

ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE
ENGINEERING AND TECHNOLOGY

**POLY(ACRYLONITRILE-CO-METHYLACRYLATE)/PEDOT CORE-SHELL
NANOCOMPOSITE AND NANOFIBERS**

M.Sc. THESIS

Ömer EROĞLU

Department of Nanoscience and Nanoengineering

Nanoscience and Nanoengineering Programme

JANUARY 2014

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(513111011)**

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Thesis Advisor: Prof. Dr. A. Sezai SARAC

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

**POLY(ACRYLONITRILE-CO-METHYLACRYLATE)/PEDOT KAPSÜL
YAPILI NANOKOMPOZİT VE NANOFİBERLERİ**

YÜKSEK LİSANS TEZİ

**Ömer EROĞLU
(513111011)**

Nano-Bilim ve Nano-Mühendislik Ana Bilim Dalı

Nano-Bilim ve Nano-Mühendislik Programı

Tez Danışmanı: Prof. Dr. A. Sezai SARAÇ

OCAK 2014

Ömer EROĞLU, a **M.Sc.** student **ITU Graduate School of Science Engineering and Technology** of student ID 513111011, successfully defended the **thesis/dissertation** entitled “**POLY(ACRYLONITRILE-CO-METHYLACRYLATE)/PEDOT CORESHELL NANOCOMPOSITE AND NANOFIBERS**”, which he prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

Thesis Advisor : **Prof. Dr. A.Sezai SARAC**
Istanbul Technical University

Jury Members : **Prof. Dr. Yücel ŞAHİN**
Yıldız Technical University

Assoc. Prof. Dr.Fatma Nese KOK
Istanbul Technical University

Date of Submission : 16 December 2013

Date of Defense : 22 January 2014

To my family and grandfather,

FOREWORD

I would like to express my gratitude to my thesis supervisor, Prof. Dr. A.Sezai SARAÇ for his continuous encouragement, guidance, helpful critics and discussions in my studies.

I would like to give my special thanks to my laboratory friends Timucin BALKAN, Zeliha GÜLER, Başak DEMİRCİOĞLU, Burcu SAYINLI, Keziban HÜNER, Hacer DOLAŞ, Diğdem Giray AYTAÇ, Dilek SUADİYE, Mehmet Tolga SATICI, Nurullah UYKUN, Uğur DAĞLI, Yahya TOPRAK and Mehmet Giray ERSÖZOĞLU, Dr. Argun T. GÖKÇEÖREN for their collaborative and friendly manner.

Most of all, I would like to thanks my relative, especially Rufat EROĞLU, Avni EROĞLU, Basri EROĞLU, Atilla ÇATALKAYA, Yaşar RAVCI. For all those times they stood by me and heartedly supported. I was able to accomplish everything in my life thanks to their eternal love.

Finally, I would like to thank all of my other friends for all their emotional assists and motivation during this extremely difficult accomplishment.

December 2013

Ömer EROĞLU
(Physics Department)

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ABBREVIATIONS

AFM	: Atomic Force Microscopy
AN	: Acrylonitrile
APS	: Amonium Persulphate
DMF	: Dimethylformamide
EDX	: Energy Dispersive X-ray Analysis
EIS	: Electrochemical Impedance Spectroscopy
FTIR-ATR	: Fourier Transform Infrared Spectroscopy –Attanuated Total Reflectance
FTO	: Fluorine Doped Tin Oxide (FTO) Glass
LiClO₄	: Lithium Perchlorate
NMR	: Nuclear Magnetic Resonance
PMA	: Polymethylacrylate
PEDOT	: Poly (3,4-ethylenedioxythiophene)
P(AN-co-MA)	: Poly(Acrylonitrile-co-Methylacrylate)
SDS	: Sodium Dodecyl Sulfate
SEM	: Scanning Electron Microscope
TEM	: Transsmission Electron Microscope Analysis

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POLY(ACRYLONITRILE-CO-METHYLACRYLATE)/PEDOT CORESHELL NANOCOMPOSITE AND NANOFIBERS

SUMMARY

Firstly, Poly(Acrylonitrile-co- Methylacrylate)/PEDOT Core Shell was synthesized from acrylonitrile (AN) 90% and Methylacrylate (MA) 10% molar ratios by emulsion polymerization in the presence of surfactive dopant sodium dodecyl sulfonate in aqueous media, using ammonium persulfate as initiator. Conductive polymers and their composites have attracted great interest for widely usage in sensors, batteries, smart windows, electronic devices, telecommunication etc. has further enhanced interest of researchers in this novel area.

In this study, we propose a method to synthesize P(AN-co-MA)/PEDOT core-shell structure. Poly(3,4-ethylenedioxythiophene) (PEDOT) is a conjugated polymer showing some properties ,i.e., conductivity, thermal stability and thermochromism etc. P(AN-co-MA) exhibited improved thermomechanical properties and higher thermal stability. Hydrophobic interfacial properties of methylacrylate provide to obtain core-shell composite structures. Firstly, Acrylonitrile-co-Methylacrylate nanocomposites were synthesized in situ via emulsion polymerization with the presence of ammonium per sulfate(APS) and surfactive dopant sodium dodecyl sulfonate(SDS). Poly(AN-co-MA) were successfully prepared with emulsion polymerization. Finally, EDOT monomer added into polymer emulsion by obtaining nano core-shell synthesized in situ polymerization. Nanocomposite is characterized by FTIR-ATR, Uv-visible Spectrophotometric, SEM, AFM, TEM and NMR measurements. Images of nanoparticles of P(AN-co-MA) and P(AN-co-MA)/PEDOT were obtained by SEM on glass surface. Synthesized P(AN-co-MA) nanoparticles dispersed in ethanol solution via ultrasonification . Subsequently they were dropped onto glass surface in order to observe nanoparticles with SEM. It showed that size of nanoparticles changed ranging from 60 nm to 139 nm According to measurements diameter of coreshell is determined as average 112 nm by showing a cauliflower structure.

Secondly, synthesized coreshell nanocomposite in situ polymerization is dissolved in DMF homogeneously. P(AN-co-MA)/PEDOT nanocomposite were dissolved as wt % 5 solution concentration in DMF to produce nanofibers with electrospinning method on aluminum template applying 12 kV with feed rate of 0.5 mL/h at Tip-to-collector distance of 15 cm. Nanofibers were produced with electrospinning method on Al template, and were characterized by SEM, Optical Microscopy and EDX. SEM results showed that average diameter of nanofibers is ~830 nm. Finally, Electrochemical Impedance measurement and cyclic voltammetry of nanofibers is performed. The EIS results were fitted with an equivalent electrical circuit for learning about nanofiber electrochemical and physical characteristics. According to circuit model, R_s , R_{ct} , W , R_c , R_{ct} refers to solution resistance, electron charge transfer, warburg Impedance, ionic charge transfer resistance and charge transfer resistance respectively. As a results, nanofibers exhibited high capacitance properties.

P(ACRYLONİTRİLE-CO-METHYLACRYLATE)/PEDOT NANOKAPSÜL YAPILI NANOKOMPOZİT VE FİBERLERİ

ÖZET

İletken polimerler son yıllarda sahip oldukları seçkin özelliklerinden dolayı araştırmacılar tarafından son derece büyük bir dikkat çekmektedir. Çünkü iletken polimerler kolay işlenebilir, ucuz üretim, biyouyumlu, esnekliği ve birçok özelliği ile çok büyük avantajlar sağlamaktadır. Özellikle teknolojinin gelişiminde iletken polimerlerin sahip oldukları bu özellikleri önemli yer tutmaktadır. Bundan dolayı elektromanyetik koruma, sensörler, güneş enerjili piller, boya karakterli güneş hücreleri, super kapasitorler, lityum-iyon bataryalar, oled led ışıklı sistemler ve bir çok alanda kullanım büyük kullanım alanı sağlamaktadır.

Önemli iletken polimerden birisi de PEDOT'dır. PEDOT elektrokromatik ve oksidasyon,biyouyumluluk,esneklik gibi seçkin özelliğiyle dikkat çekmektedir.Fakat düşük mekanik özellik,kolay kırılabilir,düşük çözünürlük gibi bazı dezavantajlara da sahiptir.Bu problemler onun kullanım alanını kısıtlamaktadır. Bu durumu aşmak için çeşitli metodlar uygulanmaktadır.Bu amaçla tezin ilk aşamasında P(Acrylonitrile-co-Methylacrylate) polimerini kullanarak etrafında Edot monomerinin yüzey aktif madde ve başlatıcı ile polimerleşmesini sağlayarak core-shell yapılı nanokompozit malzeme sentezlendi. Bu şekilde emülsiyon polimerizasyon yöntemini kullanarak labaratuvar ortamında kontrollü bir şekilde nanokompozit oluşturuldu.

Bu tez iki bölümden oluşmaktadır. Birinci bölümde P(Acrylonitrile-co-Methylacrylate) kopolimerinin sentezlenerek, etrafının Poly(3,4-ethylenedioxythiophene) ile kaplanarak, üretilen yeni coreshell yapılı nanokompozit malzeme detaylı olarak karakterize edilmiştir.Bunun için bir çok karakterize aletler kullanılmıştır.

İkinci bölümde sentezlenen nanokompozit malzemenin DMF içerisinde çözülerek elektrospinning yöntemi ile nanofiberleri alüminyum template üzerine kaplanarak karakterizasyonu yapılmıştır. Elektrospinning için gerekli parametreler ayarlanmıştır.

Sentezlediğimiz nanokompozit aynı şekilde DMF ile çözülerek elektrospinning yöntemi ile nanofiberleri FTO iletken cam üzerine kaplanılarak elektrokimyasal empedans ölçümleri incelenmiştir.

İlk olarak P(Acrylonitrile-co-Methylacrylate) sulu çözelti ortamında kontrollü bir şekilde emülsiyon polimerizasyon yöntemi ile sentezlenmiştir. Bunun için magnetic karıştırıcı üzerinde üç boyunlu balon joje içerisinde yüzey aktif madde olarak SDS saf su içerisinde çözülerek belirli oranlarda Akrylonitril, metilakrilat monomerleri reaksiyon ortamına eklenmiştir. Ardından üç boyunlu balon joje içersine saf suda çözülmüş başlatıcı olarak APS eklenmiştir. Reaksiyon 150 ml'ye tamamlayana kadar saf su eklenip, geri soğutucu takılarak 70 santigrat derecede 6 saat boyunca magnetik

kariřtırıcı üzerinde gerekleřtirilmiřtir. Ardından sentezlenen kopolimer özeltisi 10 ml’lik řiřelere ayrılarak yine aynı kopolimer özelti ortamında üzerine farklı miktarlarda Edot monomeri ve sonrasında APS eklenerek nanokompozit sentezlenmiřtir. Kopolimer ve nanokompozitli özelti metanol ile öktürölmöř olup ardından etanol ile yıkanarak kurutulmuřtur. Sentezlenen hem kopolimer hemde nanokompozitin ayrı ayrı FTIR, UV, SEM, AFM, TEM, NMR karakterizasyonları yapılarak birbirleriyle kıyaslanmıřtır. Böylece FTIR, UV ve NMR cihazlarıyla yapılan ölmömlerde nanokompozit ve kopolimer arasındaki farklılara bakılarak hem kopolimerin oluřup oluřmadığı incelendi hem de nanokompozitin yapısında PEDOT’un oluřup olumadığı arařtırılmıřtır. UV sonularına ise kopolimer ve nanokompozit DMF ierisinde özölerek bakılmıřtır. Kopolimer ile nanokompozit karřılařtırılmıřında nanokompozitin eėrisi kopolimerden farklı olarak geniř bir aralıktaki pik verdiėi görölmekte olup yaklaşık 300 nm’den sonrasında kopolimer ile aynı pikler verdiėi görölmektedir. Bu ise ortamdaki PEDOT’dan gelen pikler olduėunu ve 440 nm π - π geiř aralıėını göstermektedir. FTIR verilerine göre 2240 cm⁻¹ C $\equiv$ N AN piklerini göstermektedir. 1167 cm⁻¹ ve 1730 cm⁻¹ bandı sırasıyla MA iindeki C-O baėlarını ifade etmektedir. 1450 cm⁻¹ and 2940 cm⁻¹ pikleri C-H baėlarının etkileřimindeki titreřimlerden kaynaklanmaktadır. 3630 cm⁻¹ titreřim O-H baėına aittir. 677, 833, and 961 cm⁻¹ pikler thiophene iindeki C-S baėlarını verir. NMR sonularına göre ülü yarılmıř pikler görölmektedir. Bunlar kopolimer oluřurken AN ve MA polimerizasyondan kaynaklanmaktadır. Sonu olarak karakterizasyon verileri nanokompozitin bařarıyla sentezlendiėini göstermiřtir. AFM, SEM ve TEM ile nanokompozit ile kopolimerin yüzey řekilleri incelenerek boyutları hakkında veriler elde edildi. AFM ve SEM görüntülerine kopolimer ve nanokompozit etanol ile ultrasonifikasyon ile daėıtılarak mikropipet yardımıyla cam yüzey üzerine damlatılarak bakılmıřtır. SEM görüntülerinde kopolimer ve nanokompozit görüntüleri kıyaslanmıřtır. SEM görüntüleri nanokompozit malzemenin tanecik boyutu olarak ortalama 8 nm civarında bir kaplama olduėu gösterilmektedir. Kopolimer kaplandıktan sonra yüzeyi karnıbaharı andırmaktadır. AFM de ise sadece nanokompozitin görüntüleri elde edilmiřtir. Görüntülerde yıldız kümesini andıran sıralı paracıklar sentezlenen nanokompozite aittir. AFM görüntüsü iin nanokompozit paracıkları daha seyreklik bir ortamda daėıtılarak AFM görüntüleri cam yüzeyinden alınmıřtır. Ayrıca SEM görüntüleri kıyasladıėında büyük yüzeyler ve üzerinde nanoparacıklar görölmektedir. Bunlar SEM den de cam yüzeyine ait olduėu görölmektedir. TEM sonularına göre kopolimerin etrafının PEDOT ile kaplandıėı aıka görölmektedir. TEM görüntülerine göre i karanlık bölge kopolimer dıř aydınlık bölge PEDOT ile evrelenmiřtir.

