

ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE
ENGINEERING AND TECHNOLOGY

**POLYPYRROLE /POLY(ACRYLONITRILE-CO-METHYLACRYLATE)
NANOCOMPOSITES, NANOFIBERS AND THEIR CHARACTERIZATIONS**

M.Sc. THESIS

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Department of Nano Science & Nano Engineering

Nano Science & Nano Engineering Program

Thesis Advisor: Prof. Dr. A. Sezai SARAÇ

JUNE 2012

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

**POLİPİROL /POLİ(AKRİLONİTRİL-KO-METİLAKRİLAT) NANO
KOMPOZİTLERİ, NANOFİBERLERİ VE KARAKTERİZASYONLARI**

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To my family,

FOREWORD

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ABBREVIATIONS

μl	: Microliter
AN	: Acrylonitrile
cm	: Centimeter
DBSA	: Dodecyl benzen sulfonic acid
DMA	: Dynamic Mechaniz Analyzer
DMF	: Dimethyl formamide
DSC	: Differential Scanning Calorimetry
FTIR-ATR	: Fourier Transform Infrared-Attenuated Total Reflectance
g	: Gram
KPS	: Potassium Persulfate
MA	: Methyl acrylate
ml	: Mililiter
P(AN-co-MA)	: Acrylonitrile – Methyl acrylate copolymer
PAN	: Polyacrylonitrile
PPy/p(AN-co-MA)	: Polypyrrole / Poly Acrylonitrile-co-Methylacrylate composite
PPy	: Polypyrrole
Py	: Pyrrole
SEM	: Scanning Electron Microscopy
Tg	: Glass Transition Temperature

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POLYPYRROLE / POLY(ACRYLONITRILE-CO-METHYLACRYLATE) NANOCOMPOSITES, NANOFIBERS AND THEIR CHARACTERIZATIONS

SUMMARY

This study can be mainly categorized into two parts, first of all obtaining Polypyrrole/Acrylonitrile-co-Methylacrylate latexes that obtained by emulsion polymerization, secondly obtaining nanofibers by electrospinning method from the precipitated form of these nano-composites. Emulsion polymerization of Acrylonitrile (AN) and Methylacrylate (MA) was performed in the aqueous medium with the presence of surfactant Dodecyl Benzen Sulfonic Acid (DBSA) and initiator Potassium Persulfate (KPS). After copolymerization, different amounts of pyrrole droplets are added into emulsion latexes and reaction continued with the left initiator. At the end of the polymerization of polypyrrole with the AN-co-MA latexes, nanoparticles of Ppy/(AN-co-MA) are sampled and the morphology is characterized by Scanning Electron Microscopy(SEM). Also the nanoparticle size is determined by Particle Size Analyzer (light scattering) and measuring on SEM images. Nanoparticles were successfully obtained as 83-103 nm diameter changing by the different polypyrrole amounts. Then the polypyrrole containing and non-containing nanoparticle latexes are precipitated with methanol and dried in oven. Samples without polypyrrole shown a hard-plasticity, however polypyrrole containing samples are appeared as powder-like structure. Then dried composites were dissolved in Dimethyl Formamide (DMF) in a certain percent of solvent by weight and electrospun by an electrospinning device that contains a power supplier, pump, syringe and metal collector. The distance between collector and syringe, solution percentage by weight, applied voltage was not changed by trials. At the end of the electrospinning, nanofibers were obtained in the range of 200-700 nm diameter. In addition to nanofibers, the DMF containing solution of nanocomposites were poured into special surfaces and films are obtained. Nanofibers are characterized by SEM and Dynamic Mechanic Analyzer. Dried particles are characterized by both Fourier Transform Infrared-Attenuated Total Reflectance (FTIR-ATR), UV-Visible Spectroscopy and Differential Scanning Calorimetry (DSC). Uv-

Visible Spectroscopy results are examined with particle sizes and it was observed that the UV-Visible absorption is directly proportional with the particle size of nanoparticles. DSC analysis showed that the glass transition temperature is increased by the increasing pyrrole addition . The films were characterized by Dynamic-Mechanic Analyzer (DMA) as obtaining stress-strain curves, and it was obviously seen that the Young's Modulus of films are increased by increasing amounts of pyrrole added.

POLİPİROL /POLİ(AKRİLONİTRİL-KO-METİLAKRİLAT) NANO KOMPOZİTLERİ, NANOFİBERLERİ VE KARAKTERİZASYONLARI

ÖZET

İletken polimerler son zamanlarda oldukça fazla ilgi çekmeye başlamış ve iletkenlik gereken alanlarda polimerlere yönelinmesi, bu polimerlerin yeni kullanım alanlarına entegre edilmesi çalışmalarını hızlandırmıştır. İletken polimerlerin proses edilme sırasında gösterdikleri birtakım olumsuz özellikler, bu malzemelerin çeşitli polimerlerle bir araya getirilerek avantaja çevrilmesi konusunu gündeme getirmiştir. Kabuk-Öz (Core-Shell) yapının oluşturulması da bu çalışmalardan biridir. Bu çalışma temel olarak iki kategoriye ayrılabilir. İlk olarak emülsiyon polimerizasyonu yöntemiyle Polipirol/Poli(Akrilonitril-Ko-Metil akrilat) lateksinin elde edilmesi, ikinci olarak ise elde edilen lateks nano kompozit yapıdan, yapı çöktürülüp kurutulduktan sonra elektrospinning yöntemi ile nanofiber elde edilmesi gerçekleştirilmiştir. Öncelikle akrilonitril (AN) ve metil akrilatın (MA) sulu ortamda emülsiyon polimerizasyonu, ortamda yüzeyaktif madde olan dodesil benzen sülfonik asit (DBSA) ve başlatıcı potasyum per sülfat (KPS) bulunmasıyla tamamlanmıştır. Kopolimerizasyon gerçekleşikten sonra işlem sonlandırılmadan, polimerizasyon devam eder durumda iken emülsiyon ortamına farklı miktarlarda pirol (Py) damlaları eklenerek ortamda ilk polimerizasyondan kalmış olan başlatıcıyla polimerizasyona devam edilmiştir. Burada önemli olan, pirol ekleme aşamasında pirolün kopolimerleşmesi için ilave başlatıcı kullanılmamış olmasıdır, ortamda var olan başlatıcı ile işleme devam edilmiştir. Pirolün akrilonitril-ko-metilakrilat lateksi ile kopolimerleşmesi sonrasında Ppy/P(AN-co-MA)'nın lateks ortamındaki nanopartiküllerinden (henüz çöktürme ve kurutma yapılmadan) örnek alınıp, morfolojisi Taramalı Elektron Mikroskobu (SEM) ile incelenmiştir. Aynı zamanda Partikül Boyut Analiz (Işık Saçılımı) cihazı ile ve SEM görüntüleri üzerinden ölçüm alma yöntemiyle nanopartikül boyutları belirlenmiştir. Değişen polipirol miktarlarıyla başarılı bir şekilde 83-103 nm çaplarında küre şekilli nanopartiküller elde edildiği görülmüştür. Ardından polipirol içeren ve içermeyen lateksler (çöktürülmemiş nanopartikül içeren emülsiyon ortamı) metanol ile çöktürülerek fırında yapısında kalan su tamamen buharlaşmaya kadar kurutulmuştur. Polipirol

içermeyen numuneler (P(AN-co-MA)) tek parça halinde katılaşp, kırılmaz-sert-plastisite yapısı göstermiş olup, içerenler ise (Ppy/P(AN-co-MA)) biraraya yapışmayp ince toz formunda, yumuşak yapıda ortaya çıkmışlardır. Yapıya polipirol katıldığında oluşan nihai ürünün toz yapıda olması, proses edilebilmeyi kolaylaştırıcı yönde gözükmetedir; aksi takdirde materyal polipirol içermediğinde kırılmaz, bükülmez, uflanmaz bir yapıda kullanım güçlüğü çıkarmaktadır. Sonra bu kompozitler kütlece yüzde gözönünde bulundurularak belli miktarlarda DMF (Dimetil formamid) içinde çözülmüş ve güç kaynağı, pompa, şırınga ve metal kollektörden oluşan bir elektrosprin cihazında nanofiber haline getirilmiştir. Bu işlemde enjektör-kollektör arası mesafe sabit tutulmuştur. Farklı voltaj miktarlarında ön denemeler yapılmış ve her konsantrasyondaki çözeltinin nanofiberlerinin en düzenli ve damlacıksız elde edilebildiği voltaj 15 kV olarak belirlenmiştir. Deneyler 15 kV'lik voltaj ile yapılmıştır. Bu denemeler esnasında kollektör ile şırınga arasındaki mesafe, çözücü solüsyonunun kütlece yüzdesi ve uygulanan voltaj değiştirilmemiştir. Elektrosprising sonucunda SEM ile inceleme yapıldığında 200-700 nm çaplarında nanolifler elde edildiği görülmüştür. Nanofiberlere ek olarak hem polipirol içeren hem de içermeyen çöktürülmüş ve kurutulmuş nano kompozitlerin DMF çözücüsü içeren çözeltisi özel cam yüzeylere dökülmüş, fırında çözücü buharlaşana kadar kurutulmuş ve filmler elde edilmiştir. Film çözeltileri kütlece sabit oranda hazırlanmıştır ve daha fazla pirol eklenmiş olan nano kompozit malzemeden elde edilmiş olan filmlerin rengi, oluşan polipirol yoğunluğuna bağlı olarak daha koyu renk olmuştur. Nanofiberler SEM'in yanısıra DMA (Dinamik Mekanik Analizör) ile de karakterize edilmiştir. Nanofiberler DMA ile incelenmeye çalışıldığında, kollektörden toplanan nanofiberlerin çok ince ve dayanıksız olması sebebiyle bu lifler birkaç kat kalınlaştırma yoluna gidilmiştir. Bu nedenle nanofiberler kollektörün üzerinden toplandıktan sonra su ile ıslatılmış ve belirli boyutlarda iki sefer katlanıp toplamda dört kat yüzey oluşturulmuş ve şekil alması için kurutulmuştur. Malzeme suda çözünebilir olmadığı için bu işlem nanofiberlere herhangi bir zarar vermemiştir. Ancak yapılan işlemler sonucunda nanofiberler üzerinden DMA ile net bir ölçüm alınamamış olup, bunun fiberlerin karışık doğrultularda yönlenmesi ve bu sebeple lif demetinin bazı kısımlarında kırılma noktaları oluşması sebebiyle ortaya çıktığı düşünülmektedir. Kurutulmuş partiküller ise hem Fourier Dönüşüm Kızılötesi – Azaltılmış Toplam Yansıma Spektroskopisi (FTIR-ATR), hem UV-Görünür Spektroskopisi, hem de Diferansiyel Tarama

Kalorimetresi (DSC) ile karakterize edilmiştir. UV-Görünür Spektroskopisi sonuçları partikül boyutu ile ilişkilendirilerek incelenmiştir ve UV emiliminin doğrudan nanopartiküllerin boyutuyla orantılı olduğu görülmüştür. Partikül boyutu büyüdükçe ışının kırılması çoğalmış ve UV eğrilerinin başlangıç noktaları yer değiştirmiştir. UV-Görünür spektroskopisinde, kompozitlerin içinde polipirol oluşumunun varlığı açıkça görülmüştür. FTIR-ATR ölçümlerinde de nano kompozitte polipirol oluşumu görülmüştür, son materyalin içinde polipirole ait pikler ortaya çıkmıştır; bu da yapıda polipirol meydana geldiğini göstermektedir. FTIR-ATR spektrumunda p(AN-co-MA) ve PPy'ye ait pikler ayrı ayrı görüldüğü ve arada ilave bir bağ görünmediği için PPy ile p(AN-co-MA)'nın arasında kimyasal bağdan ziyade fiziksel bağ oluştuğunu düşündürmektedir. Bu da içeride p(AN-co-MA), dışarıda ise PPy oluşumu şeklinde core-shell yapının oluşmuş olabileceğini destekleyen bir sonuçtur. DSC Analizleri ortama eklenen pirol miktarı arttıkça camsı geçiş sıcaklığının arttığını göstermiştir. Bunun sebebi olarak ise yapıda oluşan polipirol ile genel yapının direncinin arttığı, buna bağlı olarak camsı geçiş sıcaklığının yükseldiği düşünülmüştür. Filmler de nanofiberler gibi DMA ile analiz edilmiş, stres-uzama eğrileri oluşturularak karakterize edilmiştir. Daha fazla Py eklenmiş kompozitten elde edilen filmler daha koyu renk, kırılkan ve parlak olurken, az Py eklenen veya hiç Py eklenmeyen nano kompozitten oluşan filmler açık renk (hatta şeffaf), daha elastik ve daha az parlak oluşmuştur. Ölçümlerin sonucunda eklenen Py ve oluşan PPy miktarı arttıkça filmlerin Young Modüllerinin arttığı açıkça görülmüştür. PPy genel olarak kristalin yapıda olduğu için polimer zincirinde esneklik göstermemektedir, dolayısıyla yapıdaki PPy miktarı arttıkça uzama olmadan dayanılan kuvvet miktarı artmış; dolayısıyla Young Modülü yüksek çıkmıştır. Tüm bu sonuçlar değerlendirildiğinde yeni bir nano-kompozit malzeme oluştuğu; PPy'nin özellikleri ile p(AN-co-MA)'nın özelliklerinin bir arada görüldüğü; PPy'nin proses edilebilirliğinin artırılarak nanofiber elde edilebildiği anlaşılmıştır. Bu malzeme ileride hem nanopartikül olarak kullanım alanı bulabilecek, hem de nanolif şeklinde kullanılabilecek potansiyele sahiptir.

1. INTRODUCTION

Conductive polymers and their composites are being interested frequently in recent years and polypyrrole is most commonly used types of conjugated conductive polymers.

Since their good conductivity properties [1] and potential applications in various fields like sensors [2–4], actuators [5, 6], catalysis[7], field effect transistors[8], light emitting diodes[9], capacitors[10] etc., conducting polymers like polypyrrole polyaniline, polythiophene, polyacetylene, poly (p-phenylene sulfide) and poly (p-phenylene vinylene) etc. have been commonly studied and used in recent years.

