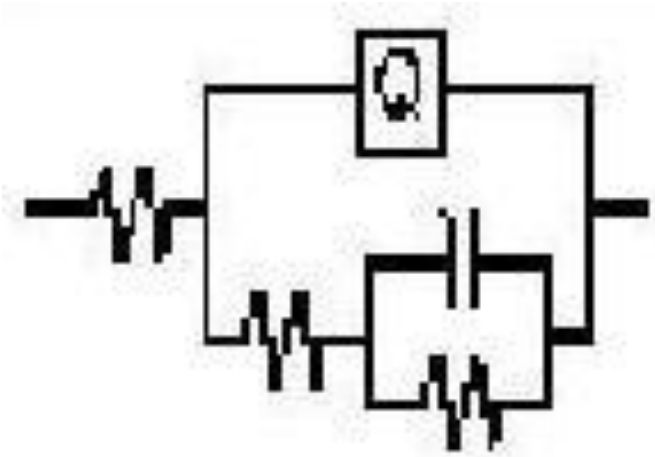


Figure 4.16: The euivalent circuit model of the electrospun nanofibers of [PANA/PAN] blends; R_s = solution and pore resistance, R_{nfb} and C_{nfb} are the resistance and the capacitance of the nanofiber; R_{ct} = charge transfer resistance; CPE is used for modelling the double layer capacitance.

5. CONCLUSION

The first objective of this theses was to obtain nanofibers of Poly(anthranilic acid)/Polyacrylonitrile blends by electrospinning method. The peaks observed in the UV-Vis spectrum were proved by the new bonds formed in FTIR spectroscopy. SEM images indicate that the diameters of [PANA/PAN] nanofibers were dependent on the amount of Poly(anthranilic acid). By the change in amount of PANA, electrospun nanofibers of [PANA/PAN] blends as small as 94±16 nm were successfully produced.

The second objective of this theses was to produce nanofibers of Polyacrylonitrile based conductive polymers with unique properties imparted by the presence of Poly(antranilic acid), which we have succeeded to obtain electrospun nanofiber of [PANA/PAN] blends for the first time. These results indicate that successful preparation of surfaces with PAN based conducting polymers are possible by using electrospinning technique. The decrease in the average values of fiber diameter was obtained via SEM images taking into account the diameter of the PAN. The diameters for the fibers were calculated from an average of 25–30 measurements on individual fibers. The electrochemical behaviour of nanofibers of [PANA/PAN] blends on ITO-PET electrode was tested through cyclic voltammetric measurements in an acidic electrolyte including of 1M HCl and cyclic voltammogram were recorded at a sweep rate of 20, 50 and 100 mV/s. The electrical properties of electrospun nanofibers were determined by electrochemical impedance measurements in monomer free solution for the first time. Experimental impedance spectra were well fitted to the calculated data which was obtained from equivalent circuit modelling with (R(Q(R(CR))). According to the results of dielectric measurements, conductivity level of [PANA/PAN] composite nanofibers was not protonated form of PANA. Two techniques were used to calculate the conductivity, EIS and BDS. Both of them gave the similar results, while BDS measurements show the conductivity at around 10E-8 with the highest frequency value, EIS

measurements indicates the conductivity with 10E-5 because of HCl used in EIS experiment. In brief, EIS can be used to estimate conductivity of the composite nanofibers, truely.

REFERENCES

[1] Handbook of Organic Conductive Materials and Polymers (Ed.: H. S. Nalwa), Wiley, New York, 1997; Handbook of Conducting Polymers (Eds.: T. A. Skotheim, R. L. Elsenbaumer, J. F. Reynolds), (2004), 2nd ed., Marcel Dekker, New York, 1998. Coontz and B. Hanson, Science 305.

[2] **H. Spanggaard and F. C. Krebs**, (2004) "A brief history of the development of organic and polymeric photovoltaics," Sol. Energy Mater. Sol. Cells, vol. 83, no. 2/3, pp. 125–146.

[3] **R. Poddar and C. Lio**, (2006) "A novel approach to fabricate a PPy/p-type Si heterojunction," Solid State Electron., vol. 50, no. 11/12, pp. 1687–1691.

[4] **M. Campos, L. O. S. Bulhoes, and C. A. Lindino**, (2000) "Gas-sensitive characteristics of metal/semiconductor polymer Schottky device," Sens. Actuators A, Phys., vol. 87, no. 1/2, pp. 67–71.

[5] **V. Saxena and K. S. V. Santhanam**, (2003) "Junction properties of Schottky diode with chemically prepared copolymer having hexylthiophene and cyclohexylthiophene units," Current Appl. Phys., vol. 3, no. 2, pp. 227–233.