Nanolif, nanofiber, ortalama lif apları nanometreler (nanometre=10⁻⁹ metre) mertebesinde olan yaklaşık olarak bir insan saı telinin binde biri kadar ince liflerdir. Genel anlamda lifler söz konusu olduėunda ‘nano’ terimi, lif apının büyüklüėü hakkında bilgi verir. Günümüzde, mevcut lif üretim teknikleriyle apı bir mikron ve altında lif üretilemediėi iin, alıřmalarda “apı bir mikron ve altındaki lifler” nanolif olarak kabul edilmektedir. Bu lifleri üretmek iin geliřtirilmiř en son teknolojilerden biri olan elektro-üretim (elektroeėirme) yöntemidir. Genelde, birok uygulama gösteriyor ki, inceleme konusu olan nanolifler kısa zaman ierisinde hayatın pek ok alanına girecektir. Polimer esaslı nanoliflerin üretimi iin en etkin ve kolay yöntem elektro-üretim (electrospinning) yöntemi olarak görölmektedir. Bunun dıřında özel ekim metodları ve gaz-buharı (vapor-grown) yöntemleri ile de nanolif üretmek mümkündür.

Nanoliflerin kullanım alanları arasında filtrasyon uygulamaları, batarya separatörleri, yara örtücüler, dış cephe kaplamaları, nefes alabilir membran kaplama uygulamaları gibi alanlar bulunmaktadır.

Electrospinning yönteminde, enerji kaynağı ve kollektör (toplayıcı levha) bir uçlarından toprak bağlantılı olduklarından, sistem kapalı devre görünümündedir. Devredeki iki elektrottan biri lif çekim çözeltisi ya da eriyiğinin içine doğru yerleştirilmekte, diğeri ise karşıdaki kollektöre bağlanmaktadır. Tüpün arka kısmına yerleştirilmiş olan bir pompa şırınga içerisindeki polimer eriğine basınç uygular. Gerekli yüksek voltaj yüksek gerilim güç kaynağından 10-40 kV mertebelerinde uygun hazırlanmış polimer çözeltisine verilir. Yüksek voltajın oluşturduğu elektrik alan içerisinde yüklenen polimer çözeltisi karşı kutup olarak topraklanmış veya zıt kutup ile yüklenmiş bir metal yüzey üzerine doğru spin hareketi ile incelenerek nanometre mertebelerinde lifler oluşturarak bir nanolif membran yüzey oluşumunu sağlar.

İkinci bölümde nanokompozit malzemenin nanofiberleri elektrosipinning yöntemi ile elde edilmiştir. İletken polimerlerin normalde kırılkan, düşük mekanik ve çözünürlük özellikler gösterdiğinden dolayı fiberleri üretilmemektedir. Bu çalışmada bu eksikliği gidermek için birçok sanayi alanında kullanılan yüksek mukavemet özellik gösteren kopolimer ile iletken polimer kaplanıp nanokompozit oluşturulmuştur. Sonrasında nanokompozit DMF içerisinde çözülerek electrospinning yöntemi ile alüminyum folyo üzerine 15 cm uzaklıkta, 12000 V güç uygulayarak şırınga yardımıyla 0.5 ml/h hızla nanofiberler üretilmiştir. Electrospinning parametre ayarları uzun bir denemeden sonra fiberlerin en iyi atılma koşulları saptanarak ulaşılmıştır. Üretilen nanofiberlerin SEM ile yüzeysel özellikleri incelenerek ortalama nanofiberlerin yarıçapları ölçülmüştür. Nanofiberlerin yüzeysel özellikleri incelendiğinde, nanofiberler saç yapısını andırmakta olup kimi yerler de porlu yüzeyler olduğu görülmektedir. SEM sonuçlarına göre nanofiberlerin yaklaşık yarıçapı 829 nm çıkmıştır. EDX analizi ile içerisindeki madde tayinleri yapılmıştır. Nanofiberlerin EDX sonuçlarına alüminyum folyo üzerinde bakılmıştır. EDX sonucuna göre PEDOT içerisindeki kükürt varlığından dolayı fiberler içerisinde iletken polimerin katıldığını göstermektedir. Ayrıca EDX sonuçları nanokapsül içerisindeki element miktarları kütlece olarak tablo içerisinde sunulmuştur.

Son bölümde sentezlenen nanokompozitlerin üç farklı zamanda aynı koşullarda ve DMF içerisinde aynı miktarda çözünmüş nanokompozit ile nanofiberlerini FTO iletken cam üzerine tamamen kaplayıncaya kadar atıldı. Elde ettiğimiz üç numunenin elektrokimyasal özelliklerini lityum per klorat sulu çözeltisi içerisinde referans elektrot olarak gümüş, karşıt elektrot olarak ise platin kullanılarak analiz edildi. Daha sonra verileri kullanarak en uygun olan $R(Q(RW))(QR)$ devre modellemesi ile sonuçlandı. Burada Q constant faz elementidir. Q değeri fiberlerin homojen bir yapıda olmadığını göstermektedir. W walburg empedansı ise iyonların yüzeye yapıştığını ifade etmektedir. Ayrıca R1,R2 porlu yüzeylerin direnci ve elektron transfer direnci olup birbirlerine seri bağlı olduğunu ifade etmektedir. Yapılan iki ayrı ölçümde FTO iletken camın elektrokimyası alındı diğer ölçümde ise nanofiber kaplanmış FTO iletken camın elektrokimyası incelendi. Daha sonra FTO iletken cam üzerindeki nanofiberlerin Cyclic Voltametry ölçümlerine lityum per klorat sulu çözeltisi içerisinde farklı tarama hızlarında incelendi. Sonuçlar birbirbiriyle kıyaslandığında üç fiber kaplı farklı numunenin elektrokimyasal ölçümleri birbirine hemen hemen yakın çıkmakta olup nanofiberler kapasitif özellik gösterdiği ortaya çıkmıştır.

1. INTRODUCTION

Discovery of conjugated polymers has attracted much interest among researchers. They can enable considerable levels of electrical conductivity applicable for use in electronic devices, batteries, electrochromic devices, optical switching devices, sensors, textiles [1]. Among the conductive polymers, poly(3,4-ethylenedioxythiophene) (PEDOT) are the most chemically stable to date. PEDOT has one of the most promising class of organic-conducting polymers owing to low oxidation potential, high stability [2], good environmental durability [3], electrochromism [4], easy doping [5], and easy synthesis. But, conductive polymers has disadvantage such as weaker in mechanical strength, softer, instability, low solubility [6-8]. Hence, nanofiber of conductive polymers cannot be easily produced and operated. To cope with this problem was prepared nanocomposite via emulsion polymerization. PAN and its copolymers are important material commercially duo to wide area application. It has unique properties such as good mechanical properties, high strength, high hardness and easily formed as fiber[9]. PAN can be used to variety area such as automobile, energy, agriculture, filtration as well. It shows that properties; slowly burn due to it has high crystalline melting point [10], resistant to most chemicals and solvents, low permeability to gases. In this study, core-shell nanocomposite is prepared using and PEDOT. P(AN-co-MA)/PEDOT characterized Fourier Transform Infrared Spectroscopy– Attenuated Total Reflectance (FTIR-ATR), Ultraviolet Visible Spectrophotometry (UV-Vis), Scanning Electron Microscopy (SEM), TEM and nanofibers were obtained from homogeneous P(AN-co-MA)/PEDOT by using electrospinning. A number of techniques including EDX, Scanning Electron Microscopy (SEM) and Optical Microscopy used for nanofiber characterization. Finally electrochemical Impedance measurements and cyclic voltametry were carried out. Therefore, nanofibers of nanocomposites have exhibited high capacitive values.

2. THEORITICAL PART

2.1 Conductive Polymer

Conductive polymers is also named as conjugated polymer due to their chemical structures. They have offered variety opportunity in consequence of their physical, chemical, electronical, optical and magnetic properties at last decade. For this, they have attracted attention for researcher. On other hand nanotechnology manipulated them in basic research and application as nanofibers, nanocoreshell, nanocomposite, nanolithographic, semiconductive products. That provides wide range of implementation such as sensors, fuel cell, organic light emitting diode[11].

2.2 Conductivity of Conjugated Polymer

Conductive polymers behave like semiconductor in term of conductivity but normally when they synthesized they indicate low conductivity because of being neutral. In order to behave them as metallic conductors, they have to be doped by a dopant during the doping process. Doping is a process of addition of electrons (reduction) or removal of electrons (oxidation) from the polymer chain. The charged species formed are able to move along the carbon chain (delocalisation) allowing electron transport and thus giving an electronically conductive material. Once doping has occurred, the charge carrying species in the delocalised π system have the mobility to move along the backbone chain. From a macroscopic perspective, conduction through a CP takes place by charge hopping both along the polymer chains and also between the macromolecules that make up individual fibres and between the fibres themselves. Doping (p or n) generates charge carriers that move in an electric field. Positive charges (holes) and negative charges (electrons) move to opposite electrodes. This provides movement of charge for electrical conductivity[12].

2.3 Applications of Conducting Polymers

Conducting polymer nanocomposites exhibit multifunctional and unique properties. Therefore, many conducting polymer nanocomposites are used in many fields, such as

nanoelectronic devices, chemical or biological sensors, catalysis or electrocatalysis, energy, ultracapacitors, ER fluids and biomedicine[14].

2.3.1 Ultracapacitors

Supercapacitor is promising energy storage device that positioned between conventional electrolytic capacitor and rechargeable batteries. Moreover, high power, high energy and long-term reliability feature of supercapacitor enable this component to use in various applications as backup power unit, auxiliary power unit, instantaneous power compensation, peak power compensation and energy storage as well[15, 16, 17, 18].(As seen in Figure 2.1)

Supercapacitors are electrochemical double layer capacitors characterized by high energy and power density. Furthermore, they consist of two electrodes surrounded by an electrolyte and separated by a separator. Since the loading capacity depends on the electrode surface, a significant performance enhancement of supercapacitors will be achieved through nanostructuring and the associated surface extension[19,20]. For the nanotechnological point of view, new materials as nanoporous substances are perfectly suitable as graphitic electrode materials in supercapacitors due to their extremely high inner surface, adjustable pore distribution and pore diameters [21, 22].

Coupling the ultrasmall separation distance with a relatively huge surface area, in ultracapacitors the ratio of available surface area to charge-separation distance has grown to an amazing 10^{12} . It is this ratio, in fact, that makes capacitors "ultra." The ability to hold opposite electrical charges in static equilibrium across molecular spacing is the important feature.

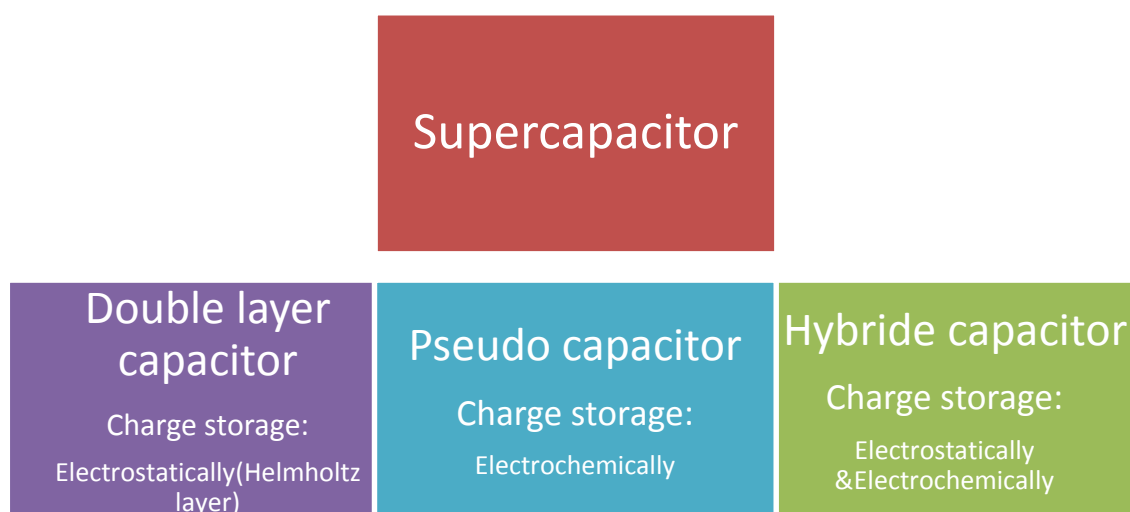


Figure 2.1: Supercapacitor varieties.

Three main factors determine how much electrical energy a capacitor can store as seen in Figure 2.2: the electrode surface area; the electrode separation distance; and the properties of the insulating layer separating the electrodes[23, 24, 25].

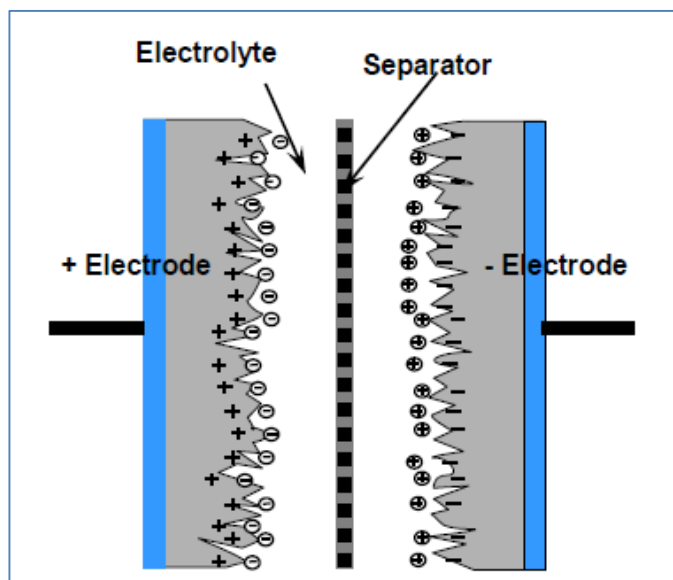


Figure 2.2: Ultracapacitor charge separation.