Although this advantages that they have, they have also some disadvantages such as being often brittle in nature and hence having difficulty to make film from them. In order to overcome these difficulties, much attention has been made in combining these conducting polymers with mechanically stable insulating polymers to give core-shell morphology. These composite particles have a wide area of applications such as antistatic coating, dampers, clutches, electrodes, separation membranes, electrochromic devices, electrochemomechanical actuators, and sensors [11, 12]. These kinds of core-shell conducting composites have two advantages which the first one depends on the type of insulating polymer used as core. These conducting polymer-coated latex particles can show very good mechanical stability. Second advantage is the amount of conducting polymer used can be greatly reduced in the shell phase, therefore the composite material maintains its conductivity without much loss [13].

Latex particles coated by conducting polymer were first reported in 1987 [14] and this study have found widespread attention [15–18]. Jianjun Wang et al. developed a core of a thermoplastic non-conducting polymer covered by a corona of a polyelectrolyte (e.g., polystyrene sulfonate, (PSS)) and into this corona (i.e., matrix) domains of a conducting polymer, polypyrrole (PPy) was embedded by oxidative polymerization of the suitable monomer (pyrrole) such that an electrical percolating Shell is formed [19]. Han Chen et al. studied the voltammetric conversion of conducting polyaniline-coated polystyrene latex particles which dispersed in aqueous

acid solution to find both a relationship between the partial reaction and particle size, but also the irreversibility of the conversion [20]. Huang Liyan et al. developed a series of mono dispersed styrene-butyl acrylate (SBA) copolymer latex particles with different butyl acrylate contents, coated with polypyrrole and studied both the effects of the concentration of polypyrrole, the butyl acrylate content in SBA copolymer and the nature of the counter-anion on the electrical conductivity of compression-moulded samples [13]. Liang Guo et al. studied and developed coated Fe₃O₄ with polystyrene particles and they used dispersion polymerization. Also they studied the effect of a cross-linking agent and the mechanism of the polymer coating [21]. Another group, Ying Wang et al. synthesized electrically conductive core-shell nanoparticles (PANI/PS-PSS) via coating poly (styrene-co-styrene sulfonate) (PS-PSS) nanoparticles with polyaniline (PANI) . They studied about the stability of the coated latexes and the conductivity of PANI/PS-PSS pellets. The role of the aniline amount was also mentioned in this literature [22].

In this study, Acrylonitrile is chosen, since it is one of the most popular monomers of chemistry and textile industry due to its common usage as a precursor of carbon fibers by copolymerizing with some other monomers. Methyl acrylate monomer is chosen for its hydrophobicity and suitability for being copolymer with acrylonitrile. Hydrophobicity is an important factor to have core-shell nanostructures in emulsion media with surfactant.

2. THEORETICAL PART

2.1 Polyacrylates

The kinds of polyacrylates are highly heat and oil resistant polymers. Several usage areas exist for acrylate and methacrylate esters that they are used to obtain polymers for textiles, latex paints, surgical cements and dental resins. The esters of acrylic and methacrylic acid are shown the formula which can be seen in figure 2.1.

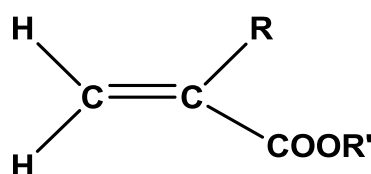


Figure 2.1 : General Formula of Acrylates

R:H bonding is considered for acrylates and R:CH₃ for methacrylates. The substituents R' can vary in a wide area: from n-alkyl chains to more complicated functional groups [23].

Esters of general acrylates are crystalline solids at ambient temperatures, then form liquid at slightly higher temperatures. They are ready to polymerize and copolymerize easily, being frequently employed in copolymers to obtain alkalisoluble polymers. The acids of acrylates are water soluble, methacrylic acid, as might be expected because of its angular methyl group, is more soluble in ester monomers, and to some extent in styrene, and as such is more useful in copolymerisation, especially if water based [24].

The first report of a polymeric acrylic ester was published in 1877 by Fittig and Paul [25] and in 1880 by Fittig and Engelhorn [26] and by Kahlbaum [27], who observed the polymerization reaction of both methyl acrylates and methacrylates. But it is a chance to O. Röhm [28] in 1901 to recognize the technical potential of the acrylic polymers. After continuing his work he got a U.S. patent on the sulfur vulcanization of acrylates in 1914 [29]. Then in 1924, Barker and Skinner [30] researched and published details of the polymerization of methyl and ethyl methacrylates. In 1927

[31], based on the extensive work of Röhm, the first industrial production of polymeric acrylic esters was started by the Röhm & Haas Company in Darmstadt, Germany (since 1971, Röhm GmbH, Darmstadt). After 1934, the Röhm & Haas Co. in Darmstadt was able to produce an organic glass (Plexiglas) by a cast polymerization process of methyl methacrylate [32]. Soon after, Imperial Chemical Industries (ICI, England), Röhm & Haas Co. (United States), and Du Pont de Nemours followed in the production of such acrylic glasses [33].

Acrylic polymers has a first-time usage as an interlining for automobile windshields, but poly(methyl methacrylate) sheet (commercial name Plexiglas, Lucite) soon became the main usage area of acrylic plastics. Poly(methyl methacrylate), chemical Formula with $[-CH_2-CH(CH_3)COOCH_3-]$, has a light transmittancy of about 92% and has good weathering resistance. It is widely used in aircraft wind shields, bathtubs [34], electron beam or ion beam resistance of them is important in the manufacture of microelectronics such as chips [35,36]. Poly(methyl methacrylate) is used as an automobile lacquer and polyacrylonitrile, $(-CH_2-CHCN-)_n$, is used as a fiber. Poly(ethyl acrylate), $(-CH_2-CHCOOC_2H_5-)_n$, is more flexible and has a lower softening temperature than PMMA. Poly(hydroxyethyl methacrylate), is used for contact lenses, and poly(butyl methacrylate) is used as an additive in lubricating oils[34].

Whilst esters of acrylic acid give soft and flexible polymers, except for those with long alkyl chains, methyl methacrylate polymerises to an extremely hard polymers. The polymers in this series become softer with increasing alkyl chain lengths up to C_{12} . The highest alkyl chain acrylics in both series tend to give side chain crystallisation.

The methacrylic ester series closely parallels the acrylics, but boiling points tend to be somewhat higher, especially with the short chain esters. Methyl methacrylate is by far the most freely available and least costly of the monomers of the series. As an alternative to the simple alkyl esters, several alkoxyethyl acrylates are available commercially, e.g. ethoxyethyl methacrylate $CH_3C(CH_3)COOC_2H_4OC_2H_5$ and the corresponding acrylate. The ether oxygen which interrupts the chain tends to promote rather more flexibility than a simple carbon atom.

Some technical perfluorinated alkyl acrylates are as following they include N-ethylperfluorooctanesulfonamido)ethyl acrylate $C_nF_{2n+1}SO_2N(C_2H_5)-CH_2O-C(O)-$

$\text{CH}=\text{CH}_2$ (n approximately 7.5, fluorine content 51.7 %), the corresponding methacrylate and the corresponding butyl derivatives. The ethyl derivatives are waxy solids, the ethyl acrylate and the corresponding methacrylate derivative having a melting range of 27–42 °C. The butyl acrylic derivative is a liquid, freezing at -10 °C. Butyl acrylate/Methyl methacrylates (BA/MMA), emulsion copolymers are versatile materials extensively used as adhesives (BA homopolymers and BA rich copolymers) and coatings (BA/MMA 50/50 wt/wt copolymers). In spite of their commercial importance, only a few literature reports dealing with the microstructural properties of BA/MMA emulsion copolymers have been published [37].

Polyacrylate elastomers can be prepared by the water emulsion system, suspension system, solvent solution method, or even the mass (bulk homogenous) polymerization process. Most are made by the water emulsion (latex) or the suspension method. Peroxides or persulfate initiated free radical systems are most commonly used in the presence of heat. Polymerization is usually taken to completion. Coagulation is best with salts, followed by water washing and drying with hot air, vacuum, or extrusion [38].

2.2 Polyacrylonitrile

Polyacrylonitrile (PAN) and copolymers of PAN have been widely studied for almost a century for commercial/ technological exploitations. PAN may be crosslinked, but also may exist without crosslinking. Crosslinking of PAN will impart some of its important physical properties, such as insolubility and resistance to swelling in common organic solvents. Recently, considerable efforts have been devoted to its processing and fiber forming technologies. Among the various precursors for producing carbon nanofibers (CNFs), PAN is the most commonly used polymer, mainly due to its high carbon yield (up to 56%), flexibility for tailoring the structure of the final CNF products and the ease of obtaining stabilized products due to the formation of a ladder structure via nitrile polymerization [39–43]. Even though acrylonitrile (AN) was known as far back as 1893, but PAN, because of difficulties in dissolving it for spinning, no progress was made in converting into a usable fiber until 1925. Acrylonitrile monomer was also useful as a copolymer with styrene, especially in a terpolymer with styrene and butadiene, known as ABS rubber. The homopolymer of PAN was developed for manufacturing of fibers in

1940, after a suitable solvent was discovered by DuPont. PAN is soluble in polar solvents like DMF, DMSO, DMAc, dimethylsulfone, tetramethylsulfide and aqueous solutions of ethylene carbonate, as well as some mineral salts. PAN forms saturated solution with 25% dissolved in DMF at 50 °C, which is high solubility compared to other solvents [44]. PAN and its copolymers are predominantly white powders up to 250 °C, at which point they become darker due to degradation. Having a relatively high T_g, these polymers have low thermal plasticity and cannot be used as a plastic material. The high crystalline melting point (317 °C) of PAN, its limited solubility in certain solvents coupled with superior mechanical properties of its fibers is due to intermolecular forces between the polymer chains. Appreciable electrostatic forces occur between the dipoles of adjacent C N groups and this intramolecular interaction restricts the bond rotation, leading to a stiffer chain [45].

PAN-based CNFs are seemingly a new class of materials used in a wide array of applications including filtration barriers, material reinforcements, garments, insulators, medical and energy storage devices, and many more. However, their unique properties make them perfect modern materials of choice across many disciplines covering engineering, medicine, and biology. The accelerating technologies of producing PAN-based nanofibers have now matured enough to overcome the drawbacks of low production rate of few grams per hour in laboratory environments to large industrial scale production. Nanofiber membranes comprising sheets of randomly oriented nanofibers show an extremely effective removal method with a high rejection rate of airborne particles by both physical trapping and adsorption. It is anticipated that the future will witness many more applications of PAN-based nanofibers in a wide variety of scientific disciplines. [46]

2.3 Methy Acrylate

The methyl acrylates are clear, colorless, volatile liquid with a slight solubility in water and complete solubility in alcohols, ethers and many organic solvents. Methacrylate esters are used to make polymers for textiles, latex paints, surgical cements and dental resins. It can be used as a co-polymer in the process of polymerization of polyanionic cellulose (PAC) polymers, to reduce the glass transition temperature of the PAC polymers. It's formula is $\text{CH}_2=\text{CHCOOCH}_3$. It have boil point 79.6 °C at 760 mmHg and have melting point about -75 °C. Although

the monomer can be polymerized under the influence of heat, light, ionic or high energy mechanisms, free radical initiation is the most commonly used method of polymerization. The skeletal formula of Methyl Acrylate is shown in Figure 2.2.

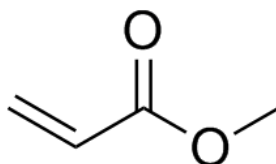


Figure 2.2 Skeletal Formula of Methy Acrylate

Methyl acrylate is a volatile chemical compound classified as a methyl ester. It has a characteristic odor used in the preparation of polyamidoamine (PAMAM) dendrimers typically. The product is highly demanded for making different industrial products. Moreover, this chemical compound is a flammable, water insoluble, colorless liquid and possess the property to mix with most organic solvents. Methyl acrylate is used in the production of coatings, elastomers, adhesives, thickeners, amphoteric surfactants, fibers, plastics, textiles and inks.. Methyl acrylate is also used in chemical synthesis. When used in latex paint formulations acrylic polymers have good water resistance, low temperature flexibility and excellent weathering and sunlight resistance.

2.4 Conductive Polymers

The discovery of conductive polymers is unique in its accomplishment as a possible substitute for metallic conductors and semiconductors. The efforts for having a tailor-made polymer in respect of its electrical, mechanical, optical and thermal properties have been pursued by several research groups.

Generally, potentiostatic conditions are recommended to obtain thin films, while galvanostatic conditions are recommended to obtain thick films. The electrochemical technique has received wider attention both because of the simplicity and the added advantage of obtaining a conductive polymer being simultaneously doped. Besides this, a wider choice of cations and anions for use as "dopant ions" is available in the electrochemical polymerisation process. Free-standing as well as self-supporting conductive polymer films of desired thickness or geometry can be obtained. Using this novel technique, a variety of conductive polymers like polypyrrole,

polythiophene, polyaniline, polyphenylene oxide pyrrole and polyaniline/polymeric acid composite have been generated. Pyrrole in aqueous acetonitrile solvent containing tetraethyl ammonium tetra-boroborate was electropolymerised in a two-electrode electrochemical cell. Polypyrrole containing the BF_4 ion (dopant) was obtained as a film deposited on the platinum electrode surface [47].