[6] **Ö. Yavuz, M. K. Ram, M. Aldissi, P. Poddar, and H. Srikanth**, (2005) "Polypyrrole composites for shielding applications," Synthetic Met., 151, 211.

[7] **N.S. Sariciftci, H. Kuzmany, H. Neugebauer, A. Neckel**, (1990) "Spectroelectrochemistry of conducting polymers," J. Chem. Phys. 92, 4530.

[8] **J.L. Camalet, J.C. Lacroix, S. Aeiyach, K. Chane-Ching, P.C. Lacaze**, (1998) "Spectroelectrochemistry of conducting polymers," Synth. Met. 93 133.

[9] **W.R. Salaneck, W.S. Huang, I. Lundstrom, A.G. Macdiarmid**, (1986) "Advances in electrochemical science and engineering," Synth. Met. 13 291.

[10] **E.W. Paul, A.J. Ricco, W.S. Wrighton**, (1985) "Resistance of polyaniline films as afunction of electrochemical potential and electrochemical potential and the fabrication of polyaniline –based microelectronic devices," J. Phys. Chem. 89 1441.

[11] **Ming-Sieng Wu, Ten-Chin Wen, A. Gopalan**, (2002) "In situ UV–visible spectroelectrochemical studies on the copolymerization of diphenylamine with anthranilic acid," Department of Chemical Engineering, National Cheng Kung University, Tainan 701, Taiwan Received 10 April 2001; received in revised form 4 May 2001; accepted 10 May 2001, Materials Chemistry and Physics 74 58–65.

[12] **M. T. Nguyen and A. F. Diaz**, (1995) "Water-soluble poly(aniline-co-oanthranilic acid) copolymers," Macromolecules, vol. 28, no. 9, pp. 3411– 3415.

[13] **M. M. Ayad, N. A. Salahuddin, A. K. Abou-Seif, and M. O. Alghaysh**, (2008) "Chemical synthesis and characterization of aniline and o-anthranilic acid copolymer," Eur. Polym. J., vol. 44, no. 2, pp. 426–435.

[14] **Nguyen MT, Diaz AF,** (1995) **"**New transition metal complexes and their ring-opened polymers," Macromolecules 28:3411.

[15] **Yan H, Wang H-J, Adisasmito S, Toshima N,** (1996) **"**Amperometric enzyme electrode for glucose determination based on poly," Bull Chem Soc Jpn 69:2395.

[16] **V.M. Jovanovic, A. Dekanski, G. Vlajnic, M.S. Jovanovic**, (1997) "Electrochemical and Surface Characterization of pH Sensor Based on Bisulfate doped Poly(pyrrole), Electroanalysis," Electroanalysis 9 564–569.

[17] **E. Hermelin, J. Petitjean, S. Aeiyach, J.C. Lacroix, P.C. Lacaze**, (2001) "Annales de chimie," J. Appl. Electrochem 31 905–911.

[18] **M. Kanungo, A. Kumar, A.Q. Contractor**, (2002) "Conducting Polymers with Micro Or Nanometer Structure ," J.Electroanal. Chem. 528 46–56.

[19] **B.A. Deore, S. Hachey, M.S. Freund**, (2004) "Self-Doped Conducting Polymers," Chem. Mater. 16 1427–1432.

[20] **M.R. Nateghi, A. Bagheri, A. Massoumi, M.H. Kazemeini**, (1998) "Handbook of advanced electronic and photonic materials and devices," Synth. Met. 96 209–212.

[21] **A.A. Karyakin, A.K. Strakhova, A.K. Yatsimibky**, (1994) "Self-doped anthranilic acid-pyrrole copolymer," J. Electroanal. Chem. 371 259–265.

[22] **J.Y. Lee, C.Q. Cui**, (1996) "Handbook of advanced electronic and photonic materials and devices," J. Electroanal. Chem. 403 109– 116.

[23] **S. Patra, N. Munichandraiah**, "Insoluble poly(anthranilic acid) confined in Nafion membrane by chemical and electrochemical polymerization of anthranilic acid", Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560012, India.

[24**] Willstater, R.; Cramer**, (1910) "Controlled polymerization of aniline at sub-zero temperatures," J. *Ber.*1910, 43: 2976; 1911, 44: 2162.

[25] **Green, A.G.; Woodhead**, (1912) "Conjugated Polymers: The Novel Science and Technology of Highly Conducting," A.E. *J. Chem. Soc.* 1910, 97: 2388; 1912, 101: 1117.

[26] **H. Letheby**, (1862) "The Pharmaceutical journal ," J. Chem. Soc., 224, 161: 1862.

[27] **M. F. Goppelsroder** (1876) "Conducting Polymers with Micro Or Nanometer Structure," Compt. Rend., 82, 331: 1876.

[28] **J. C. Chiang, A. G. MacDiarmid**. (1986) "Lower-Dimensional Systems and Molecular Electronics ," Synth. Met., 1986, 13: 193.