2.4 Electrochemical Impedance Spectroscopy (EIS)

Electrochemical impedance spectroscopy (EIS) is an efficient electrochemical technique for studying a variety of chemical, electrochemical and surface reactions. This technique is used due to the ability of the method to give information on both the bulk and interfacial properties of the polymer coated electrodes. EIS is the process of measuring impedance (complex resistance) response over a wide range of frequencies. The reason EIS provides so much information is due the response of the system changes with frequency. Thus, a broad range of information can be obtained in a single measurement. The impedance is described by an analogous equation to Ohm's law ($R = E/I$), where R is the resistance (Ohms), E is dc potential (V) and I is the current (A) in direct current (dc). This relationship is only valid for ideal resistor that does not exist in reality. Impedance is a measure the ability of a circuit element to resist the flow of electrical current. Impedance measurements are made by applying a small AC potential of known frequency (ω) with small amplitude (E_o) to a system and measuring the current and phase difference ϕ of the concomitant electrical current that develops across it. ϕ is the phase difference between the sinusoidal voltage and sinusoidal current. $\phi = 0$ for purely resistive behaviour. The consideration of phase shift makes

the impedance a more general concept than resistance. Impedance can be calculated as with Ohm's Law. impedance value varies depending on the frequencies and can be plotted as a function of frequency. This makes the technique a spectroscopic method. Since the impedance values are complex numbers, they can be represented in two different manners *i.e.* Nyquist and Bode plots. The Nyquist plot shows the data as real (Z') vs imaginary (Z'') while the Bode plot shows the amplitude and phase values over the range of frequencies. In Nyquist plot, each point gives the characteristics of the complex impedance at given frequency. However, this plot does not give the frequency value, which is the main disadvantage of the plot.

2.5 Emulsion Polymerization

Emulsion polymerization is a unique chemical process widely used to produce waterborne resins with various colloidal and physicochemical properties. Emulsion polymerization involves dispersing monomer in water with surfactants and a water-soluble initiator. The initiator forms radicals which initiate the polymerisation producing the polymer latex, a dispersion of polymer particles ($< 1\mu\text{m}$ diameter) in water.

In emulsion polymerization there are some key “ingredients”:

- The monomer must be insoluble in water and polymerizable by free radicals
- Water-soluble initiator
- Water
- Surfactant

For emulsion mechanism, above components are used. The surfactant molecules surround small amounts of monomer molecules, creating micelles. However, the usual recipe contains much more monomer than can be accommodated in micelles, so there are also large droplets of monomer that are stabilized by small amounts of surfactant. Depending on the monomer, there may also be a small amount of monomer dissolved in the water. Initiator forms free radicals in the water, where they may find a few monomers to react with. In any case, the radicals diffuse into the micelles, where they find lots of monomer but no other growing chains to cause termination for a while. The growing chain is then protected from termination until a second radical diffuses

into the micelle. Most initiators are water-soluble; therefore, the radicals are formed in the aqueous phase. These radicals are often too hydrophilic to directly enter into the organic phases. Monomer in the micelle quickly polymerizes and the growing chain terminates. Therefore, they react with the monomer dissolved in the aqueous phase, forming oligoradicals that grow slowly because of the low concentration of monomer in the aqueous phase. The entering oligoradicals find a monomer-rich environment within the micelle, and hence they grow fast forming a polymer chain. More monomer from the droplets diffuses to the growing particle, where more initiators will eventually react. Finally, the free monomer droplets vanish and all remaining monomer is located in the particles. The last product is a dispersion of polymer particles in water. It describes also be known as a polymer colloid or a latex.

2.6 Nanocomposite

Nanocomposites are a special class of materials originating from suitable combinations of two or more such nanoparticles or nanosized objects in some suitable technique, resulting in materials having unique physical properties and wide application potential in diverse areas. Nanotechnology offers physically and chemically improvement on material with nanofabrication at level nanometer. One of most important is nanocomposite owing to outstanding mechanical, thermal, optical, electrical properties according to homopolymer. Hence, they have drawn attention due to their unique properties for development of advance material. They are also gained significant improvement in material properties like thermal, mechanical of their remarkable surface area to volume ratio, good dispersion, high controlled matrix, and high surface energy[26, 27]. Thanks to their new properties has provided widely application such as drug deliver system, sensors, smart textile and novel material recently.

2.7 PAN (Polyacrylonitrile)

PAN is polymer that formed from acrylonitrile monomers as seen in Figure 2.3 via polymerization. AN monomers firstly synthesized at 1893 years by French chemist Moreau. It has ability co-polymerization with different monomers due to molecular nitrile groups(CN) such as styrene-acrylonitrile (SAN), acrylonitrile styrene acrylate,

(ASA) acrylonitrile butadiene styrene (ABS) as known ABS rubber. It also can be formed co-polymer with Methyl groups with a molecular formula of C_3H_3N .

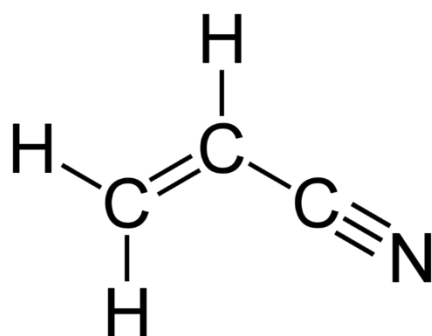


Figure 2.3: AN chemical formula.

PAN is one of most important polymer for textile industry due to it has good mechanical properties, high strength, high hardness and ease of formation as fiber[9]. Hence it can be used to variety area such as automobile, energy, agriculture, filtration. It shows properties such as slowly burning due to it has high crystalline melting point [10], resistant to most chemicals and solvents, low permeability to gases.

Polyacrylonitrile is a vinyl polymer, and a derivative of the acrylate family of polymers as seen in Figure 2.4 . It is made from the monomer acrylonitrile by free radical vinyl polymerization. PAN can be dissolved in DMF (Dimethylformamide), DMSO (Dimethyl Sulfoxide), DMAc, dimethylsulfone, tetramethylsulfide.

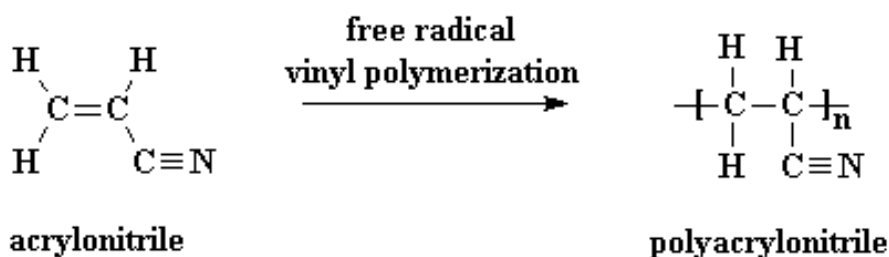


Figure 2.4: PAN chemical formula.

2.8 PMA (Polymethylacrylate)

PMA is polymer containing methacrylate groups as seen in Figure 2.5 that discovered firstly A Swiss chemist named Georg W.A. Kahlbaum. It has hydrophobic, tough, leathery and flexible properties.

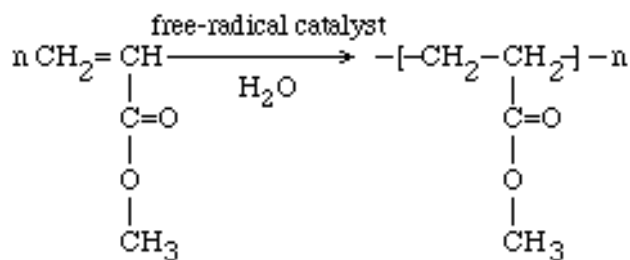


Figure 2.6: PMA chemical formula.

2.9 P(AN-co-MA) (Poly(Acrylonitrile-co-Methylacrylate))

P(AN-co-MA) is acrylonitrile's copolymer that synthesized cooperation with acrylonitrile and methylacrylate at different ratio of AN and MA, respectively as seen in Figure 2.6 . PAN is generally not used as homopolymer due to it's disadvantage that high melting point and high melt-viscosity [9,28]. For improving PAN's physical properties , its copolymers synthesized using different monomers such as butyl acrylate, methacrylate, styrene. Therefore, PAN copolymers have different crystallinity and chain packing structure e.g compare to homopolymer. PAN and its copolymers is white colour until 250 °C degree. MA provide to decrease dipole-dipole interaction between nitrile groups in AN homopolymer while forming P(AN-co-MA) copolymer[29].

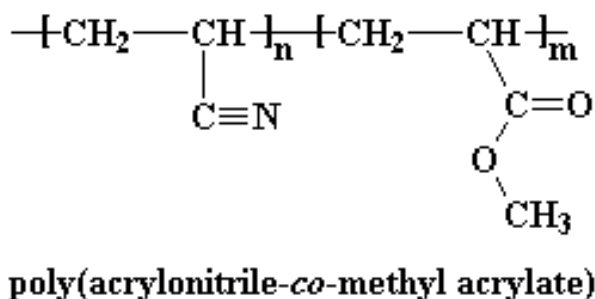


Figure 2.7: P(AN-co-MA) chemical formula.

2.10 PEDOT (Poly (3,4-ethylenedioxythiophene))

Conjugated polymers have attracted attention at last years owing to their outstanding properties. Among the conducting polymers, those based on poly(3,4-ethylenedioxythiophene) (PEDOT) as seen in Figure 2.7 have been of interest as these conducting polymers are the most chemically stable to date. Additionally, PEDOT is remarkable conjugated polymer because of having properties as good conductivity,

optical transparency, thermal stability, high flexibility, small band gap, low redox potential, environmental stability, biocompatible[30,31,32]. These properties have enabled to use them in application fields such as light emitting diodes, solar cell, sensors, biotechnology, electrochemical supercapacitors, OLEDs, flexible display[33,2,1]. PEDOT also shows perfect electrochromic properties. [2] PEDOT has disadvantage due to poor solubility and poor mechanical properties[30,1]. For this we need to improve lacking properties for increasing its efficiency combining with other chemical components such as PEDOT-PSS.

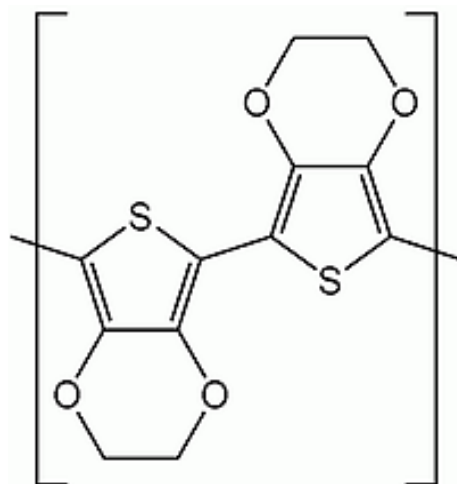


Figure 2.8: PEDOT chemical formula.

2.11 Nanofiber

Nanofibers are described as having at least a 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 have high surface area to volume ratio, high porosity, strength, reactivity, electrical and optical quality, permeability of layers[1,29]. Therefore, Nanofibers used extensively in the areas of sensors, tissue engineering, filtration, military protection clothes, micro and nanodevice, energy conversion and storage, liquid and air filtration, food and packaging, health and personal care and environmental protection, environmentally friendly biodegradable polymers, drug delivery [9,34,35]. They can be produced with variety methods such as vapor growth, arc discharge, laser ablation, chemical vapor deposition, electrospinning which provides fabricated of nanofibers more easy and efficient method than other methods.

2.12 Electrospinning

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. The Experimental setup of electrospinning shown in Figure 2.8 There are some parameters that affect forming fibers on electrospinning [35-37].

These are given following

- 1) the jet length,
- 2) solution viscosity,
- 3) surrounding gas,
- 4) flow rate,
- 5) geometry of the collector
- 6) molecular Weight Conductivity



Figure 2.9: A representative picture captured during electrospinning.

3. EXPERIMENTAL PART

3.1 Materials

Acrylonitrile (AN), Methyl acrylate (MA) were purchased from Sigma Aldrich. Ammonium persulfate (APS), Sodium dodecyl sulfonate (SDS), methanol and ethanol were all Merck reagents. EDOT was an Aldrich reagent.

3.2 Synthesis of P(AN-co-MA)

P(AN-co-MA) (Acrylonitrile 90% and Methylacrylate 10% molar ratios) was synthesized with 150ml water via emulsion polymerization using three neck flask presence of surfactant(SDS),initiator(APS) in aqueous solution. Firstly, surfactant and initiator dissolved and separated into several different bottles respectively. Subsequently, AN and MA monomers dropped into surfactant solution according to molar ratio indicated in Table 1. After, solution containing surfactant and monomers(AN and MA) mixed by magnetic stirrer ,they are transferred to three neck flask and solution of dissolved initiator was added while temperature raised 70 °C and dispersed 150 ml water in three neck flask (Figure 3.1)Synthesis performed at 70 °C temperature during six hours.

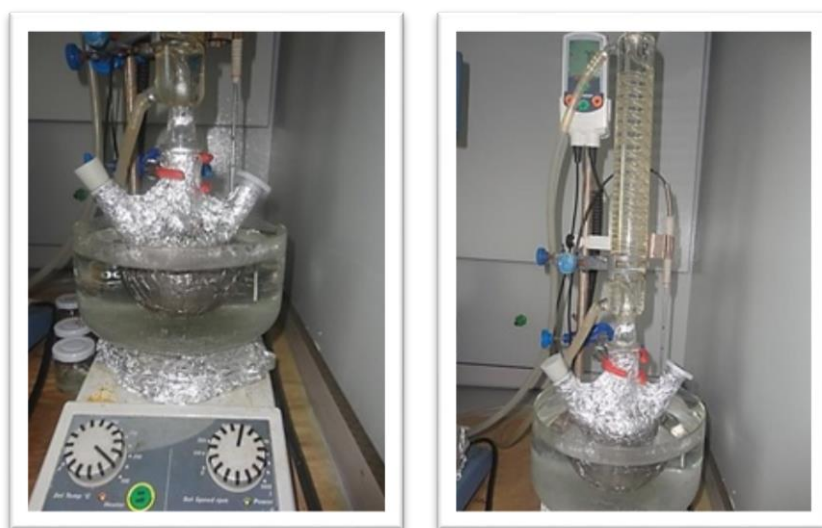


Figure 3.1: P(AN-co-MA) chemical reaction in three necked flask at 70°C temperature.

Table 1: Amount of copolymer compound for polymerization of copolymer.