Polymers were thought of as electrical insulators until the discovery that iodine-doped polyacetylene exhibited electrical conductivity many orders of magnitude higher than neutral polyacetylene. This discovery was published by [48] As a result of this pioneering work, they received the 2000 Nobel Prize in Chemistry. The development of this new class of polymeric materials continues to offer the promise of a wide range of novel applications including molecular electronics [49], actuators [50], electrochromic windows/displays [51], supercapacitors [52], transistors [53], photovoltaics [54] and corrosion protection [55]. This discovery opened up new areas of research with many commercial products now incorporating polymers as electrical conductors. For a more detailed review on the synthesis, properties and applications of conductive polymers (CPs) consult [56] CPs consist of conjugated chains containing π -electrons delocalized along the polymer backbone. In their neutral form, CPs are semiconductive materials that can be doped and converted into electrically conductive forms. The doping can be either oxidative or reductive, though oxidative doping is more common. There are three states of CPs: non-conducting (uncharged), oxidized (p-doped) where electrons are removed from the backbone, and the reduced (n-doped) (least common), where electrons are added to the backbone. The doping processes are usually reversible, and typical conductivities can be switched between those of insulators ($<10^{-10}$ S/cm) and those of metals (10⁵ S/cm) [57].

2.5 Pyrrole and Polypyrrole

Pyrrole is a heterocyclic aromatic organic compound, a five-membered ring with the formula $\text{C}_4\text{H}_4\text{NH}$. It is a colourless volatile liquid that darkens readily upon exposure to air. Pyrrole has very low basicity compared to conventional amines and some other aromatic compounds like pyridine. This decreased basicity is attributed to the delocalization of the lone pair of electrons of the nitrogen atom in the aromatic ring. Like many amines, pyrrole slowly decomposes on exposure to air and light.

Over time, it turns brown over time due to accumulation of impurities such as polypyrrole and various amine. The simplest member of the pyrrole family is pyrrole itself, a basic heterocyclic compound; colorless to pale yellow, toxic oil with pungent taste and similar to chloroform odor; insoluble in water; soluble in alcohol, ether, and dilute acids; boils at 129 - 131 °C; polymerizes in light. It is usually purified by distillation immediately before use. Pyrrole oligomers are easier to oxidize than the corresponding pyrrole monomers. The formula of pyrrole is shown in the Figure 2.3.

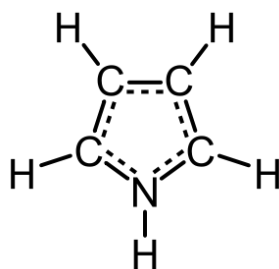


Figure 2.3: Formula of Pyrrole

Pyrrole ring system is involved in coloured products in nature. Pyrrole and its derivatives are widely used as an intermediate in synthesis of pharmaceuticals, medicines, agrochemicals, dyes, photographic chemicals, perfumes and other organic compounds. They are used in metallurgical processes. They are useful in the intensive study of transition-metal complex catalyst chemistry for uniform polymerization, luminescence chemistry and spectrophotometric analysis.

Polypyrrole (PPy) is a chemical compound formed from a number of connected pyrrole ring structures. The formula of Ppy is shown in the Figure 2.4. Polypyrroles are conducting polymers of the rigid-rod polymer host family, all basically derivatives of polyacetylene. PPy films thinner than 1 mm have different spectral properties depending on the conditions of synthesis and degree of PPy oxidation; with the increasing degree, the colour of the films changes from yellow to the blue and, ultimately, black. The stability in air of the doped PPy films is relatively high; their degradation occurs only above 150 - 300 °C. Thermal degradation of PPy starts with the loss or decomposition of dopant.

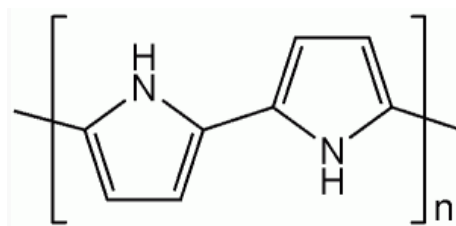


Figure 2.4 Formula of Polypyrrole

2.6 Electrospinning

As the diameters of polymer fiber materials are reduced from micrometers (e.g. 10–100 μm) to nanometers, several amazing characteristics appear such as high surface area to volume ratio (this ratio for a nanofiber can be as large as 10³ times of that microfiber), flexibility in surface functionalities, and high-qualified mechanical performance (e.g. stiffness and tensile strength) compared with any other known form of the material. These properties make the polymer nanofibers to be optimal precursors for many significant applications. In recent years, series of processing techniques such as drawing [58], template synthesis [59,60], phase separation [61], self-assembly [62,63], electrospinning [64,65], etc. have been used to obtain polymer nanofibers. Even though the term “electrospinning”, derived from “electrostatic spinning”, was used relatively recently (in around 1994), its fundamental idea dates more than 60 years earlier. Formalas published a series of patents [66–70] from 1934 to 1944, which describe an experimental setup for the production of polymer filaments using an electrostatic force. A polymer solution was entered into the electric field, then the polymer filaments were formed from the solution; between two electrodes bearing electrical charges of opposite polarity. One of the electrodes was placed into the solution and the other onto a metal collector. Once ejected out of a metal spinnerette with a small hole, the charged solution jets evaporated to become fibers which were collected on the collector. The potential difference depended on the properties of the spinning solution, such as polymer molecular weight and viscosity. If the distance between the spinnerette and the collector was short, spun fibers tended to stick to the collecting device as well as to each other, due to incomplete solvent evaporation. The schematic draft of electrospinning is shown in the Figure 2.5.

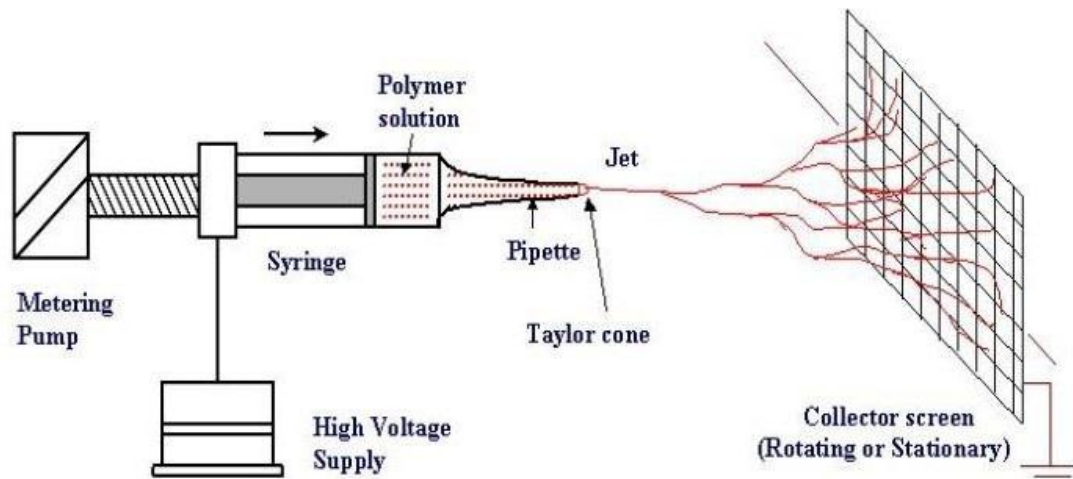


Figure 2.5 Schematic of Electro Spinning Setup

In recent years since 1980s the electrospinning process essentially similar to that described by [71] has attracted more probably due in part to a surging interest in nanotechnology, as ultrafine fibers or fibrous structures of various polymers with diameters down to submicrons or nanometers can be easily fabricated with this process.

There are mainly three components to complete the process: a high voltage supplier, a capillary tube with a pipette or needle of small diameter, and a metal collecting screen. In the electrospinning process a high voltage is used to create an electrically charged jet of polymer solution or melt out of the pipette. Before reaching the collecting screen, the solution jet evaporates or solidifies, and is collected as an interconnected web of small fibers [64,65]. One electrode is placed into the spinning solution/melt and the other attached to the collector. In most cases, the collector is simply grounded, the electric field is subjected to the end of the capillary tube that contains the solution fluid held by its surface tension. This induces a charge on the surface of the liquid. Mutual charge repulsion and the contraction of the surface charges to the counter electrode cause a force directly opposite to the surface tension. When the intensity of the electric field is increased, the hemispherical surface of the fluid at the tip of the capillary tube elongates to form a conical shape known as the Taylor cone [72]. Further increasing the electric field, a critical value is attained with which the repulsive electrostatic force overcomes the surface tension and the charged jet of the fluid is ejected from the tip of the Taylor cone. The discharged polymer solution jet undergoes an instability and elongation process, which allows the jet to

become very long and thin. Meanwhile, the solvent evaporates, leaving behind a charged polymer fiber. In the case of the melt the discharged jet solidifies when it travels in the air.

Both the dissolution and the electrospinning are conducted at room temperature with atmosphere condition. However, some polymers may cause unpleasant or even harmful smells, therefore the processes should be conducted within chambers having a ventilation system. Furthermore, a DC voltage in the range of several to several tens of kVs is necessary to generate the electrospinning. One must be careful to avoid touching any of the charged jet while manipulation. It is noted that the same polymer dissolved in different solvents may all be electrospun into nanofibers.

There are many parameters that affects the transformation of polymer solutions into nanofibers through electrospinning. These parameters include (a) the solution properties such as viscosity, elasticity, conductivity, and surface tension, (b) governing variables such as hydrostatic pressure in the capillary tube, electric potential at the capillary tip, and the gap (distance between the tip and the collecting screen), and (c) ambient parameters such as solution temperature, humidity, and air velocity in the electrospinning chamber [73].

Consequently these fibers have a large surface area per unit mass so that nanowoven fabrics of these nanofibers collected on a screen can be used for example, for filtration of submicron particles in separation industries and biomedical applications, such as wound dressing in medical industry, tissue engineering scaffolds and artificial blood vessels. The use of electrospun fibers at critical places in advanced composites to improve crack resistance is also promising.[74][75]

2.7 Emulsion Polymerization

Emulsion polymerization is a largely used process that helps to obtain waterborne resins that contains several colloidal and physicochemical properties. A hydrophobic monomer is added into the water with emulsifier and the reaction is continued with the initiation reaction by the water-soluble initiator (such as NaPS) in this free-radical non-homogenous polymerization type. [76-81]

This polymerization involves the reaction of free radicals with relatively hydrophobic monomer molecules within submicron polymer particles dispersed in a continuous aqueous phase. This unique polymerization process that is heterogeneous

in nature exhibits very different reaction mechanisms and kinetics compared to bulk or solution free radical polymerization. Surfactant is generally required to stabilize the colloidal system; otherwise, latex particles nucleated during the early stage of polymerization may experience significant coagulation in order to reduce the interfacial free energy. This feature may also come into play in determining the number of reaction loci (i.e., polymer particles) available for the consumption of monomer therein.

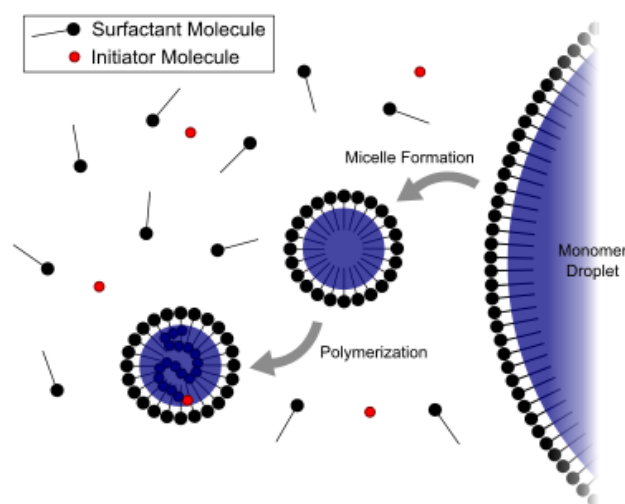


Figure 2.6 Schematic View of Emulsion Polymerization

The spontaneous latex form of particles are obtained from polymerization at the very beginning of the reaction process. These latex particles are normally 100 nm in size, and are made of many individual polymer chains. The particles do not coagulate with each other due to the surrounding of the surfactant on the particles. also the electrostatic force coming from the surfactant makes the particles repel each other.

A large oil–water interfacial area is created as the particle nuclei form and particle size increases with the continuing of the polymerization. Therefore an effective stabilizer that contains ionic and non-ionic surfactants, also protective colloid (e.g. hydroxyethyl cellulose and polyvinyl alcohol), is needed to prevent the latex particles from coagulation thanks to the physically or chemically integrated on the particle surface [82]

Since growth and stabilization, nucleation of polymer particles are controlled by the free radical polymerization mechanisms in combination with several colloidal occurrences, emulsion polymerization is considered as a relatively complex process.

The most vital characteristic behavior of emulsion polymerization is the segregation of free radicals among the separated swollen-monomered polymer particles. Faster polymerization rate and polymer with a higher molecular weight is achieved due to the reduction of the bimolecular termination of free radicals. Bulk or solution polymerization cannot provide these kinds of characteristics comes from emulsion polymerization. Final particle size and its distribution; also latex products are importantly determined by the early-stage creation of nuclei due to the short nucleation process. [83]

Emulsion polymerization can be separated into several types such as miniemulsion, microemulsion and conventional emulsion polymerization. They behave differently about particle nucleation and growth mechanisms and kinetics. El-Aasser et al. [84,85], Capek and Chern [86], Antonietti and Landfester [87] and Asua [88] are studied and reviewed miniemulsion polymerization. The review articles [89–92] are related with microemulsion polymerization.

By looking at the micelle nucleation model, examined by Harkins [93–95] and Smith and Ewart [96–98] and modified by Gardon [99,100], the model says that submicron latex particles are produced by free radicals which are captured by micelles. When the particles are completely nucleated, the number of latex particles per unit volume of water stays constant relatively till the end of the polymerization.

3. EXPERIMENTAL

3.1 Materials

Methyl Acrylate (MA), Acrylonitrile (AN), Pyrrole (Py), Dimethylformamide (DMF), Dodecyl Benzen Sulfonic Acid (DBSA) and Potassium Peroxydisulfate (KPS) were purchased from Sigma Aldrich. Methanol (CH₃OH) were obtained from Merck. NaCl was purchased from Billurtuz San. A.Ş.

3.2 Synthesis of P(AN-co-MA) Nanoparticles

0,1 mol monomer that consists of AN-MA was emulsified in aqueous media with the presence of %1 DBSA by weight of monomer amount. %50 AN-%50 MA, %60 AN-%40 MA, %75 AN-%25 MA and %95 AN-%5 MA compositions by mol were used. The reaction volume is integrated 100 ml with pure water. The monomer compositions are demonstrated at Table 3.1. The monomers are shown in the Figure 3.1.