[29] a) **A. G. MacDiarmid, A. J. Epstein. Faraday Discus** (1989) "Conducting Polymers with Micro Or Nanometer Structures," Chem. Soc., 1989, 88: 317; b) **A. G. MacDiarmid, J. C. Chiang, A. F. Richter, A. J. Epstein.** (1987) " Lower-Dimensional Systems and Molecular Electronics," Snyth. Met., 1987, 18: 285.

[30] a) **A. G. MacDiarmid, A. J. Heeger**. (1879) Synth. Met., 1879/80, 1: 101; Handbook of Conducting Polymers, Vol.1 &2 (Ed. T. A. Skotheim), Marcel Dekker, New York, 1986 b) **M. G. Kanatzidis**. (1990) ” Inorganic Chemistry in Focus III “ Chem. Eng. News, 68: 36.

[31] **A. G. MacDiarmid. Angew**, (2001) “Specialty Polymers: Materials and Applications,**”** Chem. Int. Ed., 2001, 40: 2581.

[32] a) **V. George, D. Young. J. Polym**, (1997) “Handbook of Liquid Crystals, High Molecular Weight Liquid Crystals **,”** Commun., 2002, 43: 4073 b) **M. G. Mikheal, A. B. Padias, H. K. Hall. J. Polym. Sci. Polym.** (1997) “Photochemistry ,” Chem., 35: 1673.

[33] **N. A. Zaidi, S. R. Giblin, I. Terry, A. P. Monkman**. (2004) “Russian chemical reviews,” Polymer, 45: 5683.

[34] a) **H. Goto, M. Okuda, T. Oohazama, K. Akagi. Synth**. (1999) Met., 102: 1293; b) **A. Gök, B. Sarl, M. Talu. Synth**. (2004) Met.,142: 41.

[35] a) **M. Leclerc, J. Guay, L. H. Dao, Macromolecules**, (1982) “ Handbook of Advanced Electronic and Photonic Materials and Devices,” 1982, 22: 649; b) **Y. Wei, W. W. Focke, G. E. Wnek, A. Ray, A. G. MacDiarmid. J. Phys**. (1989) “Specialty Polymers: Materials and Applications**,”** Chem. 93: 495; c) **D. Jr. MaCinnes, B. L. Funt. Synth. Met**., (1989) “Handbook of Thiophene-Based Materials: Applications in Organic Electronics,” 25: 235; d) **L. H. C. Mattoso, S. V. Mello, A. Jr. Riul, O. N. Jr. Oliverira, R. M. Faria.** (1994) ”Handbook of surfaces and interfaces of materials” Thin Solid Film, 244: 714.

[36] a) **J. Yue, A. J. Epstein. J. Am. Chem. Soc.,** (1991) “Conducting Polymers with Micro Or Nanometer Structure,” 1990, 112: 2800; b) J**. Yue, Z. F. Wang, K. R. Cromack, A. J. Epstein, A. G. MacDiarmid. J. Am. Chem. So,** “Charging of Self-Doped Poly(Anilineboronic Acid) Films Studied by in Situ.,” 1991, 113: 2665; c) **S. A. Chen, G. W. Hwang. J. Am. Chem. Soc**., “Conducting Polymers with Micro Or Nanometer Structure,” 1994, 116: 7939

[37] Y**. Cao, P. Smith, A. J. Heeger.** (1992) “Advances in Synthetic Metals: Twenty Years of Progress in Science and Technology,” 48: 91.

[38] **J. Yue, G. Gordon, A. J. Epstein.** (1992) "Conducting Polymers with Micro Or Nanometer Structure,"**,** Polymer, 33: 4409.

[39] **H. S. O. Chan, L. M. Gan, C. H. Chew, L. Ma, S. H. Seow. J. Muter. Chem**., (1993) "Conducting Polymers with Micro Or Nanometer Structure," 3: 1109.

[40] **R. E. Cameron, S. K. Clement**. (1991) "Conducting Polymers with Micro Or Nanometer Structure," U.S. Patent 5,008,041.

[41] **A. Malinauska**s, (2004) " Instıtute of chemistry," J. Power Sources 126, 214–220.

[42] **J. Yue, A.J. Esptein, J. Am. Chem. Soc**. (1990) "Conducting polymers with micro or nanometer structure," 112 2800.

[43] **J. Yue, Z.H. Wang, K.R. Cromack, A.J. Esptein, A.G. Macdiarmid, J. Am**., (1991) "Conjugated polymers and low molecular weight," ,Organic Electronic Materials, 113 2665.

[44] **K. Krishnamoorthy, A.Q. Contractor, A. Kumar**, (2002) Chem. Commun. 240.