	AN(mole)	MA(mole)	APS(mole)	SDS(mole)	Water(ml)
P(AN-co-MA)	0.16	0.01	0.00038	0.0065	150



Figure 3.2: P(AN-co-MA) solution in three necked flask after polymerization.

After all, prepared P(AN-co-MA) solution divided into 10 ml bottles as shown in Figure 3.3 a. One bottle containing P(AN-co-MA) solution precipitated with methanol and washed with ethanol then filtered by the use of filter paper. Later P(AN-co-MA) copolymer dried under vacuum at 70 °C. (Figure 3.3b) Other bottles separated for obtaining P(AN-co-MA)/PEDOT nanocomposite adding different molar ratio EDOT monomers on copolymer solution.

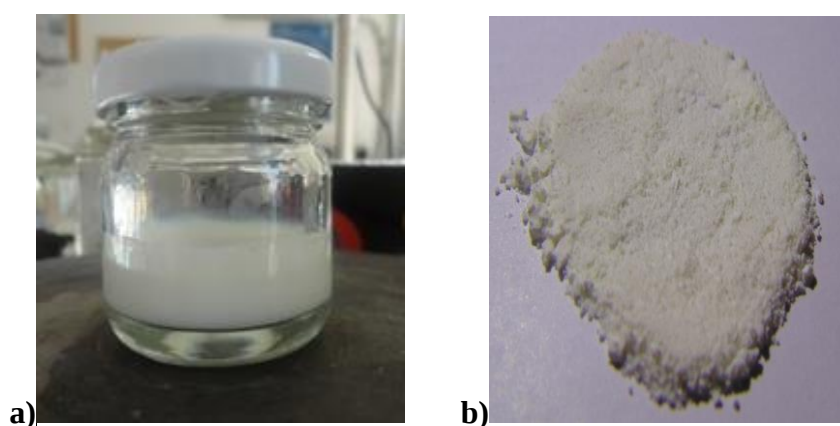


Figure 3.3: a) P(AN-co-MA) solution in 10 ml bottle b) P(AN-co-MA) copolymer after dried under vacuum at 70 °C.

3.3 Synthesis of P(AN-co-MA)/PEDOT

As explained above, to each bottles of copolymer solution variety molar ratio EDOT monomer was added for producing core shell. Firstly when EDOT monomer put into homopolymer solution, reaction performed at low yield, with the increase of different molar ratio of EDOT monomer (as shown in Figure 3.4).

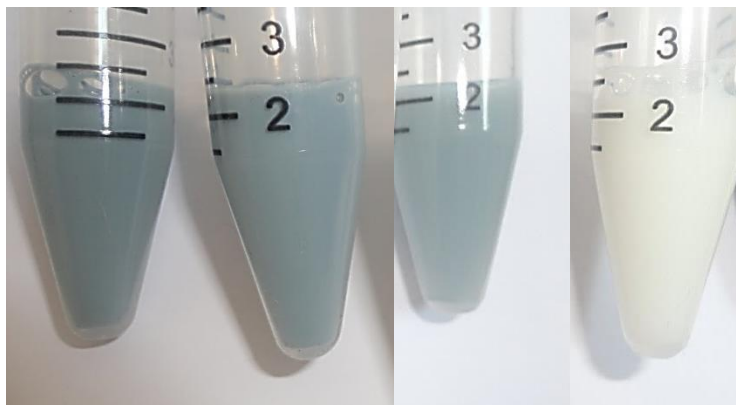


Figure 3.4: First, second, third images show in situ polymerization of EDOT 312 μl , 126 μl , 63 μl with increasing respectively with different molar ratio EDOT monomer and fourth image represents copolymer solution.

Table 2: Amount of EDOT monomer added to P(AN-co-MA) solution for first coreshell experiment.

	a)EDOT(μl)	b)EDOT(μl)	c)EDOT(μl)
P(AN-co-MA)/PEDOT	63	126	312

Therefore for coping with this problem amount of APS was increased. As a result reaction was carried out successfully after 0.0006 mol/g APS was added into P(AN-co-MA) solution. EDOT monomer added into bottles by using magnetic stirrer and at 40 °C, mixed for 12 hours (as shown in table 3). Finally, they precipitated with methanol, washed with ethanol, and dried under vacuum at 50 °C along 3 hours (as shown in Figure 3.7).

Table 3: Amount of EDOT added into P(AN-co-MA) solution for second experiment.

	a)EDOT(μl)	b)EDOT(μl)	APS(mol)
P(AN-co-MA)/PEDOT	250	500	0.00061

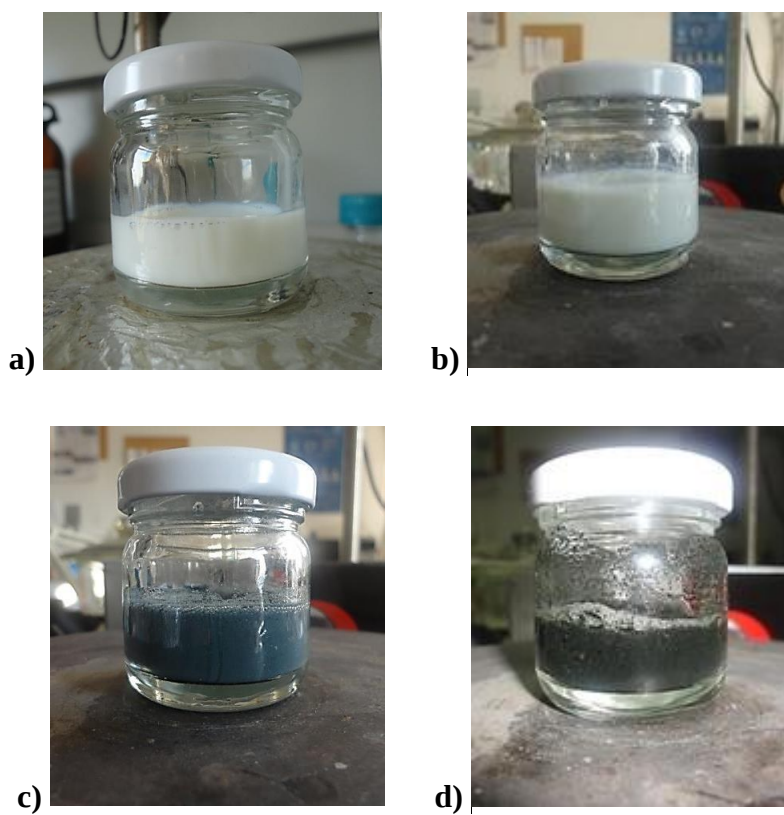


Figure 3.5: a,b,c,d show gradual polymerization of Edot in P(AN-co-MA) solution after addition of both Edot and APS.

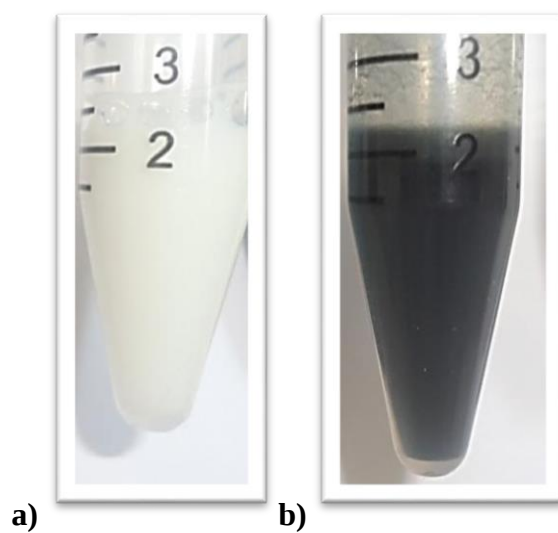


Figure 3.6: a) Image of P(AN-co-MA) solution b) Image of P(AN-co-MA)/PEDOT solution after addition of 250 µl EDOT into P(AN-co-MA) solution.



a)



b)



c)

Figure 3.7: a) P(AN-co-MA) copolymer
b) P(AN-co-MA)/PEDOT core-shell
c) P(AN-co-MA)/PEDOT nanocomposite.

4 RESULT AND DISCUSSION

4.1 FTIR-ATR Spectrophotometric Analysis

Fourier transform infrared – attenuated total reflectance (FTIR ATR) analysis of the nanocomposite and copolymer was performed by a FTIR reflectance spectrophotometer (Perkin Elmer, Spectrum One, with a universal ATR attachment with a diamond and ZnSe crystal).

As peaks shown in Figure 4.1 , AN peaks observed 2240 cm^{-1} $\text{C}\equiv\text{N}$ stretching and 1167 cm^{-1} and 1730 cm^{-1} bands respectively belong to C-O stretching and C=O stretching in MA. vibrations around 1450 cm^{-1} and 2940 cm^{-1} result from interaction of C-H stretching. 3630 cm^{-1} vibration stated to O-H stretching. Peaks 677 , 833 , and 961 cm^{-1} assigned to C-S bond in the thiophene ring [38,39].

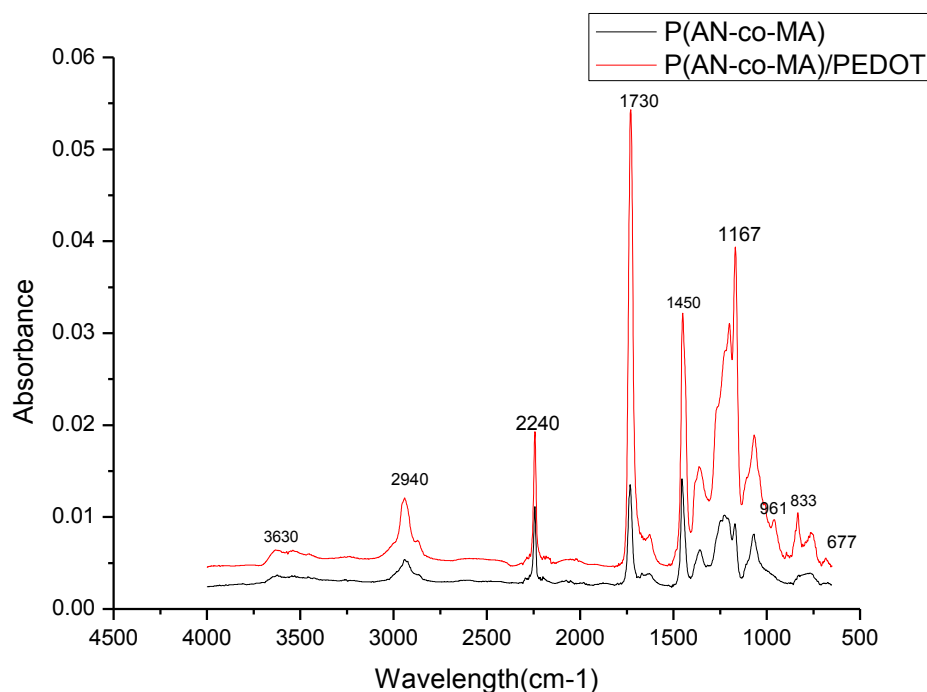


Figure 4.1: FTIR-ATR Spectrum of P(AN-co-MA) and P(AN-co-MA)/PEDOT coreshells.

4.2 UV- Visible Spectrophotometric Analyses

P(AN-co-MA)/PEDOT and P(AN-co-MA) polymers were also characterized by UV-Visible (Perkin Elmer, Lambda 45) spectrophotometric analysis. P(AN-co-MA)/PEDOT and P(AN-co-MA) polymers were dissolved wt %0.01 in DMF for analyzing by using UV-visible spectroscopy . Absorbance vs wavelength relationship of P(AN-co-MA)/PEDOT nanocomposite is shown in Figure 4.2 with a broad band between 385 and 700 nm. This peak belongs to PEDOT due to the $\pi-\pi^*$ transition band at 440 nm. Line of red related to presence of conjugated polymeric nanocomposite due to extensive range from 385 to 700 nm.

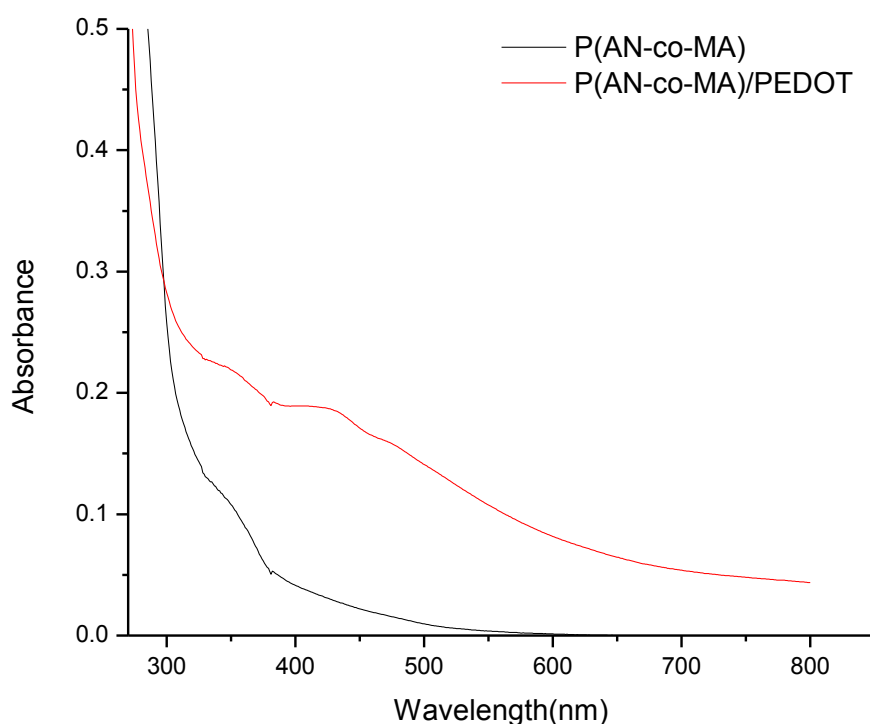


Figure 4.2: UV-Vis Spectrum of P(AN-co-MA) and P(AN-co-MA)/PEDOT core-shells wt %0.01 in DMF.