Table 3.1. : The total monomer, AN, MA, DBSA and KPS composition in feed

Total Monomer (mol)	AN (%)	MA (%)	DBSA (g)	KPS (g)
0.1	50	50	0.070	0,678
0.1	60	40	0.066	0,678
0.1	75	25	0.061	0,678
0.1	95	5	0.055	0,678

The three necked reaction flask is covered with aluminum folio in order to avoid sunlight that may start polymerization. The condenser is tied to one neck of the flask so that the evaporating monomer could be gained back. While 20 dk stirring with magnetic stirrer in the hot water bath, the temperature was increased to 70°C. Then initiator KPS is added to the emulsion and the polymerization had started. After 3 hours, the milk-like copolymer samples were taken from the emulsion to characterize

by SEM and Particle Size Analyzer. Then the reaction was ended by pouring into the copolymers into salt (NaCl). Precipitated nanoparticles were filtered through a filter paper and dried with pure water, then dried 24 hours at room temperature. Resulting nano materials are characterized by FTIR-ATR, UV-Visible Spectrometer and DSC.

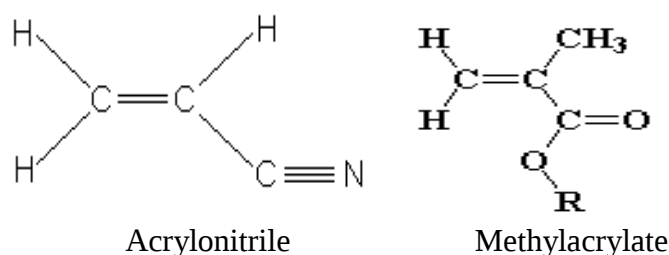


Figure 3.1 Monomers used in synthesis of Poly(AN-co-MA).

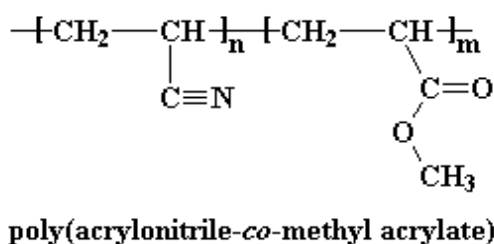


Figure 3.2 Poly(AN-co-MA) structure.

3.3 Synthesis of Ppy / Poly(AN-co-MA) Nanoparticles

AN-MA copolymers were prepared as written above. At the end of 3 hours polymerization, after waiting for equalizing the reaction with room temperature, without any initiator addition pyrrole droplets were added into the emulsion media and reaction continued 24 hours. Figure 3.3. shows the estimated mechanism of composite formation. Increasing amounts of pyrrole droplets are added as 5, 10, 15, 25, 30, 50, 60, 100, 150 and 300 microliters. Samples were taken from this latex to characterize by SEM and Particle Size Analyzer (Malvern Mastersizer Microplus Ver.2.19). And then nanoparticles were precipitated by pouring methanol into the resulting latex and the reaction were terminated. The resulting nanomaterials were characterized by FTIR-ATR, UV-Visible Spectrometer and DSC.

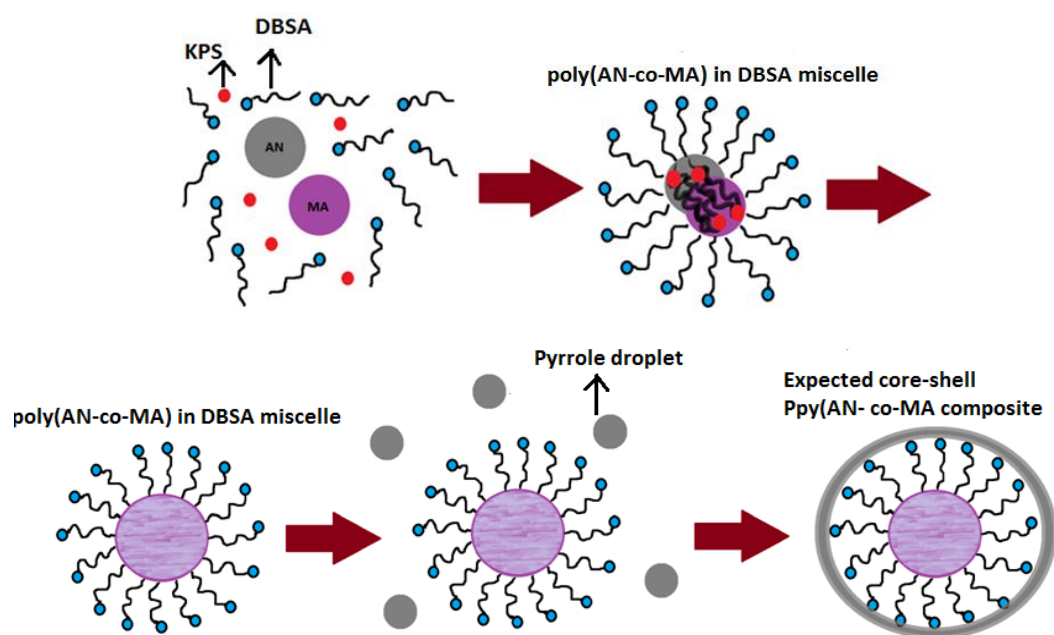


Figure 3.3 Estimated mechanism of composite formation

3.4 Preparation of Electrospinning and Film Solutions of Nano Composites

3.4.1 Electrospinning of nanocomposites

Both precipitated and dried Poly(AN-MA) and PPy/poly(AN-co-MA) nano particles were dissolved in the DMF. Solutions were prepared as about %10 by weight. 0,20 g nanoparticle and 1,6 g DMF is used. The Table 3.2. shows the composition of nanofiber solutions.

Table 3.2 : P(AN-co-MA) and PPy/ p(AN-co-MA) nanocomposite solutions used for electrospinning

Polymer	Polymer Concentration (wt%)	Solvent	Pyrrole amount that added (μ l)
P(AN-co-MA)	10	DMF	0
PPy/ p(AN-co-MA)	10	DMF	30
PPy/ p(AN-co-MA)	10	DMF	50
PPy/ p(AN-co-MA)	10	DMF	60
PPy/ p(AN-co-MA)	10	DMF	100

Each solutions were stirred at room temperature with the speed of 400 rpm for 2 hours. The electrospinning device contains a syringe pump (NE-500 model, New Era Pump Systems, Inc., USA) and DC power supplier (ES50 model, Gamma High Voltage Inc., USA). The solutions were then loaded into a 2.5 ml syringe and pumped with 0,5 ml/h speed. Applied voltage was 15 kV. In Figure 3.4, a representative picture shows the setup of the electrospinning. Obtained fibers were characterized by FTIR-ATR, SEM and DMA.

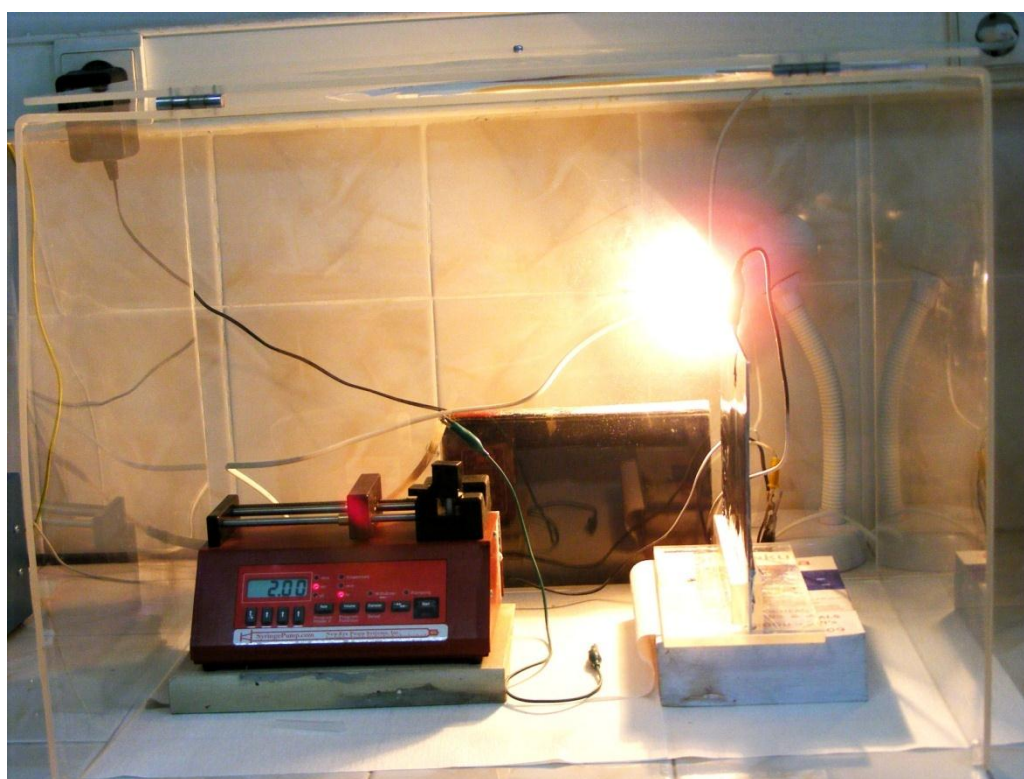


Figure 3.4 A representative picture taken during electrospinning.

3.4.2. Preparing films of nanocomposites

Both precipitated and dried Poly(AN-MA) and PPy/poly(AN-co-MA) nano particles were dissolved in the DMF. 0,40 g nanoparticle and 3,2 g DMF is used. The solutions that obtained from nanoparticles which are without-pyrrole, 30 μ l, 50 μ l, 60 μ l and 100 μ l pyrrole added were stirred 2 hours with magnetic stirrer and then poured into square pots. Figure 3.5 shows the films that obtained from different amounts of pyrrole containing PPy/p(AN-co-MA) particle solutions. They were dried in vacuum-oven 24 hours at 70°C and 24 hours at room temperature.

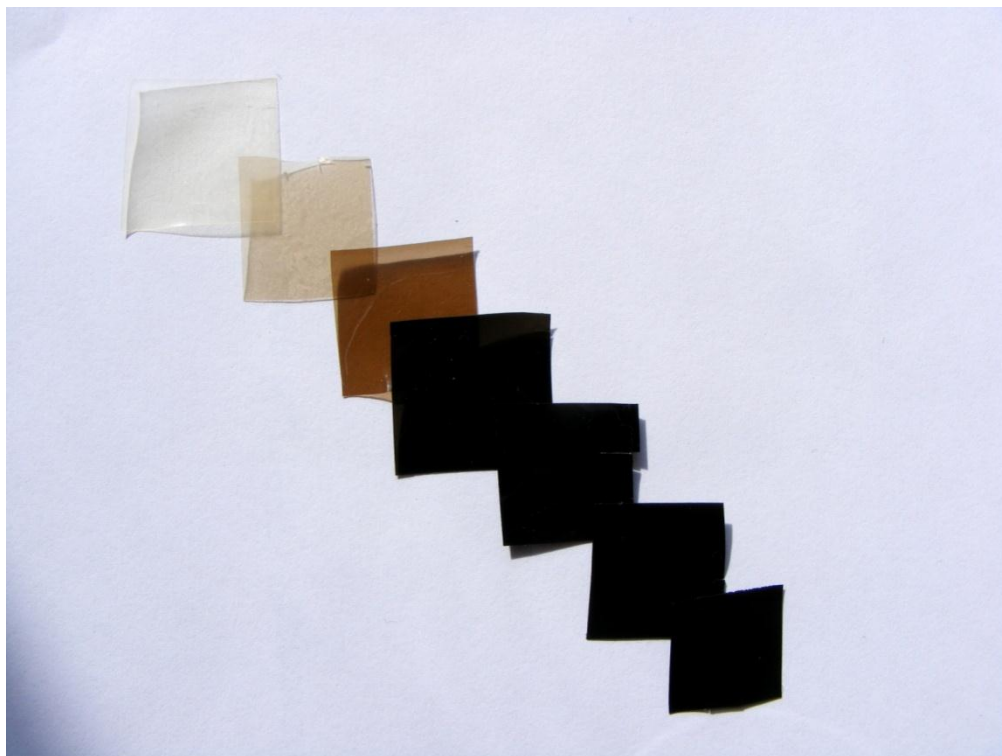


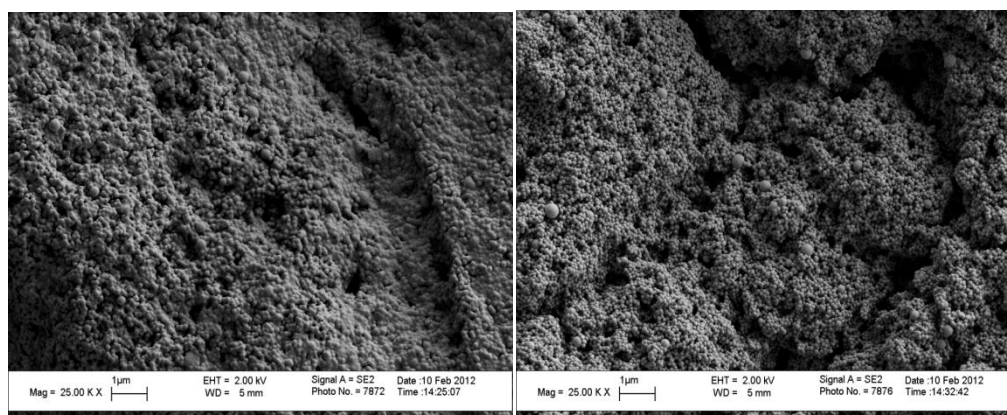
Figure 3.5 Films obtained without pyrrole addition and with different amount pyrrole addition.