[45] **S.M. Park, in: H.S. Nalwa (Ed.),** (1997) "Handbook of Organic Conductive Molecules and Polymers," vol. 3, Wiley, New York, p. 428.

[46] **AMIT BHATTACHARYA and AMITABHA DE**," (1999) Conducting Polymers in Solution—Progress Toward Processibility, J.M.S.—REV. MACROMOL. CHEM. PHYS.," C39(1), 17–56.

[47] **H. Yan, H.J. Wang, S. Adisasmito, N. Toshima, Bull.** (1996) "Synthesis of eolectrically conducting copolymers of aniline with o/m-amino," Chem. Soc., Jpn. 69 2395.

[48] **Nguyen MT, Diaz AF** (1995) "Synthesis of new water-soluble self-doped polyaniline," Macromolecules 28:3411.

[49] **Yan H, Wang H-J, Adisasmito S, Toshima N** (1996) "Novel Syntheses of Poly(*o*-aminobenzoic acid) and Copolymers of *o*-Aminobenzoic Acid and Aniline as Potential Candidates for Precursor of Polyaniline ," Bull Chem Soc Jpn 69:2395.

[50] **Malinauskas A**, (2004) "Head of Department of Organic Chemistry," J Power Sources 126:214.

[51] **Matru Prasad Dash • Minaketan Tripathy, Abhisek Sasmal, Gourang C. Mohanty, P. L. Nayak, Poly** (2010) "Anthranilic acid/multi-walled carbon nanotube composites: spectral, morphological, and electrical properties," J Mater Sci 45:3858–3865.

[52] **H. Tang, A. Kitani, T. Yamashita, S. Ito, (**1998) "Highly sulfonated polyaniline electrochemically synthesized by polymerizing aniline-2.5-disulfonic acid and copolymerizing it with aniline" , Synth. Met. 96, 43–48.

[53] **J. Yue, A. J. Epstein,** (1992), "Conducting Polymers with micro or nanometer structure", J. Chem. Soc. Chem. Commun. 21, 1540–1542.

[54] **J. Yue, Z. H.Wang, K. R. Cromack, A. J. Epstein, A. G. MacDiarmid, (**1991), **"**Organic electronic materials:conjugated polymers and low molecular weight,", J. Am. Chem. Soc. 113, 2665–2671.

[55] **X. H.Wang, J. Li, L. X.Wang, X. B. Jing, F. S.Wang, (**1995) "Polymers and composites,", Synth. Met. 69, 145–146.

[56**] K. Yamamoto, D. Taneichi,** (2000), "Electrochemical catalytic reduction of oxyjen by a self-doped polyaniline-co-po Yrphyrin complex-modified glassy carbon electrade,",**Macromol. Chem. Phys**. 201, 6–11.

[57] **A.A. Karyakin, A.K. Strakhova, A.K. atsimibky** (1994) "Self-doped polyaniline electrochemically active in neutral and basic aqueous solutions:electropolymerization of sustituted anilies," **, J. Electroanal. Chem**. 371 259–265.

[58] **P.S. Rao, D.N. Sathyanarayana,** (2003) ”Synthesis of electrically conducting copolymers of o-/m-toluidines and o-/m-amino benzoic acid in an organic peroxide system and their characterization,**”,** Synth. Met. 138 519–527.

[59**] P.A. Kilmartin, G.A. Wright,** (1997) “Conducting polymers as free radical scavengers,” Synth. Met. 88 153–162.

[60] **C. Li, S. Mu,** (2004) “Conducting polymers of aniline I.electrochemical synthesis of a conducting composite,” Synth. Met. 144 143–149.

[61] **A.A. Karyakin, I.A. Maltsev, L.V. Lukachova**, (1996) J. Electroanal. Chem. 402 217–219.

[62] **R.J. waltman, A.F. Diaz, J. Bargon,** (1984) ”Advances in electrochemical science and engineering,”, J. Phys.Chem. 88 4343–4346.

[63] **J.Y. Lee, C.Q. Cui,** (1996) “Photoelectrochemical and spectroscopic studies sulfonated polyanilines part I. Copolymers of arthanilic acid and aniline,” J. Electroanal. 403 109–116.

[64] **R.M.Q. Mello, R.M. Torresi, S.I.C. Torresi, E.A. Ticianelli, Langmuir** (2000) “Effects of adsorbed polyaniline on redox process on Mo03 surface” 16 7835–7841.

[65] **C. Moreau, Ann. Chem**. (1893) ”Journal of photochemistry and photobiology a:chemistry,” Phys. 2, 186 .

[66] **Casella, for *Rein, H*.**, ***(***1942) DRP 915 034.

[67] ***Quig, IB.:*** **American Dyestuff Rep**. (1943) “Machines and equipment,manifacture,properties,” Synthetic fibers 37 (1948) p. 879, for US-Patent registrations.

