

ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE
ENGINEERING AND TECHNOLOGY

POLY(ACRYLONITRILE-co-VINYLAETATE) /Fe₂O₃@PEDOT CORE-SHELL NANOCAPSULES AND NANOFIBERS

M.Sc. THESIS

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Polymer Science and Technology Programme

Anabilim Dalı : Herhangi Mühendislik, Bilim

Programı : Herhangi Program

JANUARY 2014

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To my family,

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ABBREVIATIONS

AFM	: Atomic Force Microscopy
AN	: Acrylonitrile
DCM	: Dichlorometane
DMA	: Dynamic Mechanical Analyser
DMF	: Dimethylformamide
DSC	: Differential Scanning Calorimetry
EIS	: Electrochemical Impedance Spectroscopy
FTIR-ATR	: Fourier Transform Infrared Spectroscopy
PAN	: Polyacrylonitrile
P(AN-co-VAc)	: Poly(Acrylonitrile-co-Vinyl acetate)
P(AN-co-VAc)/Fe₂O₃	: Core-shell nanocapsules in different amounts of Fe ₂ O ₃ ; 20, 30, 40 mg
Fe₂O₃ (20, 30, 40)	: P(AN-co-VAc)/Fe ₂ O ₃ core-shell nanocapsules with Fe ₂ O ₃ 20, 30, 40 mg
PEDOT	: Poly (3, 4-ethylenedioxythiophene)
P(AN-co-VAc)/ Fe₂O₃@PEDOT	: Core-shell PEDOT nanocapsules combined with P (AN-co-VAc)/ Fe ₂ O ₃ (40) sample
PVAc	: Poly (vinyl acetate)
SEM	: Scanning Electron Microscopy
T_g	: Glass Transition Temperature
THF	: Tetrahydrofurane
TEM	: Transmisson Electron Microscopy
TGA	: Thermal Gravimetric Analysis
UV-Vis	: Ultraviole Visible Spectrophotometer

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Hata! Yer işareti

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POLY(ACRYLONITRILE-co-VINYLAETATE) /Fe₂O₃@PEDOT CORE-SHELL NANOCAPSULES AND NANOFIBERS

SUMMARY

In the purpose of the first part of my thesis, synthesis of P(acrylonitrile-co-vinylacetate)/Fe₂O₃ core-shell nanocapsules with uniform size and morphology was constituted by using nanoemulsion polymerization technique that comprise of coating P(AN-co-VAc) as shell into Fe₂O₃ nanoparticles as core. As an initial, a free radical copolymerization of acrylonitrile (AN)-vinyl acetate (VAc) with increasing amounts of Fe₂O₃ nanoparticles as being 20, 30, 40 mg and without nanoparticles was synthesised by nanoemulsion polymerization using Triton X-100 as surfactant and polyvinylpyrrolidone (PVP) as stabilizer and capping agent. To obtain P(AN-co-VAc)/Fe₂O₃ core-shell nanocapsules and P(AN-co-VAc), all of the reactions were terminated with methanol during 3 hours. The nanocapsules and copolymer were characterized in terms of chemical composition, surface morphology, particle size, thermal and mechanical properties and conductivity by using FTIR-ATR (Fourier Transform Infrared - Attenuated Total Reflectance) spectrometer, UV- visible spectrophotometer, XRD (X-ray diffraction), SEM (Scanning Electron Microscopy), TEM (Transmission Electron Microscopy), AFM (Atomic Force Microscopy), TGA (Thermal Gravimetric Analysis), DSC (Differential Scanning Calorimetry), DMA (Dynamic Mechanical Analysis) and Parstat Electrochemical Analyser via EIS measurement (Electrochemical Impedance Spectroscopy). After synthesis of the nanocapsules, they were used to fabricate nanofibers with dissolving in DMF/THF (1:1) via electrospinning method. The nanocapsules or the powders of P(AN-co-VAc)/Fe₂O₃ obtained by washing with ethanol and subsequently drying were firstly used to prove the polymerization in FTIR-ATR. Then, the behaviours of polymers in UV-Visible spectrophotometer were examined by taking samples from emulsion medium and dissolving in DMF. To understand crystallinity of the powder polymers and display the presence of Fe₂O₃ inside the polymers, they were performed by XRD. With meseasurements of viscosity of the copolymer and nanocapsules, specific and intrinsic viscosity values were calculated by ubbelohde viscometer. In order to show particle sizes and core-shell structure of P(AN-co-VAc) and the samples of P(AN-co-VAc) with 20,30 and 40 derivations of Fe₂O₃, SEM and TEM were utilized. According to the results of young modulus obtained from DMA, P(AN-co-VAc) is the highest brittle material and the range continues as P(AN-co-VAc)/Fe₂O₃ (30), P(AN-co-VAc)/Fe₂O₃ (40). Therefore, results of toughness which is defined as the area under stress-strain curves are that the highest toughness belongs to P(AN-co-VAc)/Fe₂O₃ (20) because of the property of more strain and also range of others proceeds as P(AN-co-VAc), P(AN-co-VAc)/Fe₂O₃ (30) and P(AN-co-VAc)/Fe₂O₃ (40) due to the properties of brittleness. The nanofibers were morphologically investigated via SEM for diameters of them and EIS for electrical properties in detail. The electrochemical results of the nanofibers were adjusted to an equivalent curcuit, R (Q(R(CR))), by modelling.