4. RESULTS AND DISCUSSION

4.1. Nanoparticle Characterization

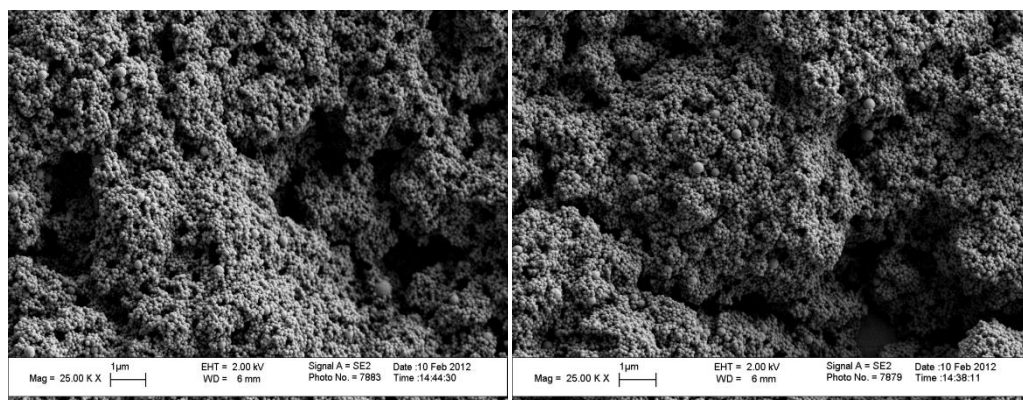
4.1.1 SEM analysis of P(AN-co-MA) and PPy/p(AN-co-MA) nanoparticles obtained from emulsion latexes

Nanoparticles sampled from emulsion latexes that obtained from participated nanoparticle solvents were characterized morphologically by Scanning Electron Microscope (LEO SUPRA 35 VP) and the samples for the SEM measurements are coated with gold (Ion Sputter Metal Coating Device, MCM-100). Nanoparticles were dripped onto a glass surface and then dried at room temperature. After that samples were coated with gold in order to use SEM e-beams effectively.



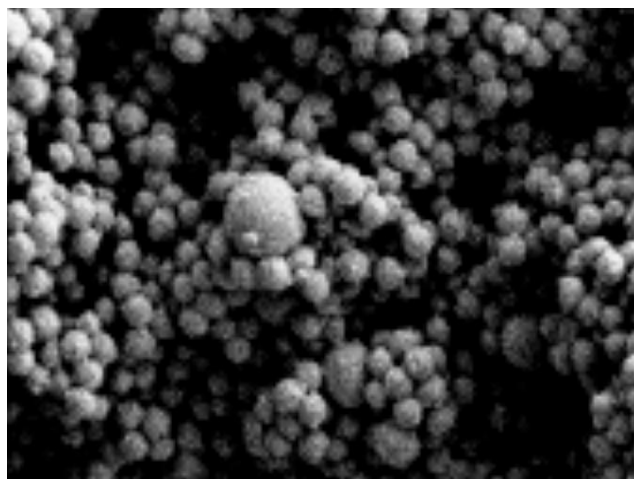
a) No pyrrole

b) 30 ul pyrrole added



b) 50 ul pyrrole added

c) 60 ul pyrrole added



d) The zoomed image of nanoparticles

Figure 4.1 The SEM images of both with addition of pyrrole and without addition of pyrrole

Figure 4.1. shows the SEM images of P(AN-co-MA) and PPy/p(AN-co-MA) nanoparticles obtained from emulsion latexes. Spherical structures occurred by the emulsion polymerization method, by the stirring in high rpm of magnetic stirrer. After addition of pyrrole into the emulsion media while reaction is continuing may provide a core-shell structure since the surfactant DBSA create a micro-reactor vessel by providing micelle formation where the monomers are encapsulated in. Polymers are macromolecular chains consisting of many subunits that are formed by consecutive additions of monomer. Diblock copolymers, in particular, have two characteristic subunit types in a single non-repeating AB pattern. [101-103] Amphiphilic diblock copolymers consist of two regions with substantially different solubility properties. For example, a polymer composed of a hydrophobic poly(methyl acrylate) and a hydrophilic poly(acrylic acid) block can aggregate into micellar structures upon introduction to an aqueous solution.[104] In this fashion, the hydrophobic region of the amphiphilic molecule initiates micellization by collapsing to form the core, while the hydrophilic block forms a protective shell. [105] Smaller surfactant molecules used as detergents and emulsifiers have long been studied in determining the size, shape, and physical properties of various micelles. [106-107] Relatively high concentrations of surfactants have been observed for micelle formation.[108]

Under these information's light, it is considered that in this study hydrophobic part of the surfactant molecules may adsorb on the produced conducting polymer, a surfactant thus becoming a part of the resulting material. Therefore, p(AN-co-MA)

may be encapsulated in the DBSA miscelle by the hydrophobic tail, since the MA monomer is hydrophobic too. Then Pyrrole may be polymerized by the adsorption on the surface on the miscelle. As seen in the Table 4.1., nanoparticle sizes are decreased by the addition of pyrrole first; but then increased by the increasing amount of pyrrole added. The concentration at which a block copolymer achieves micellization is referred to as the critical aggregation concentration (CAC). Copolymers are more ideal for micellar applications than surfactants due to decreased CAC requirements. [109] Lower copolymer concentrations necessary for micelle formation were determined to be a function of dispersion, hydrogen bonding, and electrostatic intermolecular forces associated with the hydrophobic block. [110-112]

When the CAC is reached for a copolymer, small polymeric micelles form. The micelles then coalesce as local concentrations of copolymer are further increased. [113-114] Micelle dissolution can then be triggered by a change in temperature, pH, salt concentration, or light intensity. [115-116]

Table 4.1. : P(AN-co-MA) and Ppy/ p(AN-co-MA) latex nanoparticle sizes measured on SEM images

Nanoparticle from latex	Added Pyrrole Content (μ l)	Particle Size (nm)
P(AN-co-MA)	0	103,70
Ppy/(AN-co-MA)	30	83
Ppy/(AN-co-MA)	50	90
Ppy/(AN-co-MA)	60	94

4.1.2 Particle size analysis of P(AN-co-MA) and PPy/p(AN-co-MA) nanoparticles obtained from emulsion latexes

To analyze particle size of nanoparticles, another method is used by Particle Size Analyzer (Light Scattering) - Malvern Mastersizer Microplus Ver.2.19. Samples that containing different amount of pyrrole addition were taken from emulsion latexes and sent to the Organik Kimya A.Ş. in order to analyze particle size. As seen in the Figure 4.2. the colour of latex nanoparticles that sampled from emulsion media changes into darker by increasing pyrrole addition. This means that the

polymerization of pyrrole occurs apparently. Thus, the dark blue-blackish colour of polypyrrole is appeared sample by sample.

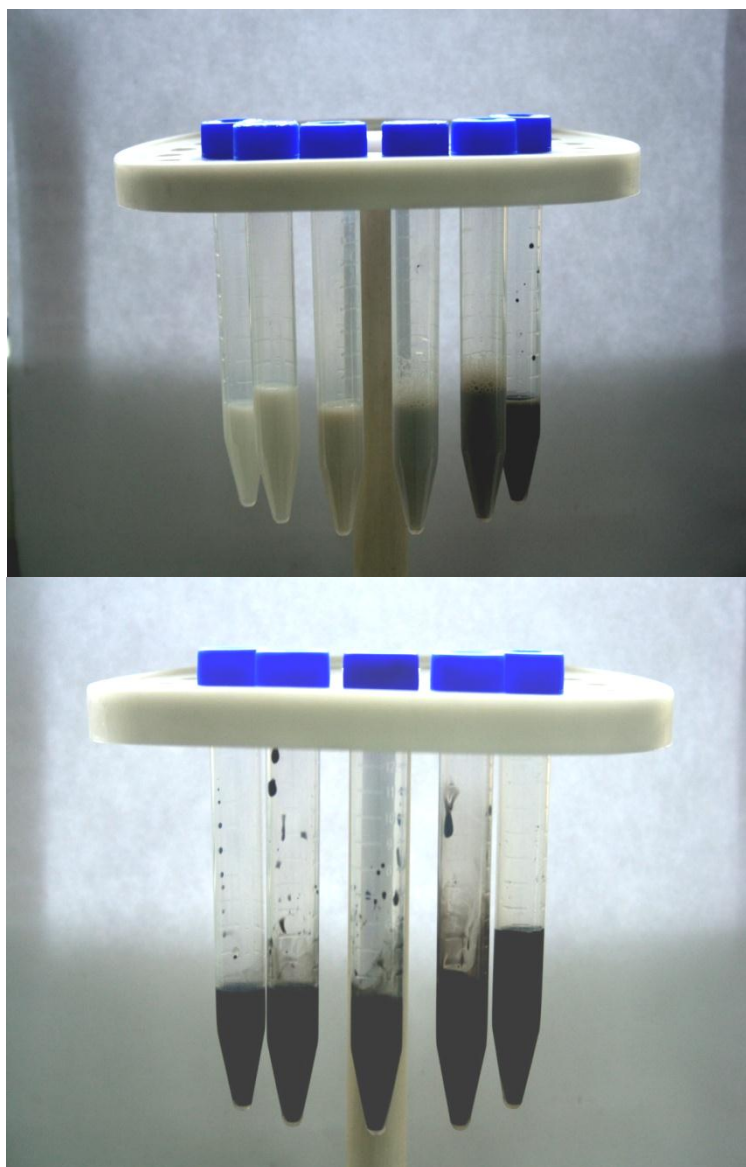


Figure 4.2 The colour change of latex nanoparticles that sampled from emulsion media by increasing pyrrole addition.

By increasing amounts of polypyrrole in the structure, particles get bigger as shown in the Table 4.2. These diameters were measured by Particle Size Analyzer and differs from SEM images, this may be caused from the aggregation due to electrostatic structure of polypyrrole.

According to Quajai et al, in the range of 60-90 nm Ppy nanoparticles can be obtained by microemulsion process. It is observed that when a nanosizer is used to

measure the particle sizes, the average particle size is found to be in the range of 180-1300 nm. This value is much more bigger than the measurement of SEM images, this means Ppy particles tend to form an aggregation. The polymerization conditions affect the aggregation degree. For instance when the SDS-doped Ppy was synthesized at room temperature without stabilizer; high degree of aggregation was indicated and average particle size was found 1300 nm. However, when it is synthesized at low temperature, the particle size is observed as 180 nm. This is because of the restricted mobility of the surfactant that leads to the decrease in the inner volume of micelles that encapsulate the monomer and the oxidant. Reduced micelle volume results in reduced nanoparticle size [117].

Table 4.2. : P(AN-co-MA) and PPy/ p(AN-co-MA) latex nanoparticle sizes measured by Particle Size Analyzer

Nanoparticle from latex	Added Pyrrole Content (μl)	Particle Size (nm)
P(AN-co-MA)	0	118
PPy/(AN-co-MA)	5	119
PPy/(AN-co-MA)	15	124
PPy/(AN-co-MA)	25	145
PPy/(AN-co-MA)	30	9340
PPy/(AN-co-MA)	50	9550
PPy/(AN-co-MA)	60	15500
PPy/(AN-co-MA)	150	15510
PPy/(AN-co-MA)	300	52680

4.1.3 FTIR-ATR characterization of P(AN-co-MA) and PPy/p(AN-co-MA) nanoparticles obtained after precipitating and drying the emulsions

FTIR analysis of dried P(AN-co-MA) and PPy / p(AN-co-MA) nanoparticles after precipitation were carried out with FTIR-ATR reflectance spectrophotometer (Perkin Elmer, Spectrum One, with a Universal ATR attachment with a diamond and ZnSe crystal) as seen in the Figure 4.3.



Figure 4.3 FTIR-ATR reflectance spectrophotometer in Electropol & Nanotech Laboratory

4.1.3.1. FTIR-ATR characterization of p(AN-co-MA)

Powder samples were taken and analyzed. The FTIR-ATR spectra of p(AN-co-MA) and PPy/(AN-co-MA) are shown in Figure 4.4 and it was recorded in the absorbance mode. Peak at 3430 cm^{-1} shows the N-H stretching from p(AN-co-MA) [118], peak at 1449 cm^{-1} refers to C-H bending [119] from p(AN-co-MA), peaks at 2954 and 1055 cm^{-1} are assigned to C-H stretching from p(AN-co-MA) [120] [121]. The peak at 2242 cm^{-1} is the characteristic of $\text{C}\equiv\text{N}$ nitrile group from AN [121]. C=O stretching from MA can be seen at 1726 cm^{-1} as a characteristic [118]. The strong absorption peak here is appearing in every spectrum of the copolymers is associated with carboxyl groups. The peak at 1634 cm^{-1} may be coming from O-H bending. [122]

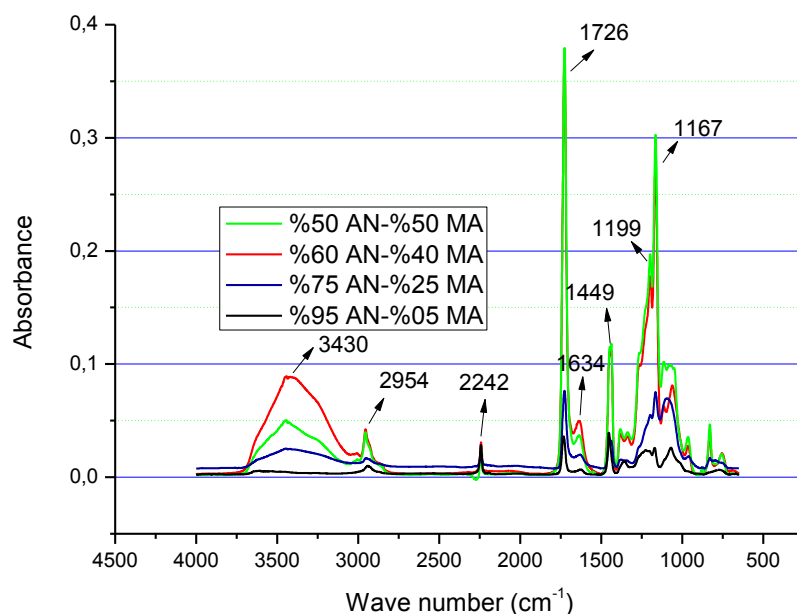


Figure 4.4 FTIR-ATR spectra of p(AN-co-MA) nanoparticles

The graph at Figure 4.5 is the absorbance value ratio at the characteristic peaks of AN and MA. The AN amount in the structure is increasing step by step by the increasing feed of AN monomer to the emulsion media. As the absorbance values are taken from the graph, the relationship between polymerization rates may be calculated from the ratios.