[68] ***Koch,PA.:*****Textil-Rdsch**. (1950) “Machines and equipment , manifacture, properties,” Synthetic fibers 5 p. 414 and 486.

[69] ***Hunyar, A.;*** **et al.: Faserforsch. u. Textiltechn., also see** “Machines and equipment , manifacture, properties” Synthetic fibers [252-260].

[70] ***Roney, M.:*** **Modern Textiles (**1971) "Contemporary authors," [237], and *Fourne, F:* Chemiefasern, p. 369.

[71] Courtaulds Fibres Ltd., Coventry/UK.

[72] **Toho Rayon Co., Ltd.**,"International competitive benchmarks and financial gap analysis," Tokyo and Mishima/Japan.

[73] **Charles E. Carraher, Jr.**, Giant Molecules Essential Materials for Everyday Living and Problem Solving, 2nd Edition, WILEY.

[74] **Quingling, C., Xin, C., Liansheng, M., and Wencai.C.** (1999). " Polymers of acryclic acid,methacrylic acid,maleic acid and their derivatives ," Catal. Today, 51: 141.

[75]**Yury Gogotsi**, (2006) "Nanomaterials," Nanotubes and nanofibers, TA418.9.N35N3577, Taylor & Francis Group.

[76] **FANG Jian, NIU HaiTao, LIN Tong & WANG XunGai**, (2008) " Applications of electrospun nanofibers, Chinese Science Bulletin "| vol. 53 | no. 15 | 2265-2286.

[77] **Suat Cetiner, Fatma Kalaoglu and Hale Karakas** , "Electrospun Nanofibers of Polypyrrole-Poly(Acrylonitrile-co-Vinyl Acetate)" Textile Research Journal Vol 0(0): 1–9 DOI: 10.1177/0040517510365953.

[78] **Seeram Ramakrishna, Kazutoshi Fujihara, Wee-Eong Teo, Thomas Yong, Zuwei Ma, and Ramakrishna Ramaseshan (**2006), "Electrospun Nanofibers: Solving Global Issues, Materials," Today, volüme 9, number 3.

[79] **Nandana Bhardwaj, Subhas C. Kundu** (2010) "Electrospinning: A fascinating fiber fabrication technique" 28 325–347.

[80] **G. M. Bose**, (1745) Recherches sur la cause et sur la varitable theorie de lectricite, Wittenberg.

[81] **Lord Rayleigh, Philos. Mag**. (1882), "Acoustics of bells," 14, 184 – 186.

[82] **J. F. Cooley**, (1902) "Progress and resources of Heron Lake," US 692,631.

[83] **W. J. Morton**, (1902).”Journal of nervous and metal disease” US 705,691.

[84] **J. F. Cooley**, (1903). “Progress and resources of Heron Lake,” US 745,276.

[85] **K. Hagiwaba, O. Oji-Machi, K. Ku**, (1929) ”Electrospinning:Materials,processing and applications,” Jpn 1,699,615.

[86] **A. Formhals**, (1934) “Electrospinning:materials,processing and applications,” US 1,975,504.

[87] **W. Simm, K. Gosling, R. Bonart, B. von Falkai**, (1972) ”Textile technology digest” GB 1346231.

[88]**M. Jacobsen**, (1991), ”Modern pharmaceutical ındustry : a primer,” Chemiefasern/Textilind. 36 – 41.

[89] **J. Doshi, G. Srinivasan, D. Reneker,** (1995) “Tenth rolduc polymer meeting,” News Polym 20, 206 – 207.

[90] **Andreas Greiner and Joachim H. Wendorff**, (2007) “Electrospinning: A Fascinating Method for the Preparation of Ultrathin FibersAngew.” Chem. Int. Ed. 2007, 46, 5670 – 5703.

[91] **Kidoaki S, Kwon IK, Matsuda T.** (2005) “Mesoscopic spatial designs of nano and microfiber meshes for tissue-engineering matrix and scaffold based on newly devised multilayering and mixing electrospinning techniques. Biomaterials” 2005;26:37–46.

[92] **Liang D, Hsiao BS, Chu B.** (2007) “Functional electrospun nanofibrous scaffolds for biomedical applications. Adv Drug Deliv Rev,” 59:1392–412

[93] **Nagapudi K, Brinkman WT, Leisen JE, Huang L, McMillan RA, Apkarian RP, et al.** (2002) “Photomediated solid-state cross-linking of an elastin-mimetic recombinant protein polymer,” Macromolecules 35:1730–7.

[94] **Taylor GI. Electrically Driven Jets. Proc R Soc Lond,** (1934–1990), “Electrically driven jets,” A Math Phys Sci 1969;313, 453-75.