4.3 ^1H NMR Spectra Of P(AN-co-MA) Copolymers

Copolymer was dissolved in DMSO for NMR measurement. As seen in Figure 4.3, It indicated that composite contain MA range from 3.6 to 3.8 ppm because of triplet peaks. Peak between 1.63 and 2.25 ppm belong to methylene group for both AN and MA, other peaks between 2.6 and 3.25 ppm show methine of both comonomers. Water in DMSO is exhibited 3.3 ppm peaks. Also 2.5 ppm peak is belongs to DMSO. [13]

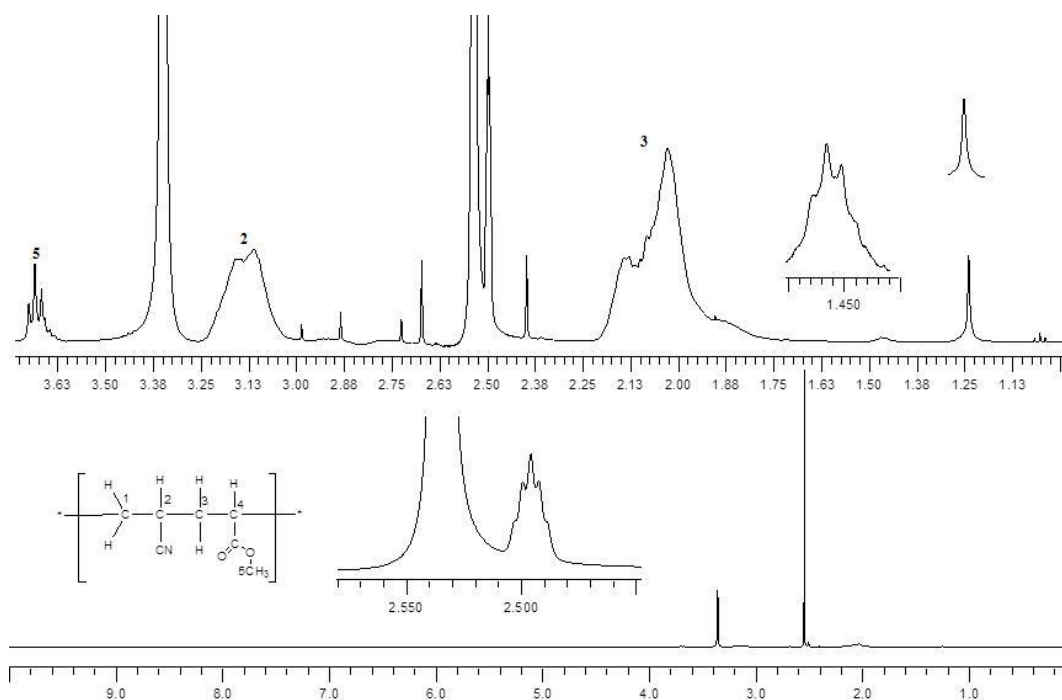


Figure 4.3: ^1H NMR spectra of P(AN-co-MA) copolymers.

4.4 Scanning Electron Microscope

Images of nanoparticles of P(AN-co-MA) and P(AN-co-MA)/PEDOT were obtained by SEM on glass surface. Synthesized P(AN-co-MA) nanoparticles dispersed in ethanol solution via ultrasonification. Subsequently they were dropped onto glass surface in order to observe nanoparticles with SEM. It showed that size of nanoparticles changed ranging from 60 nm to 139 nm as given Table 4. When morphological properties of nanoparticles of P(AN-co-MA) examined, it can be clearly seen that surface of copolymer is smooth especially when compared to P(AN-co-MA)/PEDOT nanocomposite. PEDOT is formed onto P(AN-co-MA) like cauliflower. (as shown in Figure 4.4 and in Figure 4.5). Therefore P(AN-co-MA)/PEDOT nanocomposite synthesized successfully via emulsion polymerization and covered around P(AN-co-MA) with PEDOT as a core shell structure.

Table 4: Average size of coreshell nanoparticles measured with image programme.

	P(AN-co-MA)	P(AN-co-MA)/PEDOT
Average size of nanoparticles (nm)	107.44 $\pm$ 34	115.28 $\pm$ 39

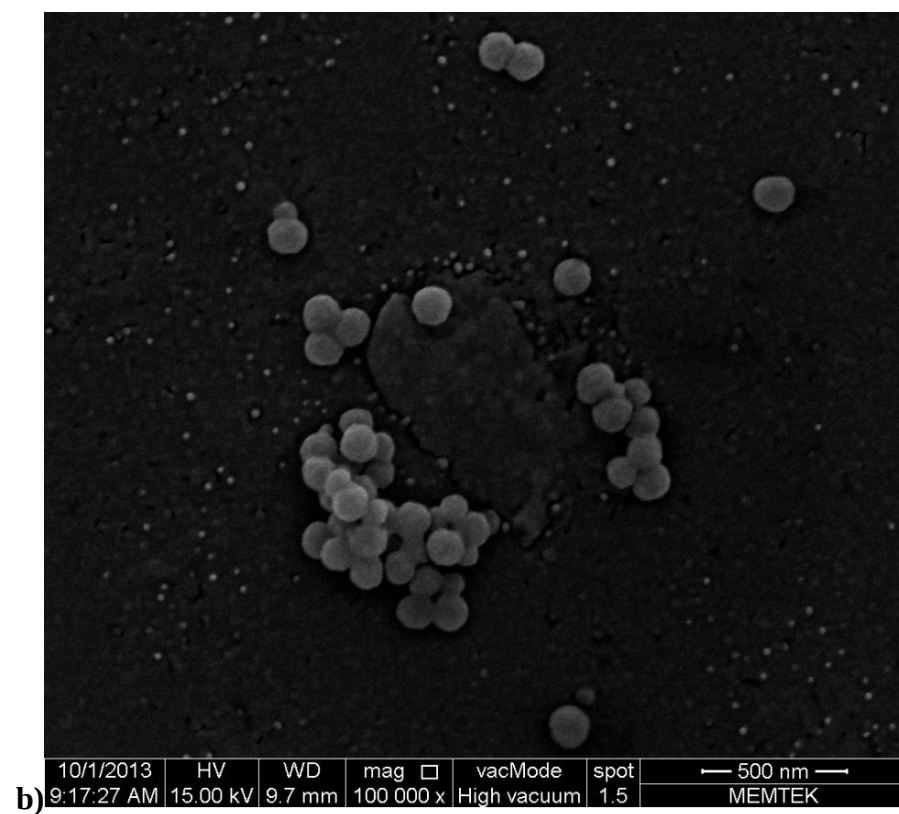
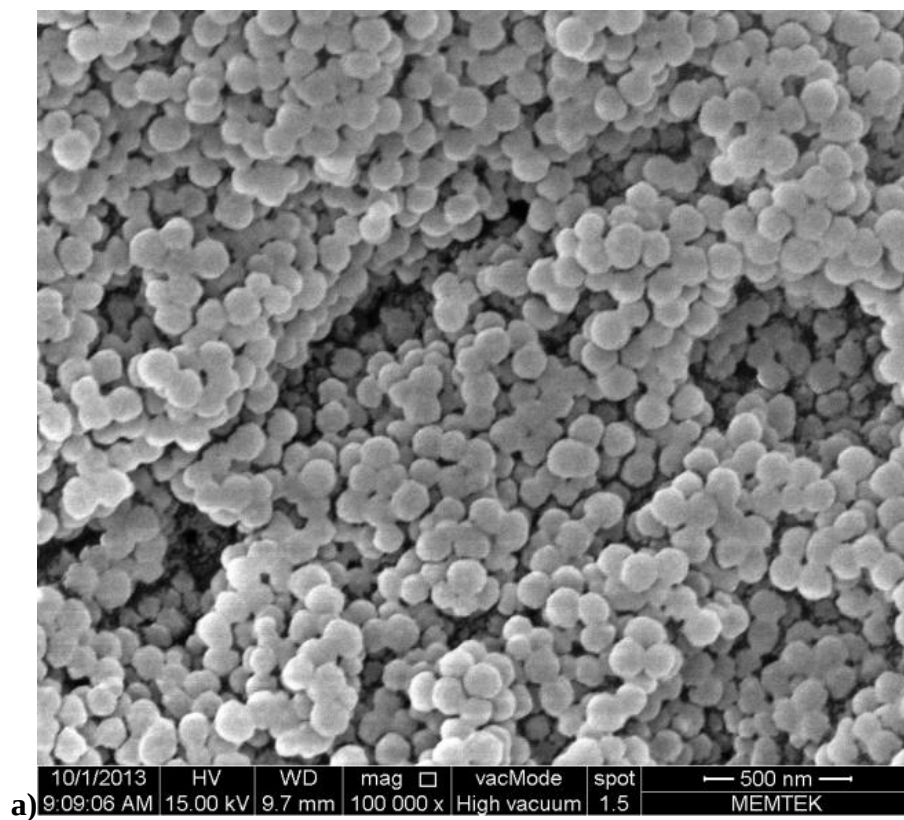


Figure 4.4: a) SEM images of P(AN-co-MA) copolymers.
b) SEM images of P(AN-co-MA) copolymers.

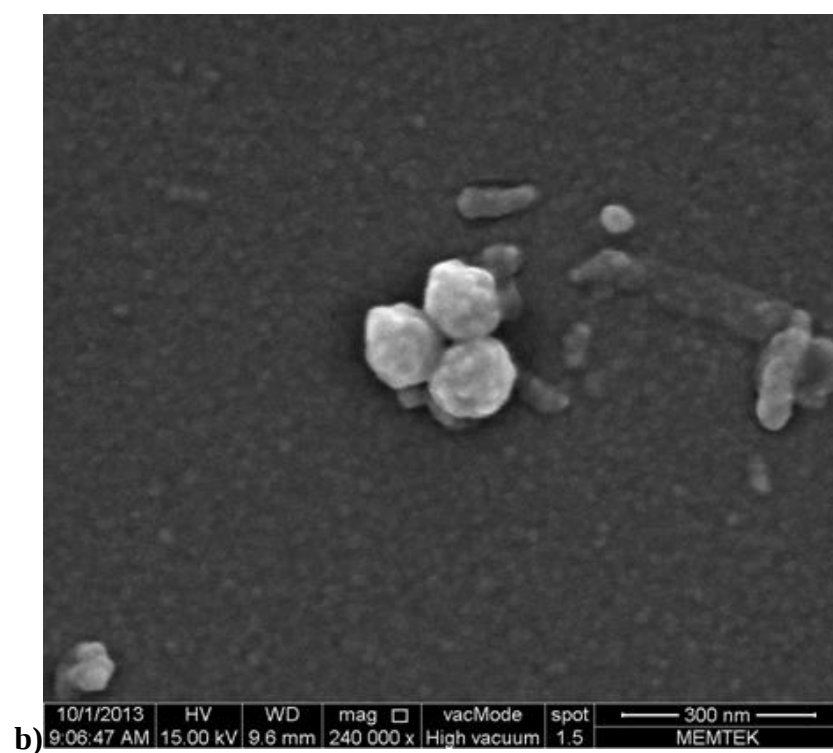
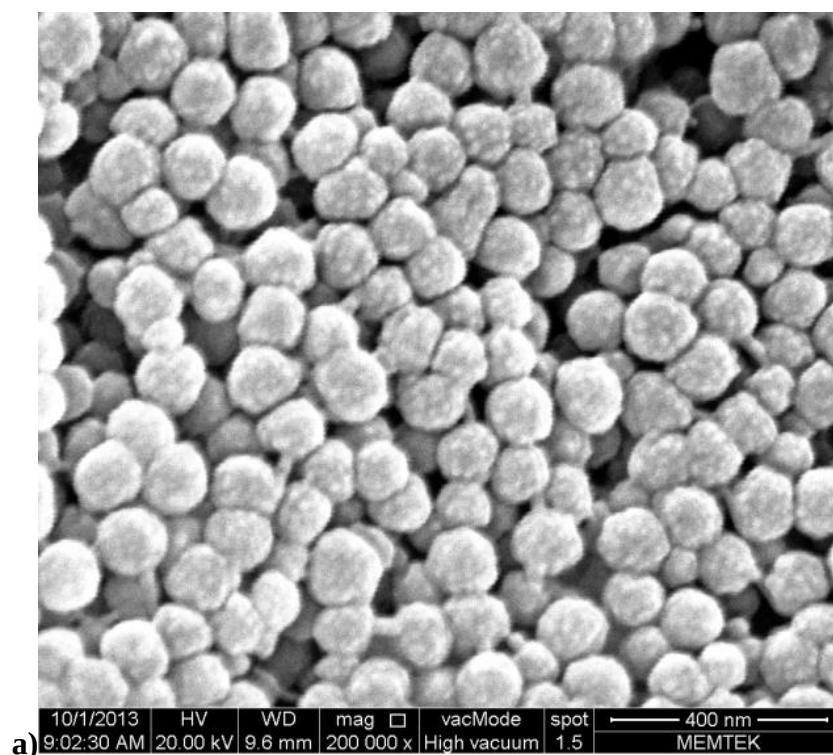


Figure 4.5: a) SEM images of P(AN-co-MA)/PEDOT coreshell (400x zoom)
b) SEM images of P(AN-co-MA)/PEDOT coreshell (300x zoom).

According to SEM images (as shown in Figure 4.6 a,b), coreshell structure vanished with increasing amount of EDOT due to aggregation of PEDOT particles with each other during polymerization.