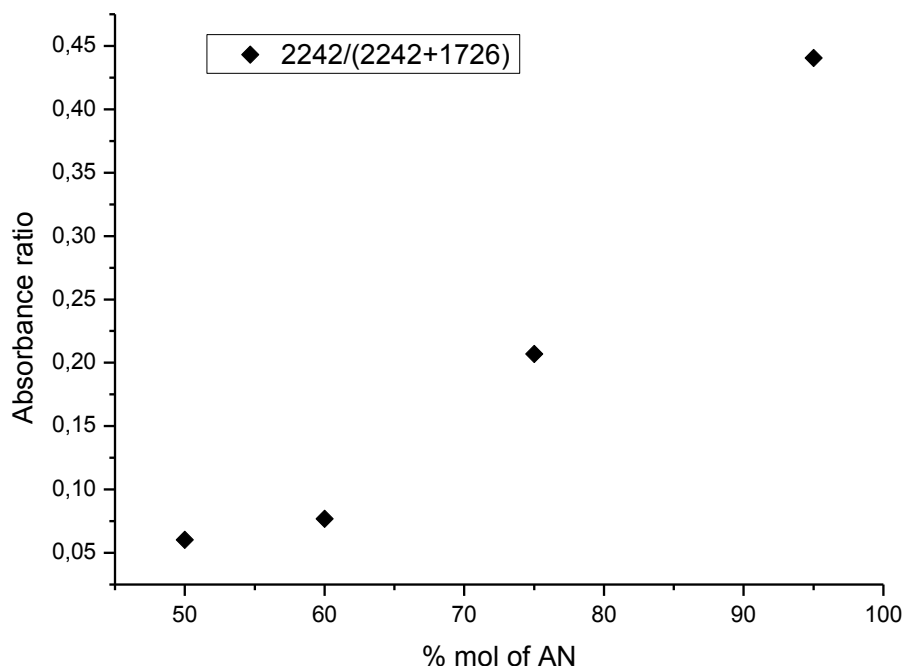


Figure 4.5 The absorbance ratio of C≡N (2242) / C=O stretching (1726)

4.1.3.2. FTIR-ATR characterization of PPy / p(AN-co-MA)

The characteristic peaks can be easily seen by the FTIR-ATR graphs of PPy / p(AN-co-MA) nanoparticle powders in the Figure 4.6. The peak at 1554 cm^{-1} shows the PPy ring vibration [123] and also peak at 1449 cm^{-1} shows the PPy ring vibration (C=C stretching) too [124]. At the 1166 cm^{-1} C-H in-plane deformation is observed [124]. 1045 cm^{-1} peak refers to N-H in-plane deformation [124]. Peaks at 967 and 911 cm^{-1} are the =C-H out of plane vibration [125]. The appearance of the peak at 1554 cm^{-1} above a certain pyrrole addition concentration is due to the Polypyrrole formation in the structure strongly. Figure 4.7 indicates that the 1554 cm^{-1} peak is appearing and increasing sample by sample as the added pyrrole amount is increased up to $300\text{ }\mu\text{l}$.

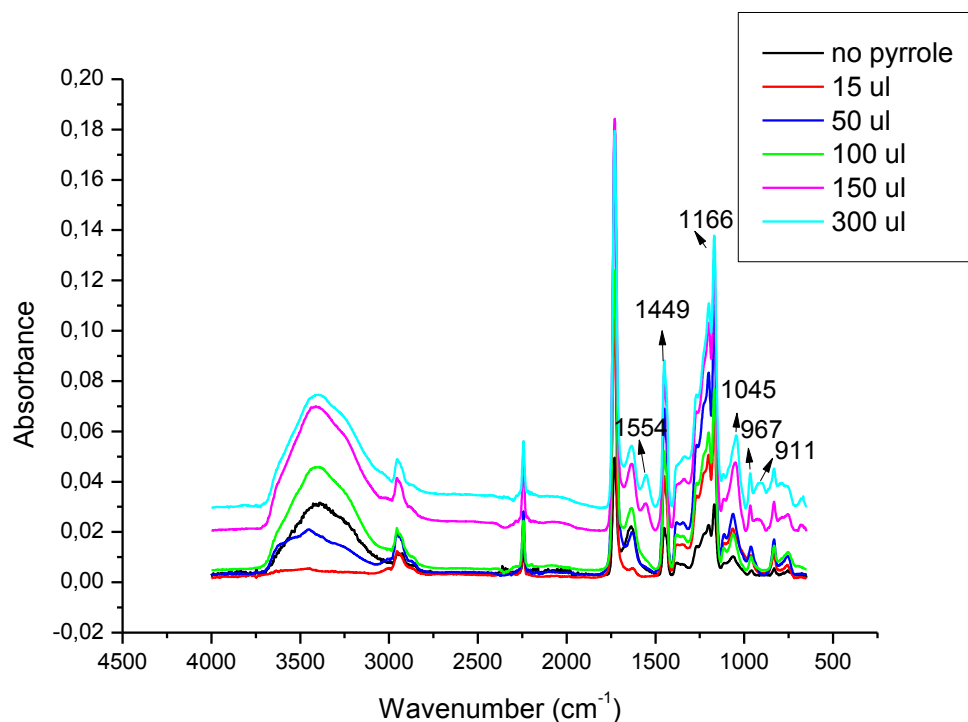


Figure 4.6 FTIR-ATR spectra of PPy / p(AN-co-MA) nanoparticles by increasing amounts of polypyrrole

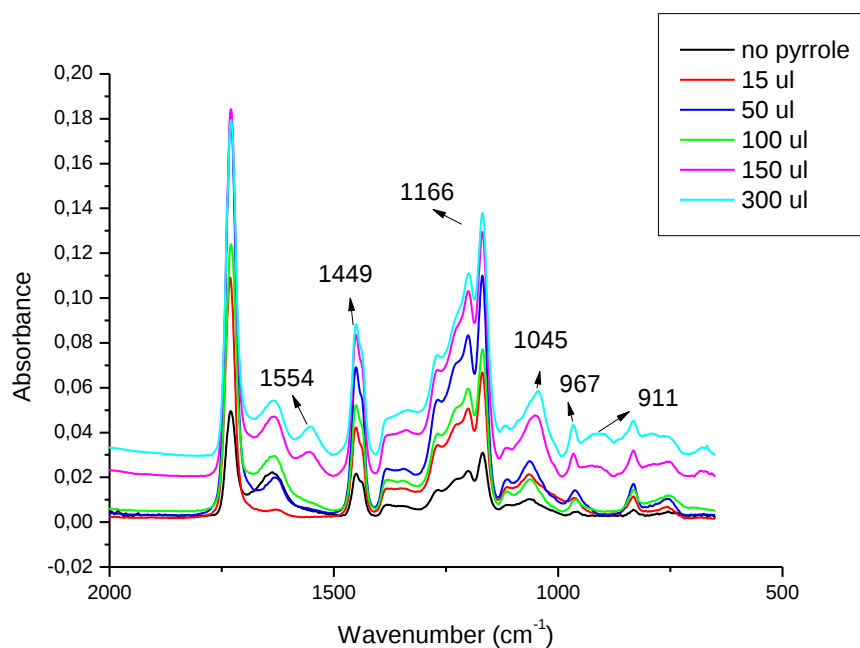


Figure 4.7 The appearing peak at 1554 cm^{-1} due to the increasement of pyrrole addition.

In the figure 4.8, the absorbance ratio of Polypyrrole's characteristic peak to Acrylonitrile's peak refers to the increasement of polypyrrole in the structure.

Acrylonitrile amount is held constant. The increase at the 1553 cm^{-1} ring vibration is obvious but the increase of the 1449 cm^{-1} ring vibration is not clear. This is probably because of the existence of overlapping peaks.

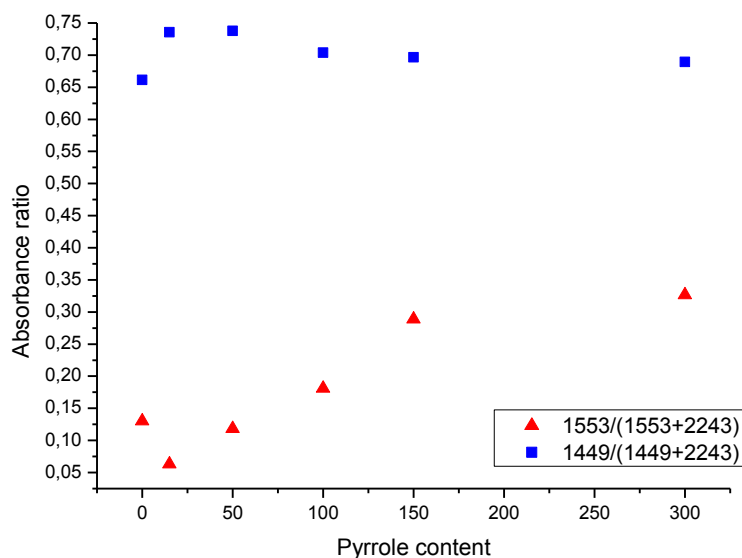


Figure 4.8 The 1553 and 1449 cm^{-1} (PPy ring vibration) ratio to 2243 cm^{-1} ($\text{C}\equiv\text{N}$ formation of AN)

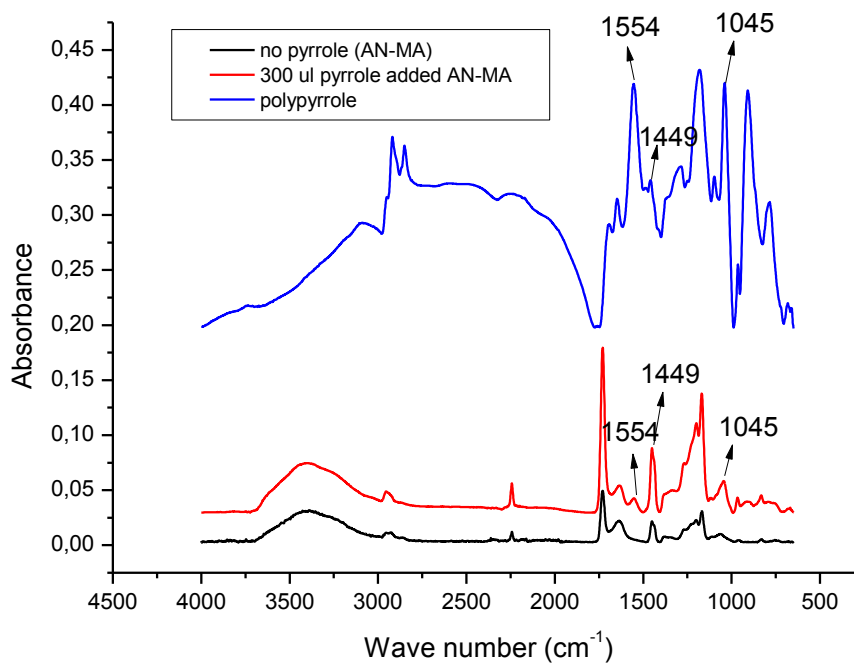


Figure 4.9 The comparison of pure PPy obtained at the same emulsion conditions without matrix of PPy / p(AN-co-MA) and P(AN-co-MA)

In the Figure 4.9, the pure PPy that obtained with the same emulsion reaction conditions with the P(AN-co-MA) and PPy / p(AN-co-MA) particles. When we look at the pure PPy's characteristic peaks, we can see these peaks in the composite nanoparticles spectrum too. This means pyrrole is successfully polymerized by one step within the matrix: P(AN-co-MA).

4.1.4 UV-Visible Spectroscopy characterization of P(AN-co-MA) and PPy/p(AN-co-MA) nanoparticles obtained after precipitating and drying the emulsions

The UV-Visible Spectroscopy characterization is achieved by using the Perkin Elmer Lambda 45 UV-Visible Spectrometer. After precipitation and drying of emulsions, 0.01 g powder nanoparticle is dissolved in 8 ml DMF and after calibration of the spectrometer with pure DMF, the measurements were taken. In Figure 4.10 the UV-Visible Spectrometer is seen in the Electropol&Nanotech Laboratory.



Figure 4.10 The UV-Visible Spectrometer in the Electropol&Nanotech Laboratory.

The UV-Visible spectroscopy results shows the absorbance increase by the increasing pyrrole addition into the reaction media. 0, 5, 10, 15, 25, 30, 50, 60, 100, 150, 300 microliters of pyrrole added nanoparticles were analyzed and after 150 microliter PPy added, the characteristic peak at 460 nm appears and shows the π - π^* transition band in the polypyrrole. [126] This peak appears at 150 μ l and 300 μ l pyrrole added samples as seen in the Figure 4.11.

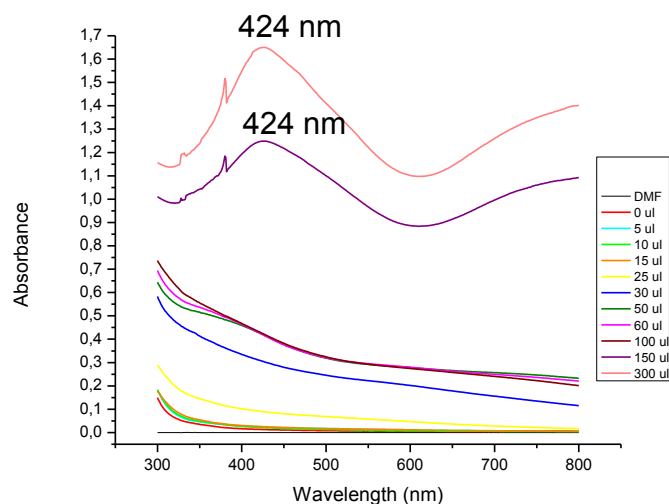


Figure: 4.11 The UV-Visible spectrum of pure DMF, p(AN-co-MA) and increasing amounts of polypyrrole containing PPy/p(AN-co-MA) nanoparticles in DMF solution.