[95] **Sun ZC, Zussman E, Yarin AL, Wendorff JH, Greiner A**. (2003) "Compound core-shell polymer nanofibers by co-electrospinning." Adv Mater , 15:1929–32.

[96] **Adomaviciute E, Milasius Rimvydas** (2007) The influence of applied voltage on poly (vinyl alcohol) nanofibre diameter." Fibers Text East Eur;15:64–5

[97] **Chong EJ, Phan TT, Lim IJ, Zhang YZ, Bay BH, Ramakrishna S, et al.** (2007) "Evaluation of electrospun PCL/gelatin nanofibrous scaffold for wound healing and layered dermal reconstitution." Acta Mater 3:321–30. Chun I, Reneker DH, Fong H, Fang X, Deitzel J, Tan NB.

[98]**Li D, Xia Y**. (2004) "Electrospinning of nanofibers: reinventing the wheel." Adv Mater;16: 1151–70.

[99]**Deitzel JM, Kleinmeyer J, Harris D, Tan NCB.** (2001) "The effect of processing variables on the morphology of electrospun nanofibers and textiles." Polymer;42:261–72.

[100] **Sukigara S, Gandhi M, Ayutsede J, Micklus M, Ko F.** (2003) " Regeneration of Bombyx mori silk by electrospinning—part 1:processing parameters and geometric properties." Polymer 2003;44:5721

[101] **Deitzel JM, Kleinmeyer J, Harris D, Tan NCB**." (2001) The effect of processing variables on the morphology of electrospun nanofibers and textiles." Polymer 2001;42:261–72.

[102] **McKee MG, Layman JM, Cashion MP, Long TE.** (2006) "Phospholipid non-woven electrospin membranes." Science;311:353–5.

[103] **Sukigara S, Gandhi M, Ayutsede J, Micklus M, Ko F.** (2003) "Regeneration of Bombyx mori silk by electrospinning—part 1:processing parameters and geometric properties." Polymer;44:5721–7.

[104] **Larrondo L, Manley RSJ.** (1981) "Electrostatic fiber spinning from polymer melts. I. Experimental observations on fiber formation and properties." J Polym Sci, Polym Phys Ed a;19:909–20.

[105] **Deitzel JM, Kleinmeyer J, Harris D, Tan NCB** (2001) "The effect of processing variables on the morphology of electrospun nanofibers and textiles." Polymer ;42:261–72.

[106] **Doshi J, Reneker DH.** (1995) "Electrospinning process and applications of electrospun fibers." J Electrost ;35:151–6.

[107] **Hohman MM, Shin M, Rutledge G, Brenner MP.** (2001) "Electrospinning and electrically forced jets. II. Applications." Phys Fluids;13:2221–36.

[108] **Haghi AK, Akbari M.** (2007) "Trends in electrospinning of natural nanofibers." Phys Status Solidi 2007;204:1830–4.

[109] **Fong H, Liu WD, Wang CS, Vaia RA.** (2002) "Generation of electrospun fibers of nylon 6 and nylon 6-montmorillonite nanocomposite." Polymer;43:775–80.

[110] **Hayati I, Bailey AI, Tadros TF.** (1987) "Investigations into the mechanisms of electrohydrodynamic spraying of liquids. 1. Effect of electric-field and the environment on pendant drops and factors affecting the formation of stable jets and atomization." J Colloid Interface Sci ;117:205–21.

[111] **Baumgarten PK.** (1971) "Electrostatic spinning of acrylic microfibers." J Colloid Interface Sci ;36:71–9.

[112] **Reneker DH, Chun L**. (1996) "Nanometre diameters of polymer, produced by electrospinning." Nanotechnology 7:216–23.

[113] **Zhang C, Yuan X, Wu L, Han Y, Sheng J**. (2005) "Study on morphology of electrospun poly (vinyl alcohol) mats." Eur Polym J 2005b;41:423–32.

[114] **Buchko CJ, Chen LC, Shen Y, Martin DC.** (1999) "Processing and microstructural characterization of porous biocompatible protein polymer thin films." Polymer; 40:7397–407.

[115] **Deitzel JM, Kleinmeyer J, Harris D, Tan NCB**. (2001) "The effect of processing variables on the morphology of electrospun nanofibers and textiles." Polymer; 42:261–72.

[116] **Demir MM, Yilgor I, Yilgor E, Erman B.** (2002) **"**Electrospinning of polyurethane fibers." Polymer; 43:3303–9.

[117] **Megelski S, Stephens JS, Chase DB, Rabolt JF.** (2002) "Micro-and nanostructured surface morphology on electrospun polymer fibers." Macromolecules; 35:8456–66.