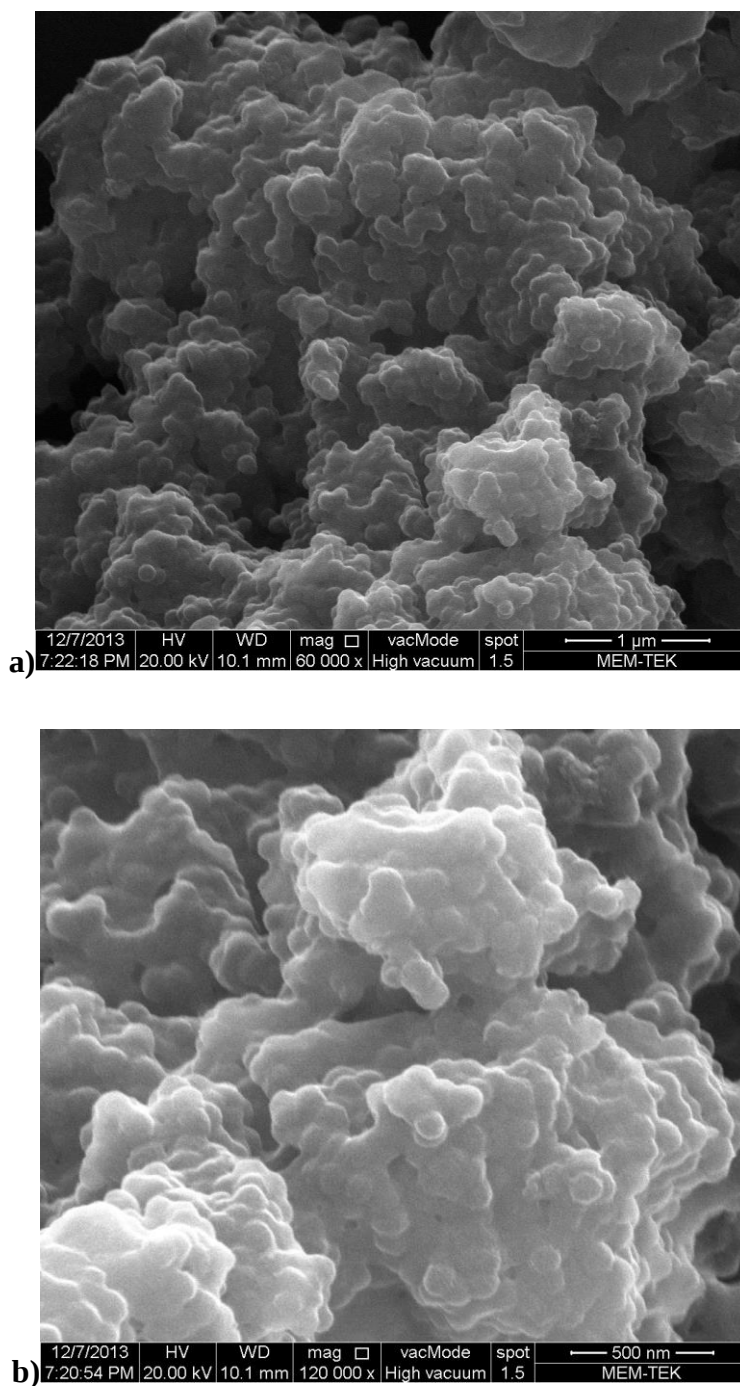


Figure 4.6: SEM images of P(AN-co-MA)/PEDOT nanocomposite after addition of 500 μ l EDOT(with high amount of EDOT)(a and b shows different scale of images).

4.5 Atomic Force Microscopy(AFM)

To observe the surface morphology of coreshell nanostructured nanocomposite was viewed on glass surface by Atomic Force Microscopy. The same coreshell nanocomposite structure was observed with SEM as analyzed by AFM and TEM.

AFM measurements of P(AN-co-MA)/PEDOT on glass surface indicated that nanoparticles are formed during the polymerization process. AFM shows same image with SEM on 6 μm area of glass surface. A further zoom into this area about 3 μm is exhibited in Figure 4.9 as three dimensional representation. This view indicates that the coreshell nanostructured nanocomposite is placed over the glass surface around big spot and it has approximate diameter of coreshell of 120 nm. As shown in Figure 4.7 and in Figure 4.8 , sum of nanoparticles seen on glass surface corner as a big spot.

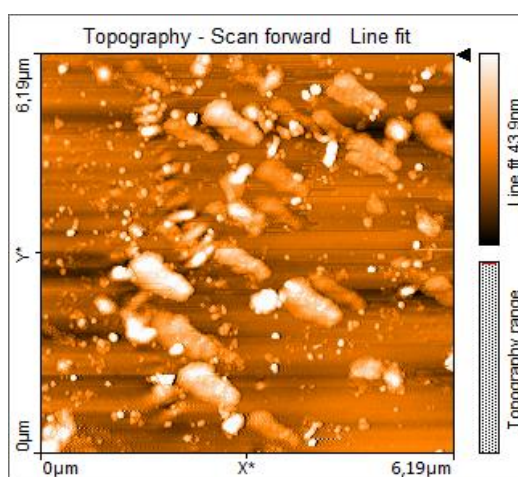


Figure 4.7: AFM image of P(AN-co-MA)/PEDOT coreshells 6x6 μm area on glass surface.

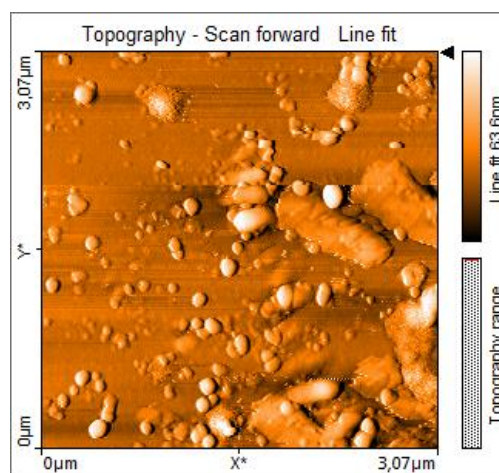


Figure 4.8: AFM image of P(AN-co-MA)/PEDOT coreshells 3.07x3.07 μm area on glass surface.

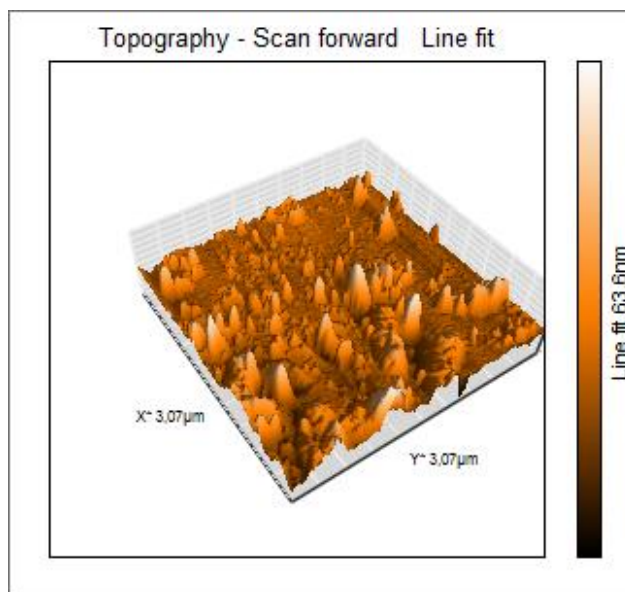


Figure 4.9: AFM 3D image of P(AN-co-MA)/PEDOT coreshells 3.07x3.07 μm area on glass surface.

4.6 Transsmision Electron Microscope analysis (TEM)

Characterization of the coreshell nanostructured nanocomposite morphology is further analyzed by performing TEM as seen in Figure 4.10. Also as shown in Figure 4.11 high magnification TEM images show the presence of the coreshell structured nanocomposite formed with in situ polymerization.

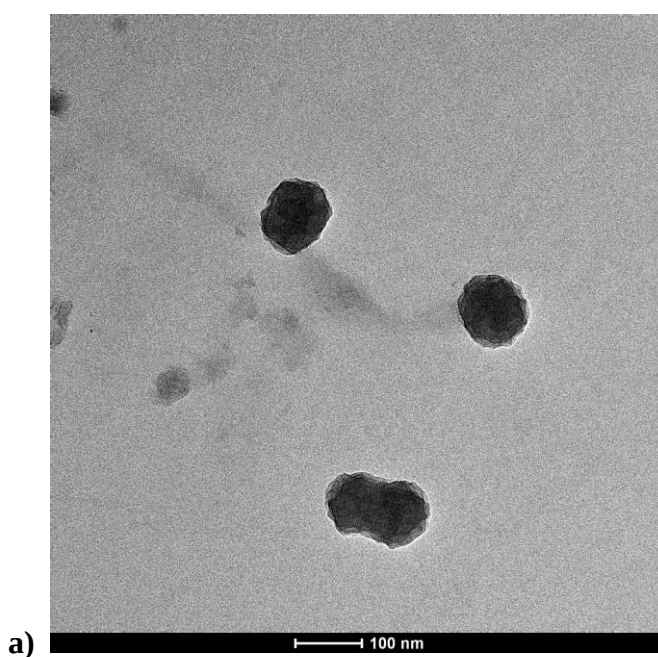


Figure 4.10: a) TEM images of P(AN-co-MA) copolymer
b) TEM images of P(AN-co-MA) copolymer.

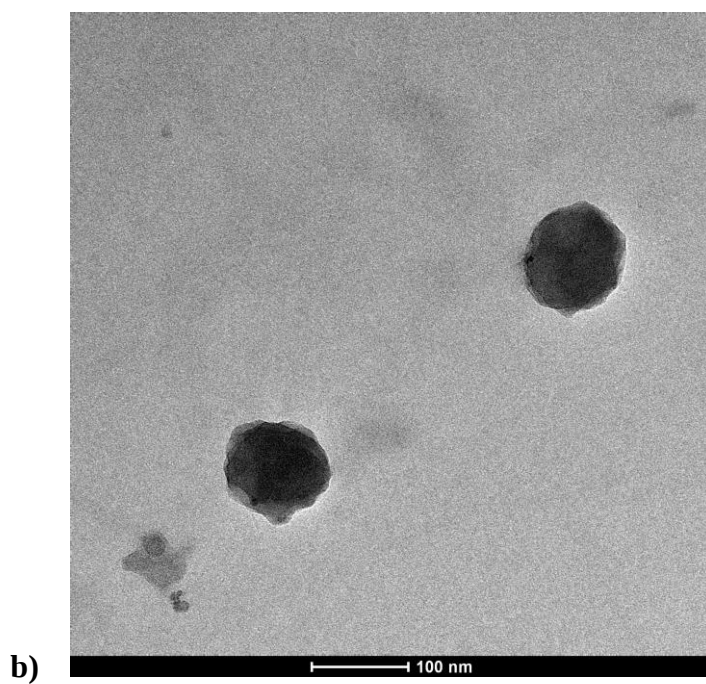


Figure 4.10 (continued): a) TEM images of P(AN-co-MA) copolymer
b) TEM images of P(AN-co-MA) copolymer.

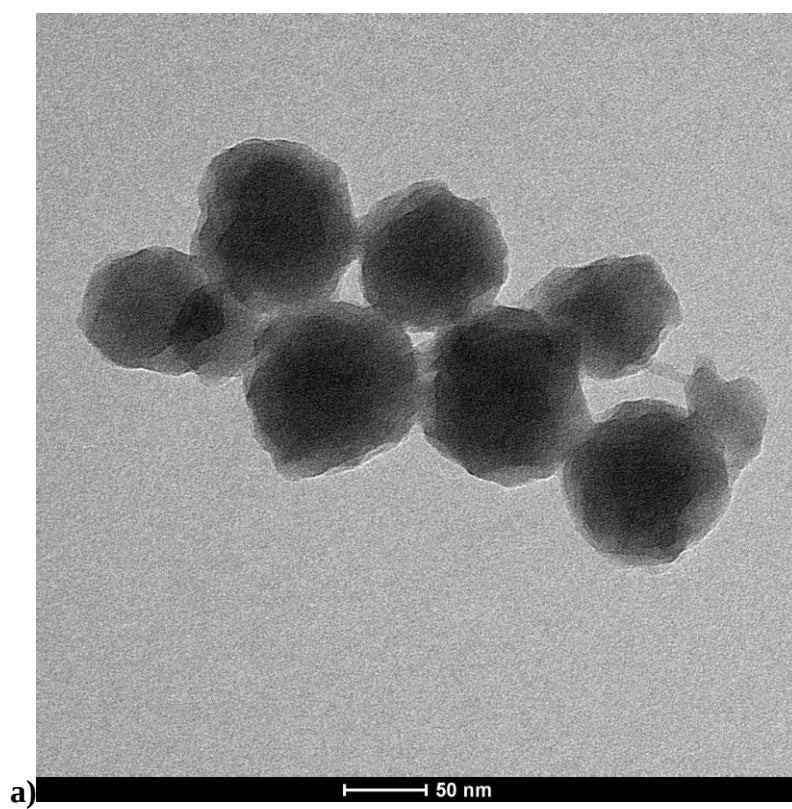


Figure 4.11: a) TEM images of P(AN-co-MA)/PEDOT coreshell
b) TEM images of P(AN-co-MA)/PEDOT coreshell
c) TEM images of P(AN-co-MA)/PEDOT coreshell.