4.1.5. The relationship between UV-Visible spectroscopy reflectance and particle size of nanoparticles

As Bernard Van Eerdenbrugh writes in his study, UV-Visible light is a effective method to catch and follow the micron and sub-micron particle sizes in an aqueus medium. [127]

Scattering techniques totally suffer from the disadvantage that in order to obtain a reliable estimate of particle size, measurements should be made at a range of lowdisperse - phase volume fractions and should be extrapolated to infinite dilution in order to avoid the problems encountered as a result of particle-particle interactions. However, the dilution of a microemulsion containing a surfactant is often problematic, due to the partitioning of the surfactant between the various phases, which often leads either to a change in the microstructure of the system or, in extreme cases, the disappearance of the microemulsion droplets [128]. All in all, scattering studies on microemulsion systems are often carried out in the concentrated microemulsion region and an appropriate model is then used to correct the results for particle-particle interactions. [129]

In any scenario where small (submicron) absorbing particles are present in the medium being analyzed, caution should be exerted when using UV/Vis fiber-optics for quantification of dissolved concentrations. [130]

As seen in the figure above, the spectrum curves does not start from the same point. There is a probability of light reflection due to the size of the particle. The amount of scattered and reflected particles is a function of particle size. In that sense UV-Visible Spectroscopy can be correlated with light scattering method. If the absorbance of a certain point is correlated with the results of particle size analysis, a proportionality will be seen on these two kinds of characterization. Figure 4.12 and 4.13 shows the probable reflection on the spectrum and the certain point at the 325 nm to choose the absorbance values. Also the Table 4.3 indicates the proportional increasement of particle size and absorbance at the probable reflectance point as the Figure 4.14.

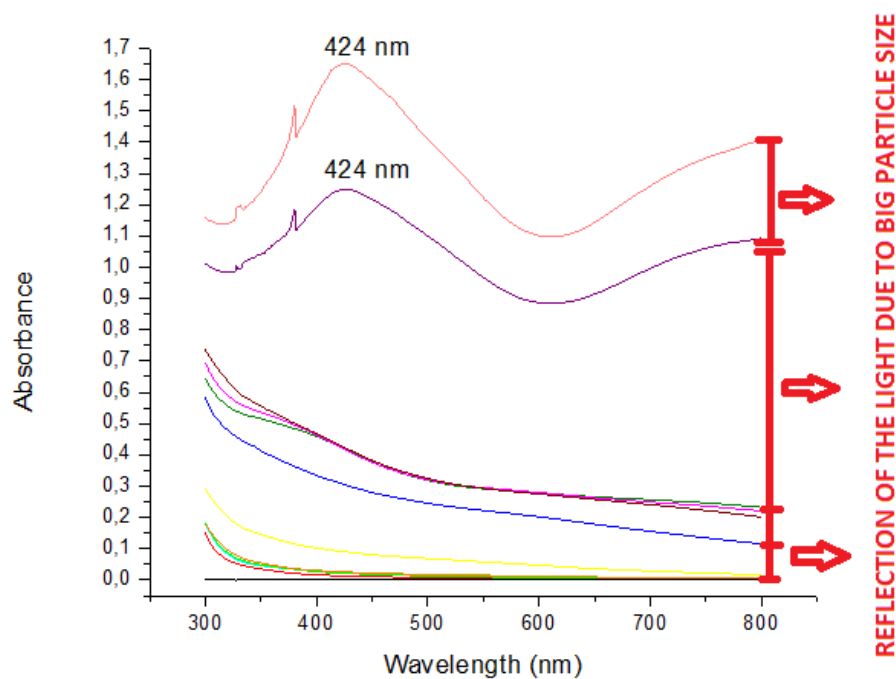


Figure 4.12 The probable reflection on the spectrum

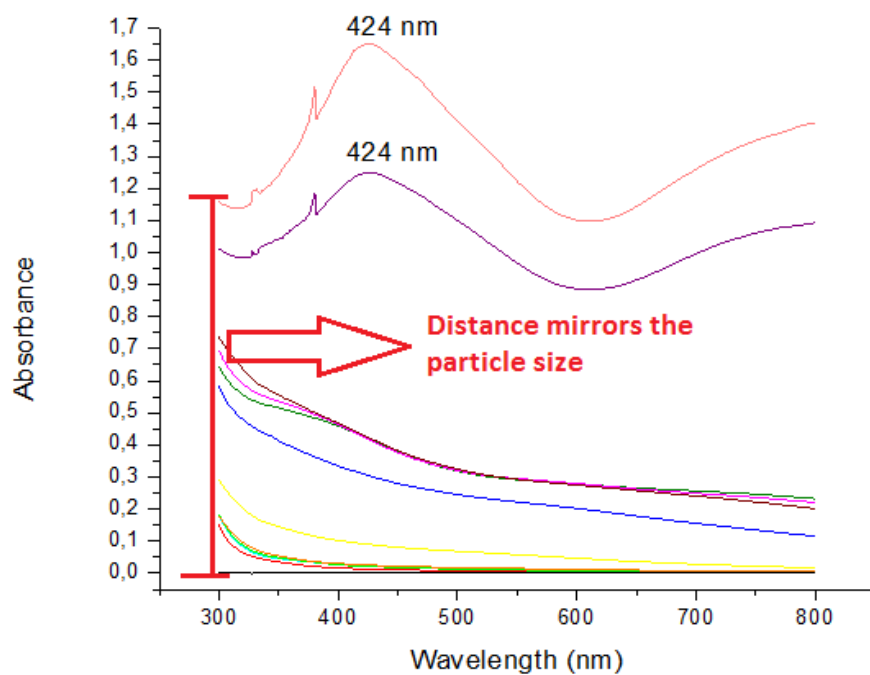


Figure 4.13 The certain point to examine the reflection

Table 4.3: The comparison of the absorption at the 325 nm, pyrrole amount and particle size

Added Pyrrole (μl)	UV Absorbance at 325 nm	Particle Size by Particle Size Analyzer(nm)
0	0,0678	118
5	0,0838	119
15	0,1842	124
25	0,4635	145
30	0,5429	9340
50	0,5799	9550
60	0,9846	15500
150	1,1459	15510
300	0,0678	52680

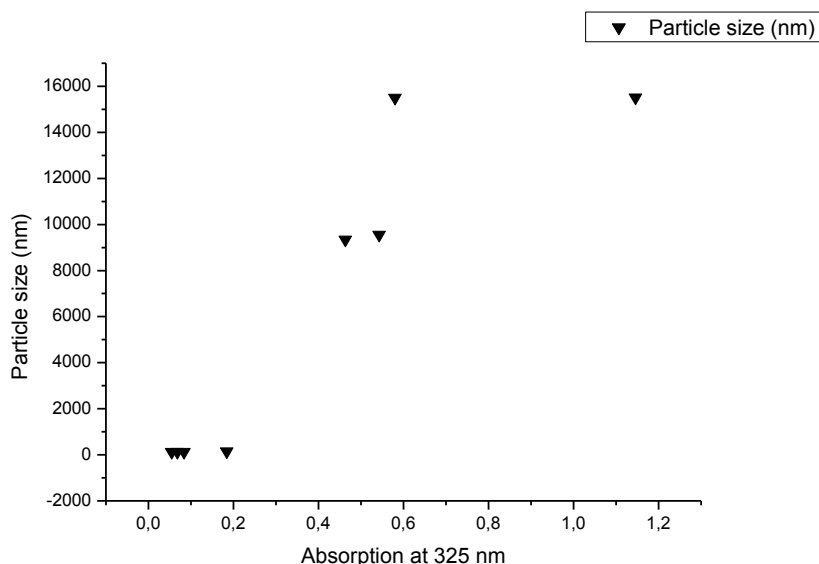


Figure 4.14 The proportional increase of the particle size in relation with the UV absorbance at 325 nm.

4.1.6. Differential scanning calorimetry analysis of p(AN-co-MA) and PPy / p(AN-co-MA) nanoparticles

T_g values of the p(AN-co-MA), 30 μ l pyrrole added PPy / p(AN-co-MA) and 100 μ l pyrrole added PPy / p(AN-co-MA) were determined as the Figure 4.15 and Table 4.4. By the polypyrrole entrance to the structure, the stiffness and relatively hard processability occurs, therefore T_g is higher at more PPy containing samples. Sanderson et al has studied effect of process variables on the initiation temperature and exothermic heat for the copolymerization of acrylonitrile and methylacrylate. According to this study, the reaction of AN-MA copolymerization gives an exothermic peak on the DSC curves according to the stabilization process. [131] Our results are parallel to the Sanderson's results for AN-MA copolymers. (Effect of process variables on the initiation temperature and exothermic heat for the copolymerization of acrylonitrile and methylacrylate.

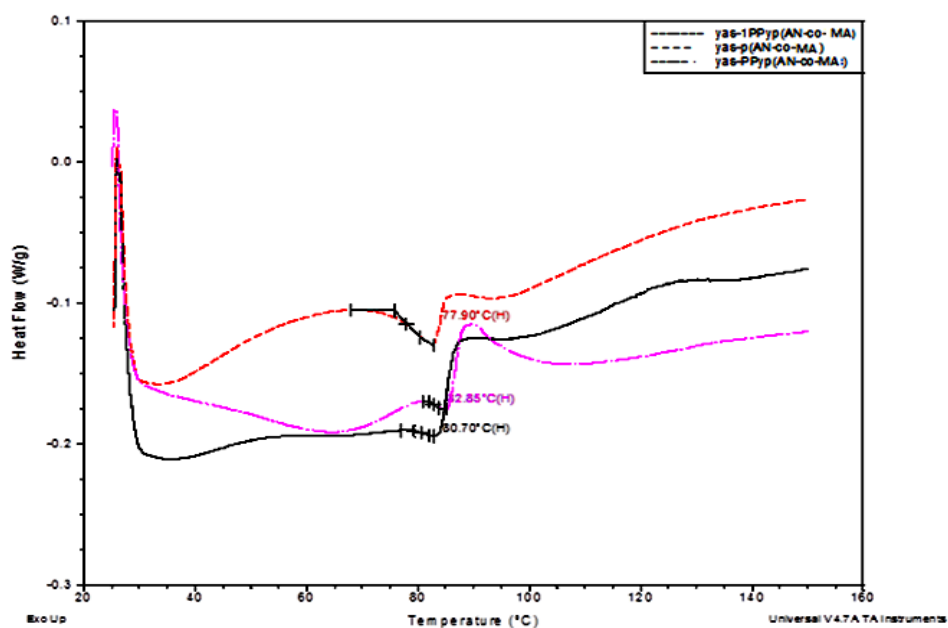


Figure 4.15 The Tg values of nanocomposites as increasing order.

Table 4.4: The increasing Tg values according to increasing pyrrole addition

Added pyrrole(μ l)	Tg (°C)
0	77,9
30	80,7
100	82,85

4.2. Nanofiber and Film Characterizations

4.2.1. Nanofiber characterization

Nanofibers were characterized by SEM and DMA (Dynamic Mechanic Analyzer). After nanofibers were coated with gold, the sem images were taken. Figure 4.16 shows the SEM images of no-pyrrol added, 30, 50, 60, 100 μ l pyrrole added sample nanofibers.

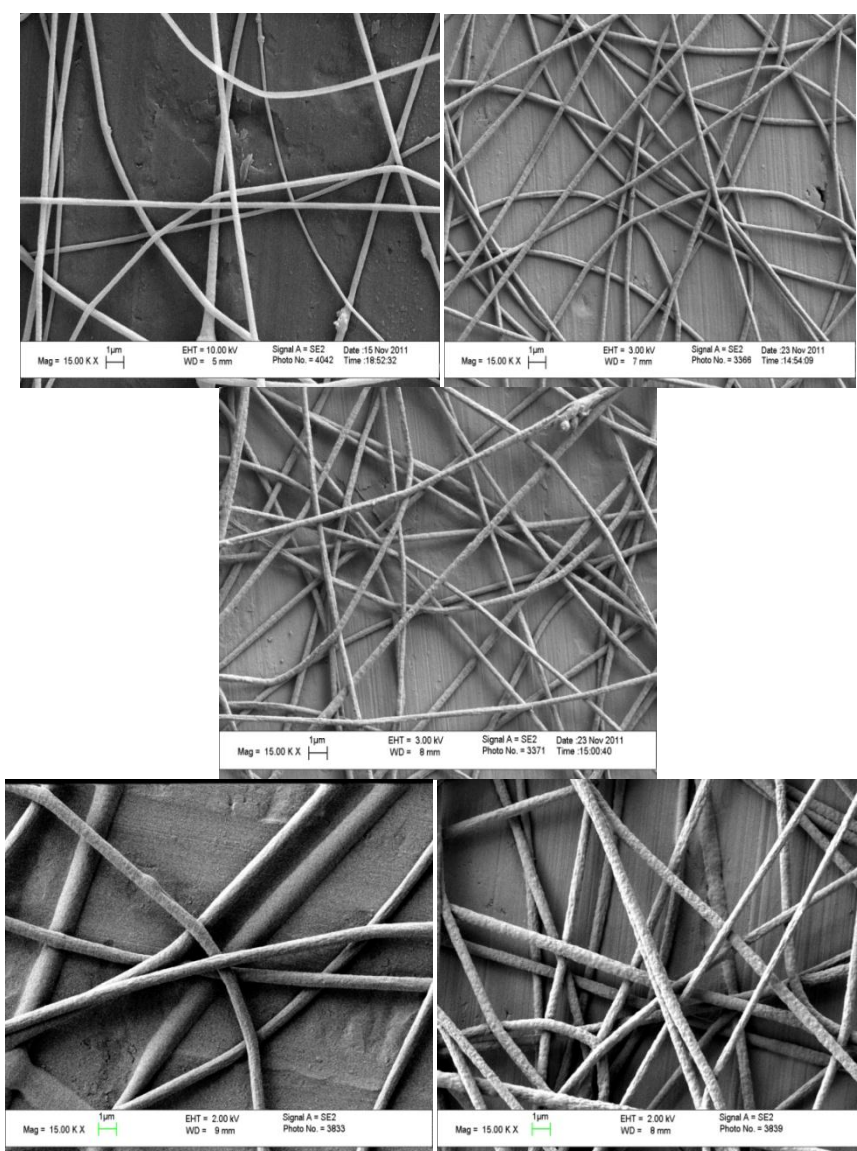


Figure 4.16 The SEM images of left to right: 0, 30, 50, 60, 100 μl pyrrole added samples.