[118] **Lee JS, Choi KH, Ghim HD, Kim SS, Chun DH, Kim HY, et al**. (2004) "Role of molecular weight of a tactic poly (vinyl alcohol) (PVA) in the structure and properties of PVA nanofabric prepared by electrospinning." J Appl Polym Sci; 93:1638–46.

[119] **Mo XM, Xu CY, Kotaki M, Ramakrishna S.** (2004) "Electrospun P (LLA-CL) nanofiber: a biomimetic extracellular matrix for smooth muscle cell and endothelial cell proliferation." Biomaterials; 25:1883–90.

[120] **Katti DS, Robinson KW, Ko FK, Laurencin CT.**" Bioresorbable nanofiber-based systems for wound healing and drug delivery: optimization of fabrication parameters." J Biomed Mater Res 2004;70B:286–96.

[121] **Pawlowski KJ, Barnes CP, Boland ED, Wnek GE, Bowlin GL.** "Biomedical nanoscience: electrospinning basic concepts, applications, and classroom demonstration." Mater Res Soc Symp Proc 2004;827:17–28.

[122] **Haghi AK, Akbari M.** (2007) "Trends in electrospinning of natural nanofibers." Phys Status Solidi; 204:1830–4.

[123] **Larrondo L, Manley RSJ.** (1981) "Electrostatic fiber spinning from polymer melts. I. Experimental observations on fiber formation and properties." J Polym Sci, Polym Phys Ed 1981a;19:909–20.

[124] **Larrondo L, Manley RSJ**. (1981) "Electrostatic fiber spinning frompolymermelts. II. examination of theflowfield in an electrically driven jet." J PolymSci, PolymPhys Ed 1981b;19:921–32.

[125] **Larrondo L, Manley RSJ**. (1981) “Electrostatic fiber spinning from polymer melts. III. Electrostatic deformation of a pendant drop of polymer melts.” J Polym Sci, Polym Phys Ed 1981c;19:933–40.

[126] **Yordem OS, Papila M, Menceloğlu YZ**. (2008) “Effects of electrospinning parameters on polyacrylonitrile nanofiber diameter: an investigation by response surface methodology.” Mater ;29:34–44.

[127] **Yuan XY, Zhang YY, Dong CH, Sheng J**. (2004) “Morphology of ultrafine polysulfone fibers prepared by electrospinning.” Polym Int;53:1704–10.

[128] **Megelski S, Stephens JS, Chase DB, Rabolt JF**. (2002) “Micro-and nanostructured surface morphology on electrospun polymer fibers.” Macromolecules; 35:8456–66.

[129] **Zong X, Kim K, Fang D, Ran S, Hsiao BS, Chu B.** (2002) “Structure and process relationship of electrospun bioadsorbable nanofiber membrane.” Polymer 2002a;439:4403–12.

[130] **Wang X, Um IC, Fang D, Okamoto A, Hsiao BS, Chu B.** (2005) “Formation of water-resistant hyaluronic acid nanofibers by blowing-assisted electro-spinning and non-toxic post treatments.” Polymer 2005b;46:4853–67.

[131] **Sundaray B, Subramanian V, Natarajan TS, Xiang RZ, Chang CC, Fann WS**. (2004) “Electrospinning of continuous aligned polymer fibers.” Appl Phys Lett 2004;84:1222–4.

[132] **Li D, Wang Y, Xia Y.** (2004) “Electrospinning nanofibers as uniaxially aligned arrays and layer by layer stacked films.” Adv Mater;16:361–6.

[133] **Xu CY, Inai R, Kotaki M, Ramakrishna S**. (2004) “Aligned biodegradable nanofibrous structure: a potential scaffold for blood vessel engineering.” Biomaterials;25:877–86.

[134] **Doshi J, Reneker DH**. (1995) ”Electrospinning process and applications of electrospun fibers.” J Electrost;35:151–6.

[135] **Geng X, Kwon OH, Jang J.** (2005) "Electrospinning of chitosan dissolved in concentrated acetic acid solution." Biomaterials;26:5427–32.

[136] **Jalili R, Hosseini SA, Morshed M**. (2005) "The effects of operating parameters on the morphology of electrospun polyacrilonitrile nanofibres." Iran Polym J;14:1074–81.

[137] **Casper CL, Stephens JS, Tassi NG, Chase DB, Rabolt JF.** (2004) "Controlling surface morphology of electrospun polystyrene fibers: effect of humidity andmolecular weight in the electrospinning process." Macromolecules;37:573–8.

[138] **Baumgarten PK.** (1971) "Electrostatic spinning of acrylic microfibers." J Colloid Interface Sci;36:71–9.