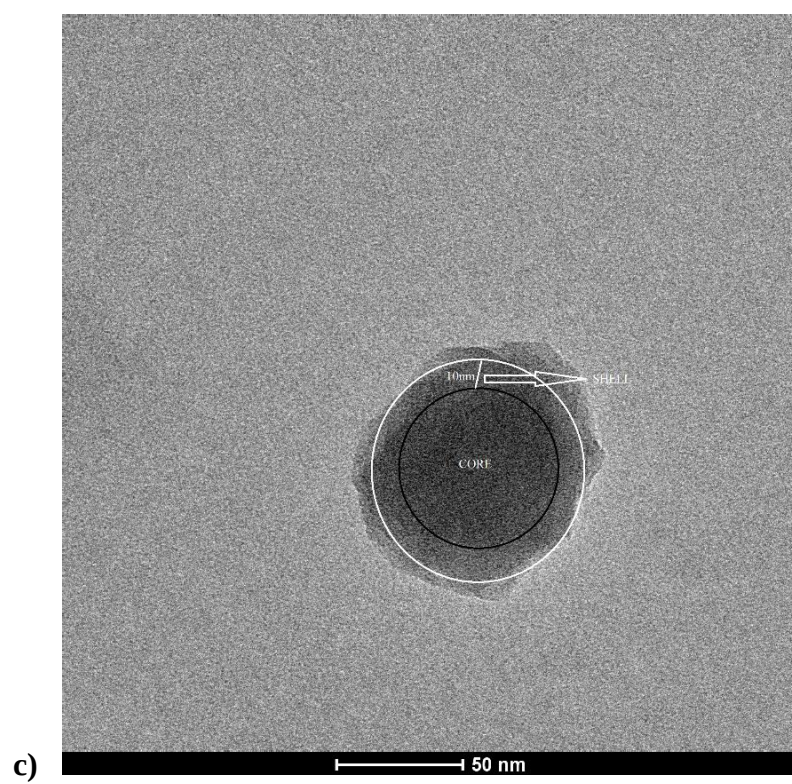
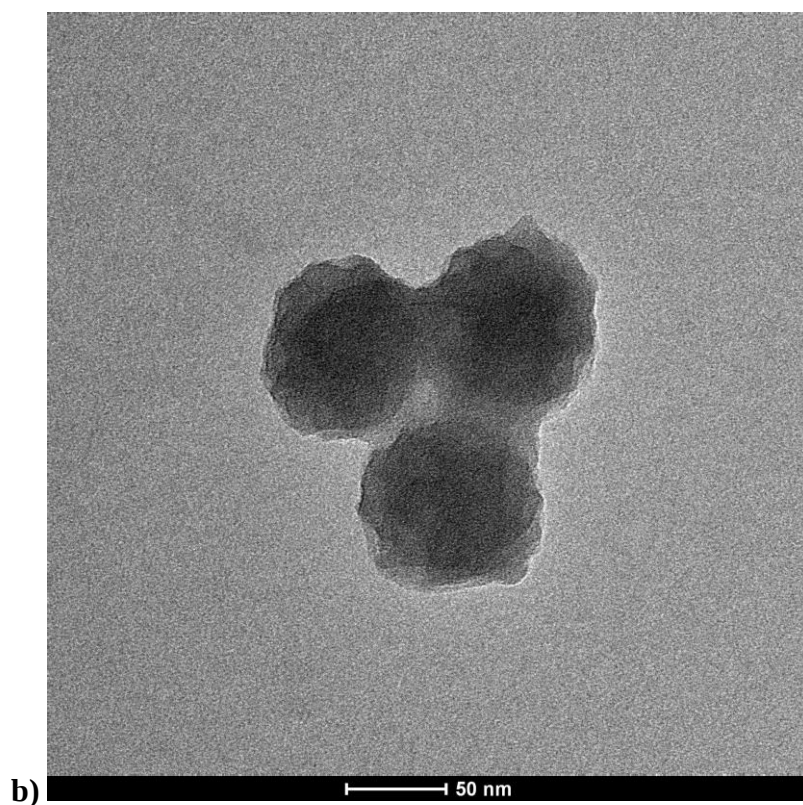


Figure 4.11(continued): a)TEM images of P(AN-co-MA)/PEDOT coreshell
b)TEM images of P(AN-co-MA)/PEDOT coreshell
c)TEM images of P(AN-co-MA)/PEDOT coreshell.

4.7 Nanofibers of P(AN-co-MA)/PEDOT

Conductive polymers have disadvantage such as weaker in mechanical strength, fragile, instability, lower resolution capability [6-8]. Hence, nanofiber of conductive polymers cannot be easily produced and operated. Therefore nanocomposite was formed with conductive polymer in order to deal with this problem and gain new properties such as increasing mechanical properties and solubility.

As shown in Figure 4.12, P(AN-co-MA)/PEDOT nanocomposite were dissolved as wt % 5 solution concentration in DMF to produce nanofibers with electrospinning method on aluminum template applying 12 kV with feed rate of 0.5 mL/h at Tip-to-collector distance of 15 cm. (Table 5)



Figure 4.12: Dissolved P(AN-co-MA)/PEDOT and P(AN-co-MA) in DMF for electrospinning.

Table 5: Electrospinning Parameters.

	Electrospinning Parameters
Applied voltage	12 KV
Solution concentration	Wt %5
Feed rate	0.5 ml/h
Tip-to-collector distance	15 cm

4.8 Characterization Of Nanofiber

4.8.1 Optical microscope

As shown in Figure 4.13, nanofibers are viewed significantly to understand their fiber and morphologic properties with optical microscopy. According to this image, nanofibers formed successfully by electrospinning and they dispersed homogeneously on aluminum template.



Figure 4.13: Optical Microscopy Images of Nanofibers Wt %5 P(AN-co-MA)/PEDOT

4.8.2 Scanning electron microscope

According to SEM images of nanofibers they formed morphologically like hair. Some places on nanofiber have porous surface as seen in Figure 4.14. Average size of nanofibers are founded to be 829 nm using image programme in Table 6.

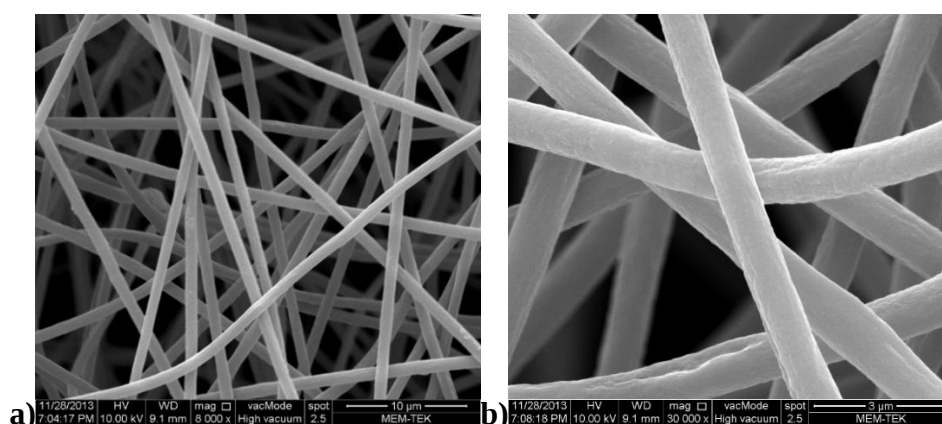


Figure 4.14: SEM Images of Nanofiber of Wt %5 P(AN-co-MA)/PEDOT (a,b,c,d represents different scale image).

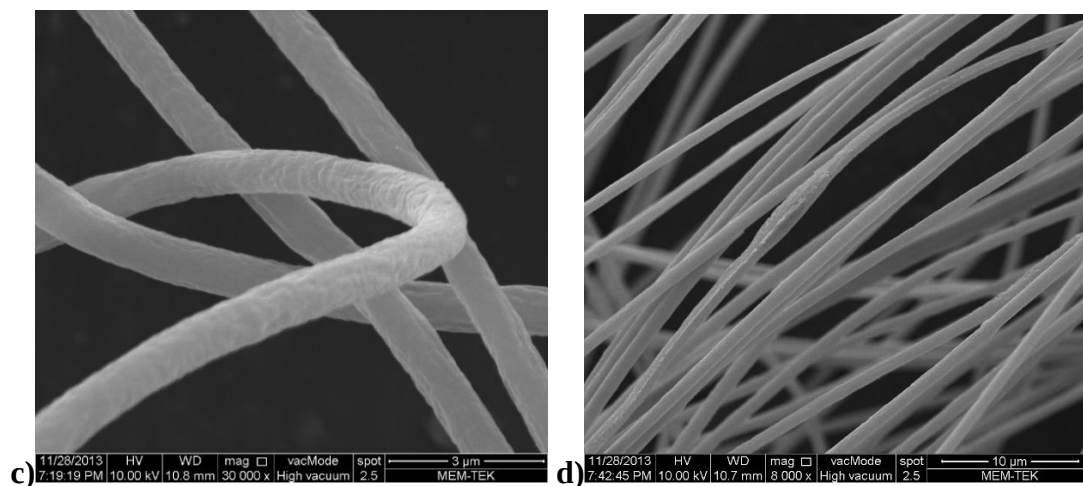


Figure 4.14(continued): SEM Images of Nanofiber of Wt %5 P(AN-co-MA)/PEDOT (a,b,c,d represents different scale image).

Table 6: Average diameter of nanofibers.

	Nanofiber
Average size of nanofibers(nm)	829.36±20

4.8.3 Energy dispersive X-ray analysis (EDX)

To determine the chemical composition of nanofibers(in Table 7) on aluminium template EDX was used. According to EDX results in Figure 4.15 N,C,O,S elements were found in nanofibers. So ‘N’ components belong to ‘AN’ and ‘S’ was belong to PEDOT . Also, Al belong to aluminium template under nanofibers.

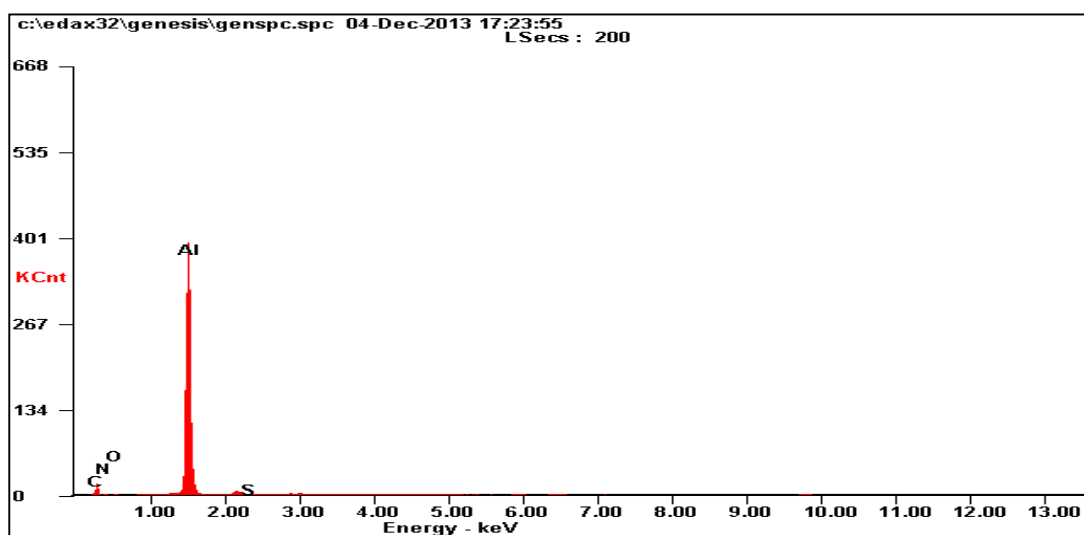


Figure 4.15: EDX analyze of Nanofibers of Wt %5 P(AN-co-MA)/PEDOT The spectrum of the nanocomposite containing signals from C, N, O and S further confirm the existence of PEDOT and P(AN-co-MA).

Table 7: The percentage of each element provided by SEM EDS in nanofibers.

<i>Element</i>	<i>Wt %</i>	<i>At %</i>
C K	37.18	55.07
N K	05.01	06.36
O K	00.99	01.10
Al K	56.71	37.40
S K	00.11	00.06

4.8.4 Electrochemical impedance spectroscopy (EIS)

EIS measurement of nanofibers is determined in %0.01 M LiClO₄ solution on ITOPET with a platinum wire as a counter electrode, and a Ag wire as a quasi-reference electrode by Parstat 2263 Electrochemical Analyser via electrochemical impedance spectroscopy measurement. The Nyquist, Bode Magnitude, Bode Phase and admittance data of the EIS is measured in the frequency range 0.01 Hz–100 kHz using Z SimpWin V3.10, AC-impedance data analysis software program. An excellent agreement between experimental results and the parameters was observed with Chi-square.

The EIS results were fitted with an equivalent electrical circuit for learning about nanofiber electrochemical and physical characteristics. As seen in Figure 4.16 R_s, R_{ct}, W, R_c, R_{ct} refers to solution resistance, electron charge transfer, warburg Impedance, ionic charge transfer resistance and charge transfer resistance respectively. C_{pe1} and C_{pe2} is also attributed to constant phase element for porosity and surface, double layer capacitance, respectively. Nanofibers containing PEDOT have been doped by ClO₄ ions during EIS measurement so it shows resistivity to ionic charge transfer(R_c) [3]. On other hand, warburg Impedance is observed due to electrons diffusion onto porous of nanofibers. Thus, C_{PE1} evaluated as ionic charge capacitor because of the surface morphologies of nanofibers such as porosity, polarity[40]. R_{ct} indicates the charge transfer resistance of nanofibers on FTO glass. C_{PE2} denoted the double-layer capacity of nanofiber electrode [20,41,32]. Impadance Q calculated as following ; **(4.8)**

$$Z_{CPE} = \frac{1}{Q(i\omega)^\alpha}, \quad (4.8)$$

If n value is equivalent to $n=1$, system has ideal capacitor, a capacitor can be treated as a pure good capacitor, but $0.5 < n < 1$ value indicates the deviation from ideal capacitor and ideal dielectrics behavior [5,42].

As shown in Figure 4.17, nyquist and bode phase values indicates that nanofibers have capacitive behavior. For EIS measurement, three nanofiber pattern prepared on FTO glass with electrospinning method at the same conditions and then measured their electrochemical impedance values from the equivalent circuit model in Table 8.