Table 4.5: Average diameter and standart deviation of diameters according to added pyrrole amount

Added Pyrrole Amount(μl)	Average Diameter (nm)	Standard Deviation
0	597	62
30	263	47
50	345	30
60	699	37
100	307	129

Table 4.5 indicates that while pyrrole addition is increased, average diameter mostly in a range of decrease. However the standard deviation has a minimum base point which indicates the regularity of the fiber diameter has reach a minimum value and then increase while pyrrole addition is increased. Figure 4.17 shows that, when polypyrrole is appeared in the nanoparticles, this polypyrrole affects nanofibers too and provides a porous surface to the nanofibers.

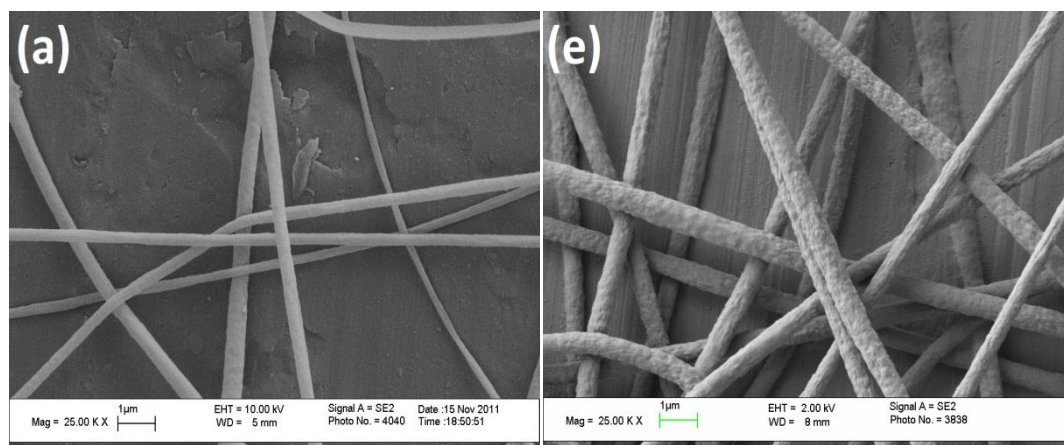


Figure 4.17 (a) is the nanofiber that not contains polypyrrole and non-porous, (e) is the nanofiber that contains polypyrrole and porous

Also Dynamic Mechanic Analyse is observed by TA Instruments DMA Q 800. Nanofibers were too weak to dynamically measure under stress, therefore nanofiber sheets were bended 4 times as seen in the figure 4.18 and then measurement was achieved. The two clamps of the DMA held the nanofiber sheet and applied a force to measure the strength of the materisl by the terms of stress and strain However, due to the breaking points that caused by bending, the measurement was not healthy. The results are given in the graph in Figure 4.19. Young's modulus were calculated as stress/strain.

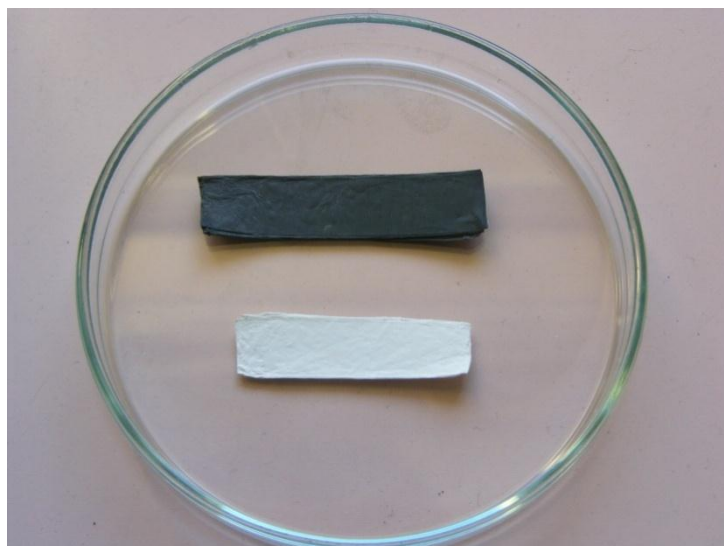


Figure 4.18 The 4 times bended nanofiber sheets. Upper: PPy / p(AN-co-MA)
Lower: p(AN-co-MA)

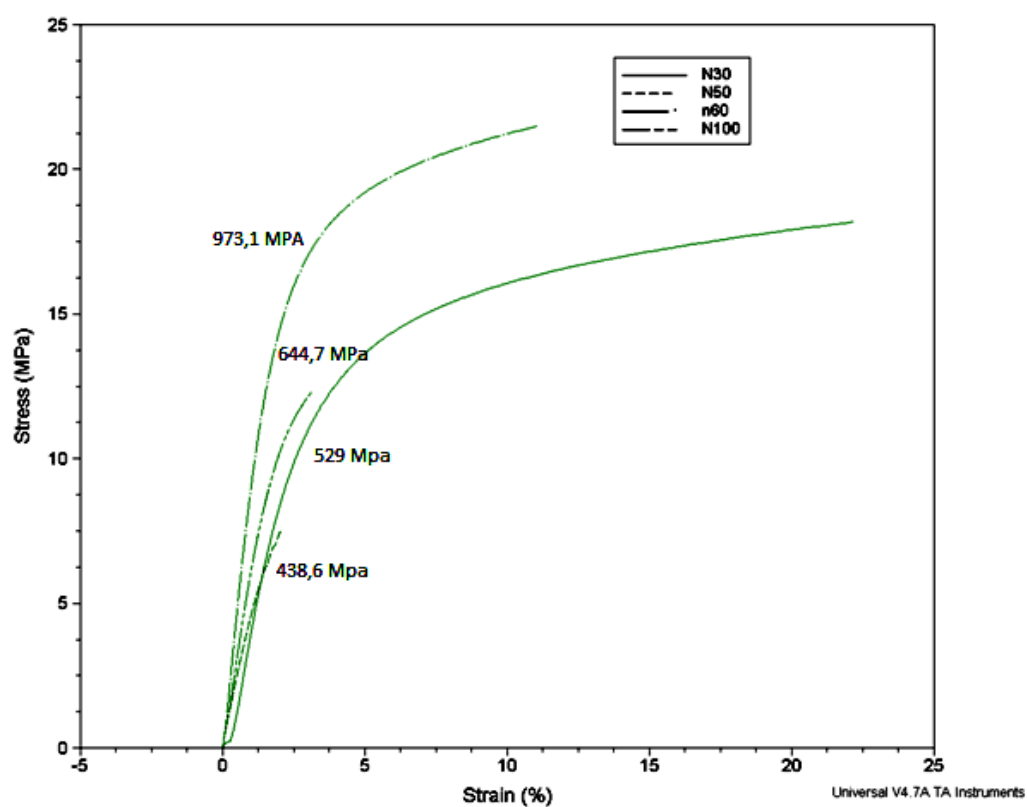


Figure 4.19 The stress-strain curves and Young's Modulus of nanofibers.

4.2.2. Film characterization

The films were characterized by Dynamic Mechanic Analyzer (DMA). As polypyrrole is brittle and stiff, when the polypyrrole formation in the structure is increased, the elasticity and elongation of the film decreased. Therefore the Young's Modulus is increasing by the increasing amount of polypyrrole in the chemical structure. This indicates that the PPy film remains all through in the glassy state and does not exhibit any transition (glass-rubbery) in the investigated temperature range (25 °C to 250 °C) and thus the PPy film is hard and brittle and is not soft and does not show any flexibility in the backbone chain of the polymer. [132] The films are shown in the Figure 4.20 as Polypyrrole formation – increasing order. And the graph in the Figure 4.21 shows the stress-strain curves and Young's Modulus of the films.

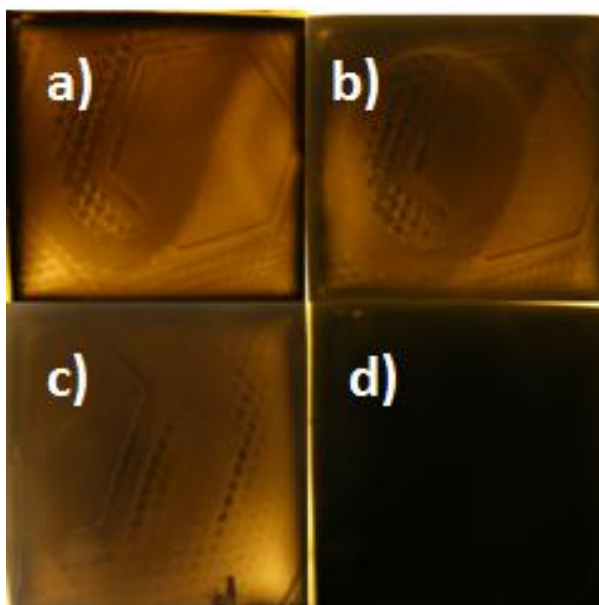


Figure 4.20 Films that obtained from a)30 μ l b)50 μ l c)60 μ l d)100 μ l pyrrole added nanoparticles

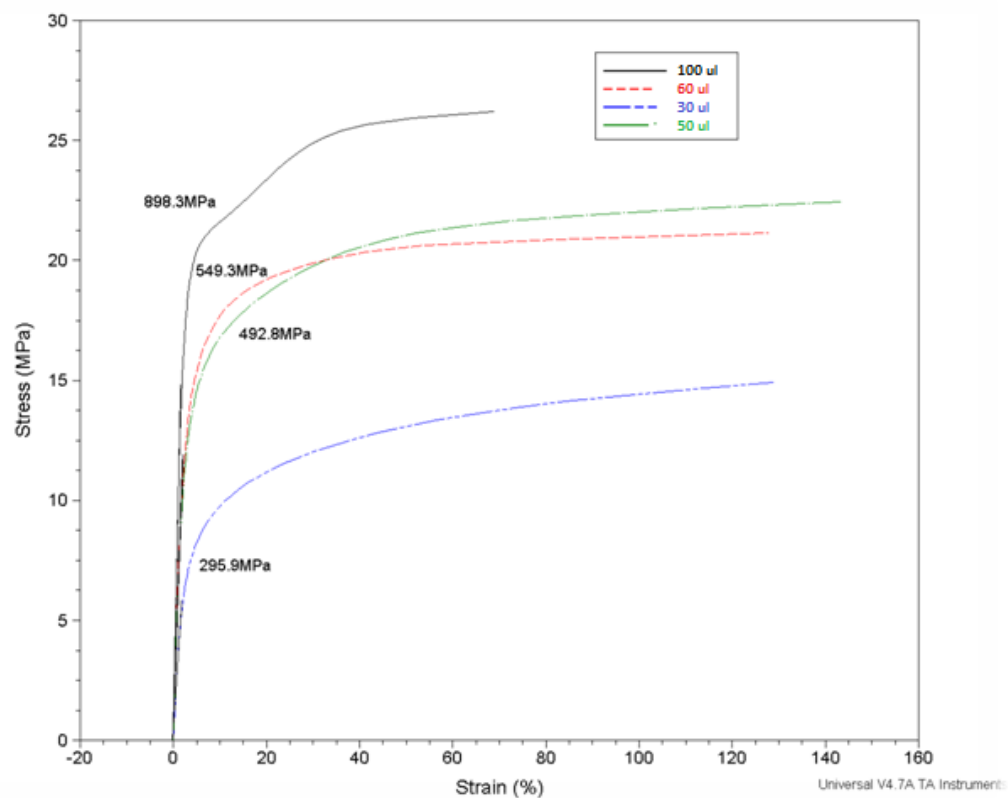


Figure 4.21 Stress-strain curves and Young's Modulus of the films, from highest to lowest: obtained from 100 μl , 60 μl , 50 μl , 30 μl pyrrole added nanoparticles.

5. CONCLUSIONS

To conclude this thesis by the strategic points, first of all a one-step polymerization is achieved without any initiator addition to the reaction media. Polypyrrole containing nano composites were obtained from the emulsion media after the copolymerization of p(AN-co-MA) nanoparticles, without terminating the reaction. Nano spheres were characterized by SEM and Particle Size Analyzer, also the powder of these nano composites were analyzed by FTIR-ATR spectroscopy, UV Visible Spectroscopy and also (DSC) it was observed that pyrrole had successfully polymerized in the structure. After nanoparticle characterization, nanofibers of obtained nanocomposite were electrospun without facing any difficulty. Polypyrrole's characteristic properties were appeared such as brittleness, stiffness and having high Young's modulus by characterizing the nanofibers with DMA. Also films that prepared from the nanoparticles were examined by DMA and it was seen that by the entering of polypyrrole in the structure, the stress that material can carry without elasticity increased and this means the Elasticity (Young's) modulus increased too. The suitable nanofiber formation of the nanomaterial provides processibility to the polypyrrole containing nano composites without brittleness.

This copolymers can be used as processible for many applications if the conductivity studies has been carried out successfully, such as biosensors, ion selective membranes, conductive nanocoatings, and all nanofiber flexibility needed areas.

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- **Yerlikaya Y., Sarac A. S., 2012:** Nanofibers and Characterizations of Polypyrrole /Poly(Acrylonitrile-co-Methylacrylate) Composites, NANOSEA 2012 4th International Conference on Nano-Structures Self Assembly, 25-29 June 2012, S. Margherita di Pula, Sardinia, ITALY