[139] **Christian Burger,1 Benjamin S. Hsiao,1,2 and Benjamin Chu1,2**, (2006) "NANOFIBROUS MATERIALS AND THEIR APPLICATIONS," Annu. Rev. Mater. Res. 36:333–368

[140] **Arun Kumar Singh, Rajiv Prakash, A.D. D. Dwivedi, and P. Chakrabarti**, (June 2008) "Electronic Properties and Junction Behavior of Polyanthranilic Acid/Metal Contacts", IEEE Electron Device Letters, Vol. 29, No. 6, pp. 571-574.

[141] **Matru Prasad Dash, Minaketan Tripathy, Abhisek Sasmal, Gourang C. Mohanty, P. L. Nayak,** (2010) "Poly(anthranilic acid)/Multi-wall carbon nanotube composites: spectral, morphological, and electrical properties", Springer Science+Business Media, J Mater Sci 45:3858-3865.

[142] **B. L. Rivas, C. O. Sanchez,** (2003) " Poly(2-) and 3-aminobenzoic acids) and Their Copolymers with Aniline: Synthesis, Characterization, and Properties", Polymer Department, Faculty of Chemistry, University of Concepcion, Casilla 160-C, Chil, Journal of Applied Polymer Science, Vol. 89, 2641-2648.

[143] **My T. Nguyen and Arthur F. Diaz,** (1995) "Water-Soluble Poly(aniline-co-o-anthranilic acid) Copolymers", Macromolecules, 28 (9), pp 3411–3415.

[144] **Bhavana Gupta, Rajiv Prakash**, (2011) "Synthesis of functionalized conducting polymer "polyanthranilic acid" using various oxidizing agents and

formation of composites with PVC", Polymers for Advanced Technologies, Volume 22, Issue 12, pages 1982–1988.

[145] **H. S. O. Chan, S. C. Ng, W. S. Sim, K. L. Tan, B. T. G. Tan,** (1992) "Preparation and characterization of electrically conducting copolymers of aniline and anthranilic acid: evidence for self-doping by x-ray photoelectron spectroscopy", Macromolecules, 25 (22), pp 6029–6034

[146**] S. Patra, N. Munichandraiah**, "Insoluble poly(anthranilic acid) confined in Nafion membrane by chemical and electrochemical polymerization of anthranilic acid", Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560012, India

[147] **M.R. Nateghi,M. Borhani,** (2008) "Preparation, characterization and application of poly anthranilic acid-co-pyrrole", Reactive & Functional Polymers 68 153-160.

[148] **K. Ogura*, H. Shiigi, M. Nakayama, A. Ogawa,** (1999) "Thermal properties of poly(anthranilic acid) (PANA) and humidity-sensitive composites derived from heat-treated PANA and poly(vinyl alcohol)", Journal of Polymer Science Part A: Polymer Chemistry Volume 37, Issue 23, pages 4458–4465

[149**] Norizah Abdul Rahman, Marija Gizdavic-Nikolaidisa, Sudip Ray, Allan J. Easteal, Jadranka Travas-Sejdic,** (2010) "Functional electrospun nanofibres of poly(lactic acid) blends with polyaniline or poly(aniline-co-benzoic acid)", Synthetic Metals, 160 2015–2022.

[150**] Wei Sun, Qing Cai, Peng Li, Xuliang Deng, Yan Wei, MingMing Xu, Xiaoping Yang,** (2010) "Post-draw PAN–PMMA nanofiber reinforced and toughened Bis-GMA dental restorative composite", dental materials 2 6 873–880.

[151] **Wei Pan, Sheng Lin Yang, Guang Li, Jian Ming Jiang,** (2005) "Electrical and structural analysis of conductive polyaniline/polyacrylonitrile composites", European Polymer Journal 41 2127–2133.

[152**] Ming-Sieng Wu, Ten-Chin Wen∗, A. Gopalan,** (2002) "In situ UV–visible spectroelectrochemical studies on the copolymerization of diphenylamine with anthranilic acid," Materials Chemistry and Physics 74 58–65

[153] **S. Patra, N. Munichandraiah,** (2005) **"**Insoluble poly(anthranilic acid) confined in Nafion membrane by chemical and electrochemical polymerization of anthranilic acid", Synthetic Metals, 150 (3). pp. 285-290

[154] **Dongxue Han, Jixia Song, Xuefeng Ding, Xiaoyu Xu, Li Niu**, (2007) "Fabrication and characterization of self-doped poly(aniline-co-anthranilic acid) nanorods in bundles," Materials Chemistry and Physics 105 380-384

[155] **M. M. E. Jacob and A. K. Arof**, (2000), Electrochim. Acta, 45, 1702.

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PUBLICATIONS/PRESENTATIONS ON THE THESIS

▪ GİRAY D., BALKAN T., SARAC A. S.., 2011: Nanofibers of Poly(anthranilic acid)/Polyacrylonitrile Composites, Nano TR VII 7th Nanoscience and Nanotechnology Conference, June 29, 2011 İstanbul, Turkey.