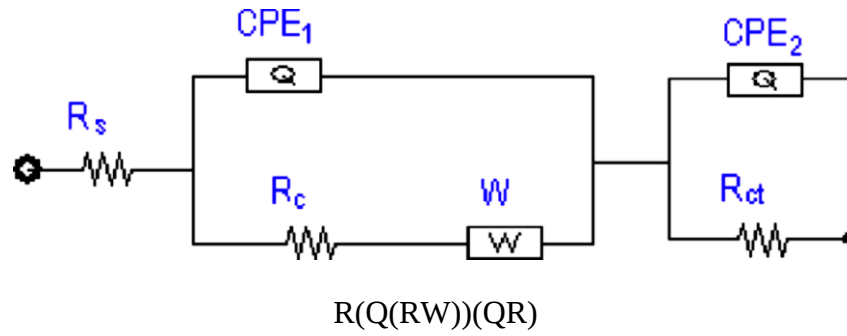
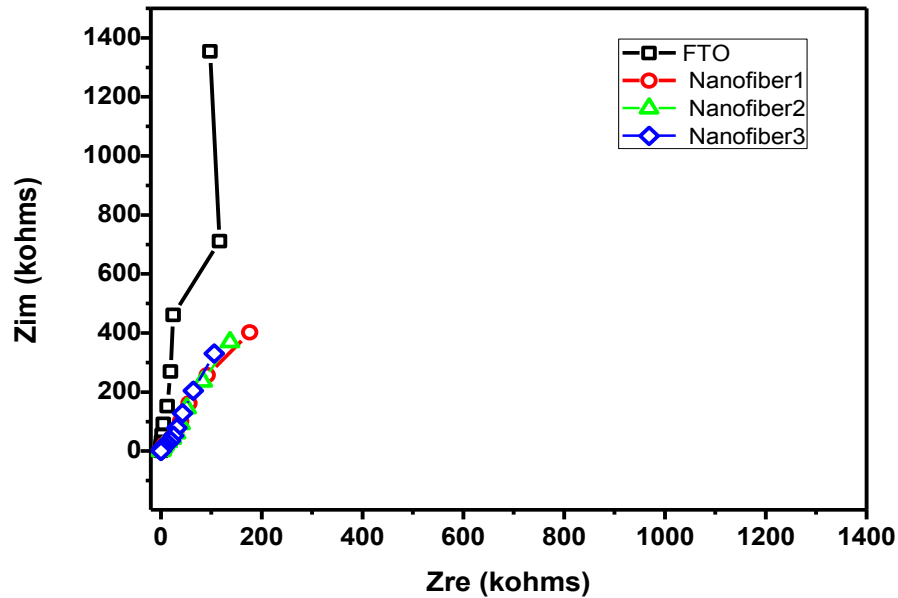
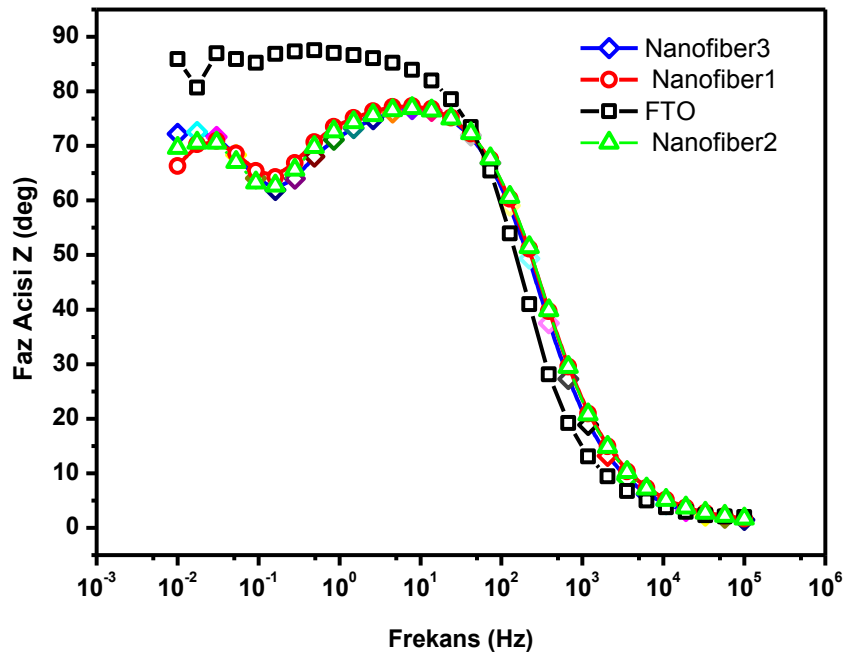


Figure 4.16: The equivalent circuit model of the electrospun nanofibers of P(Acrylonitrile-co-Methylacrylate)/PEDOT nanocomposite; R_s solution and pore resistance, R_c and C_{PE2} are the resistance and the capacitance of the nanofiber; R_{ct} is charge transfer resistance; C_{PE1} is used for modelling the double layer capacitance.

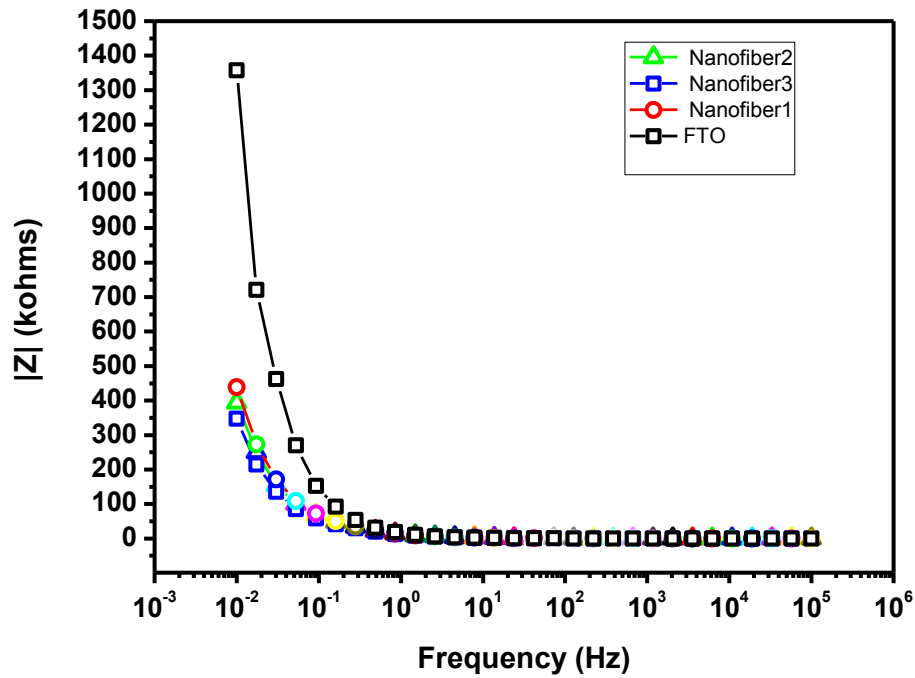


a)

Figure 4.17: (a) Nyquist plots, (b) bode phase, (c) Bode Magnitude d) Admittance indicating that measured and calculated datas well fitted to each other

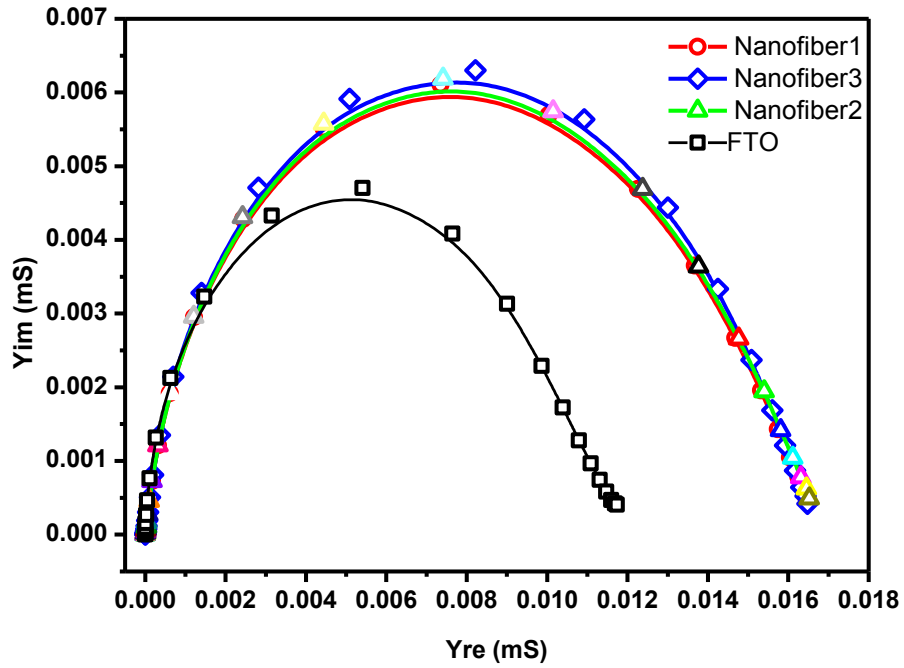


b)



c)

Figure 4.17(continued): (a) Nyquist plots, (b) bode phase, (c) Bode Magnitude (d)Admittance indicating that measured and calculated datas well fitted to each other.



d)

Figure 4.17(continued): (a)Nyquist plots, (b) bode phase, (c) Bode Magnitude (d)Admittance indicating that measured and calculated datas well fitted to each other.

Table 8: Content of dependence of parameters calculated from the equivalent circuit model for the electrospun nanofibers of P(Acrylonitrile-co-Methylacrylate)/PEDOT.

	Nanofiber1	Nanofiber2	Nanofiber3
$R_s [\Omega \text{ cm}^2]$	62.26	62.52	62.91
$CPE_1 [\text{mF cm}^{-2}]$	$4.005 \cdot 10^{-5}$	$3.729 \cdot 10^{-5}$	$3.225 \cdot 10^{-5}$
n	0.8	0.8	0.8
$R_{CT} [\Omega \text{ cm}^2]$	$5.042 \cdot 10^5$	$1.062 \cdot 10^6$	$8.047 \cdot 10^5$
$W_{Yo}/(S \text{ s}^{-n} \text{ cm}^{-2})$	$4.45 \cdot 10^{-6}$	$8.443 \cdot 10^{-6}$	$7.111 \cdot 10^{-6}$
$CPE_2 [\text{mF cm}^{-2}]$	$2.55 \cdot 10^{-5}$	$2.308 \cdot 10^{-5}$	$2.437 \cdot 10^{-5}$
n	0.8508	0.8457	0.8422
$R_c [\Omega]$	$3.024 \cdot 10^4$	$4.259 \cdot 10^4$	$5.964 \cdot 10^4$
chi squared	$6.601 \cdot 10^{-4}$	$8.853 \cdot 10^{-4}$	$3.875 \cdot 10^{-4}$
sample area in square cm x^2	1	1	1

4.9 Cyclic Voltammetry

The electrochemical behaviour of nanofibers of P(AN-co-MA)/PEDOT nanocomposite on FTO glass electrode was tested through cyclic voltammetric measurements in %0.01 M LiClO₄ solution.

Different scanning rates were used to investigate the dynamic property of P(AN-co-MA)/PEDOT nanofibers. Cyclic voltammetry (CV) was carried out at a scanning rate of 20-100 mV/s between -0.3 and 1 V. As is shown in Figure 4.18, curves of CV is proportional to the scan rates which shows an electric charge-transfer controlled process. With increasing scan rates increases electrical capacitance. [43,46]. High surface area and presence of PEDOT result a high current during oxidation and reduction indicating well reversibility the dependence of anodic and cathodic charges.[44,45]. Figure 4.18 indicates the stability of the film coating on FTO glass with increasing the number of cycles in monomer free solution. Also the CVs demonstrates the better doping of Cl⁻, ClO₄⁻. Further detailed electrochemical study on these fibers are in progress.

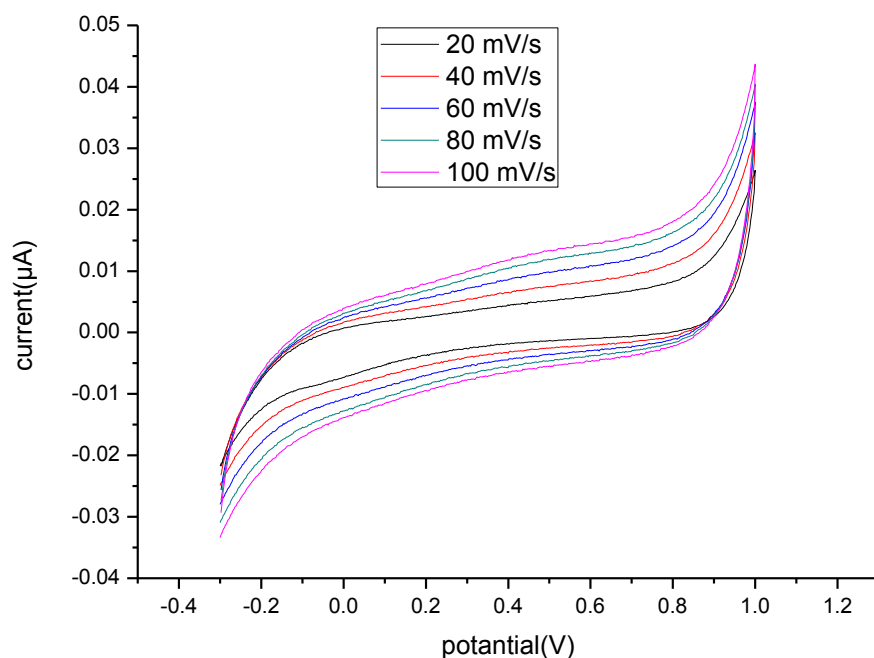


Figure 4.18: Cyclic voltammograms of nanofibers of P(AN-co-MA)/PEDOT nanocomposite on FTO glass electrode using %0.01 M LiClO₄ solution at five extreme sweep rates (a) 20 mV/s (b) 40 mV/s (c) 60 mV/s (d) 80 mV/s (e) 100 mV/s

5. CONCLUSIONS

We synthesized successfully P(Acrylonitrile-co-Methylacrylate)/PEDOT Coreshell Structured Nanocomposite as first objective of thesis. According to FTIR , UV, NMR spectroscopic data of nanocomposite have contained chemical compositions of P(Acrylonitrile-co-Methylacrylate) and PEDOT. SEM and AFM images give clear indication of coverage of P(Acrylonitrile-co-Methylacrylate) with PEDOT like cauliflower structure and they provide information about size of nanocomposite with approximately 115 nm using image program. In the second part of thesis, Nanofibers produced with electrospinning method by dissolving in DMF wt % 5 of polymer and it was characterized by SEM, Optical microscopy, EDX and EIS. The results indicate that nanofiber have high capacitive values which measured by EIS and best fitted to $R(Q(RW))(QR)$ circuit model. Repeated EIS measurements on different nanofiber samples under same conditions show that Impedance results indicated similarity.

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doi:10.1016/j.electacta.2011.08.024

CURRICULUM VITAE



Name Surname: Ömer EROĞLU

Place and Date of Birth: MALATYA 06.07.1987

Address: Yakakent Mah. 8087/11 Sok. No:48/14 Çiğli-İZMİR

E-Mail: eroglu_3544@hotmail.com

B.Sc : Ataturk University/Physics

M.Sc. : Istanbul Technical University / Nano Science & Nano Engineering

PUBLICATIONS/PRESENTATIONS ON THE THESIS

▪EROĞLU O,UNSAL C, SARAC A. S., 2013: Synthesis and Characterizations of Polythiophene /Poly(Acrylonitrile-co-Methylacrylate) Coreshell Structured Nanocomposites, Nano TR 9 9th Nanoscience and Nanotechnology Conference, June 26, 2013 Erzurum, Turkey.