The second aim of the thesis was to synthesize P(AN-co-VAc)/Fe₂O₃@PEDOT core shell structure. For this purpose P(AN-co-VAc)/Fe₂O₃ was washed with ethanol and then dried in vacuum oven at 60°C which is used as a core. After obtaining the core-shell P(AN-co-VAc)/Fe₂O₃@PEDOT, succession polymerization was checked by FTIR-ATR. Afterwards, they were spin coated onto ITO-glass to examine conductivity properties via Parstat Electrochemical Analyser. The results of electrochemical measurements of P(AN-co-VAc)/Fe₂O₃@PEDOT showed us that they were ten times better than P(AN-co-VAc)/Fe₂O₃. In the same way, these results were adapted to an equivalent circuit [R (Q(R (QR)))].

POLY(ACRYLONITRILE-co-VINYLAETATE)/Fe₂O₃@PEDOT ÇEKİRDEK-KABUK NANOKAPSÜLLERİ VE NANOFİBERLERİ

ÖZET

Polimerik nanokapsüllerle ilgili çalışmalar hızlı gelişme gösteren alanlardan biridir. Polimerik nanokapsüller iki ana bölümden oluşur: dolgu malzemesi ve evsahibi polimer matris. 100 nm’ den daha düşük bir boyutlu inorganik partiküller çekirdek yapısı için dolgu malzemesi olarak, polimerde kabuk şeklindeki yapıyla bu partiküllerin evsahibi olarak hareket eder. Son dönemlerde, etkileşimli ve melez özellikleri sebebiyle polimerik nanokapsüllerin senteziyle ilgili olarak birçok çaba sarf edilmektedir. Polimerik nanokapsüllerin başlıca özellikleri dolgu malzemesi ve evsahibi polimer matrise bağlıdır. Bu kapsüller geleneksel kompozit malzemelerden daha iyidir. Çünkü geleneksel kompozitler yüksek oranda dolgu malzemesine ihtiyaç duyar. Polimerik nanokapsüller aynı özelliklere daha düşük orandaki dolgu malzemesiyle ve az yoğunluklu, iyi derecede şekil alabilen malzemelerin üretimiyle erişebilir.

Son yıllarda polimer manyetik nanomalzemelerle ilgili olarak Fe₃O₄/Polianilin, Fe₃O₄/Polimetil metakrilat, Fe₃O₄/Polivinil klorür, Fe₃O₄/Poliakrilamid, γ - Fe₂O₃/Polianilin, γ - Fe₂O₃/Poliimid, SnO₂/Polianilin çalışmaları ilgi çekici çalışmalardır. Bu polimerik nano malzemeleri hazırlamak amacı ile farklı yaklaşımlar keşfedilmiştir uygulanmıştır. Örnek olarak süspansiyon, in- situ, emülsiyon, mini emülsiyon, dispersiyon ve serbest radikal polimerizasyonları söylenebilir.

Polimerik nanokapsüllerin fonksiyonları dolgu malzemesine bağlıdır. Bu yüzden eğer manyetik nanopartiküller kullanılırsa elde edilen malzeme manyetik özellikler gösterir. Geçtiğimiz 30 yıl içerisinde dolgu malzemesi gibi manyetik nanopartikül içeren nano malzemelere özel bir ilgi gösterilmektedir. Manyetik ve fizikokimyasal özellikler sunan bu malzemeler, farklı uygulamalarda kullanılmak üzere elde edilmiş ve hala geniş uygulama alanlarından dolayı da araştırılmaya devam edilmektedir. Bu malzemelerin temel özellikleri kolay işlenebilir olması, düşük maliyetli üretimi, yüzeylere iyi tutunması, mükemmel derecedeki tünelleme magneto direnç yaratan fizikokimyasal özellikleri, iyi derecede film oluşumu ve bunların yanında elektriksel ve optik özellikleridir. Polimerik nanokapsüller; hücre ayrımı, tıbbi teşhisler, yüksek derecede bilgi depolama araçları, elektromanyetik cihazlar, elektromanyetik girişimi engelleme, biotıp, güvenlik ve enerji gibi uygulama potansiyeli yüksek alanlarda kullanılmaktadır.

Tezimin ilk bölümünün amacı, P(AN-co-VAc)/Fe₂O₃ çekirdek-kabuk nanokapsüllerinin eşdeğer büyüklük ve morfoloji ile nanoemülsiyon polimerizasyon yöntemiyle sentezlenmesi oluşturmaktadır. P(AN-co-VAc) ve P(AN-co-VAc)/Fe₂O₃ sentezleri sırasında ağırlıkça % 80 akrilonitril monomeri ve % 20 vinil asetat monomeri sisteme beslenmiştir. Bu oranlar %90 AN-%10 VAc, %80 AN-%20 VAc-%70 AN-%30 VAc oranlarında ön sentezler yapıp onlardan elde edilen nanofiberlerden elde edilen sonuçlara göre karar verilmiştir. Polimer yapısı çekirdek olarak görev yapan Fe₂O₃ nanopartiküllerine P(AN-co-VAc) kopolimerinin kabuk

olarak kaplanmasıyla şekillenmiştir. İlk olarak, akrilonitril-vinil asetat 20, 30 ve 40 mg değerlerindeki artan Fe_2O_3 nanopartikülleriyle ve partikülsüz olarak serbest radikal polimerizasyonuyla sentezlendi. Emülsiyon polimerizasyonunda birbirine karışmayan iki faz bulunmaktadır. Monomer fazı dağıtma fazı içinde homojen olarak dağılır. Emülsiyon yapıcı maddeler kullanılarak monomer fazı dağıtma fazı içerisinde tek düze küresel partiküller homojen halde bulunur. Sentez sırasında Triton X-100 yüzey aktif maddesi, PVP (polyvinilprrolidon) da stabilizatör ve koruma ajanı olarak kullanıldı. P(AN-co-VAc)/ Fe_2O_3 çekirdek-kabuk nanokapsülleri ve P(AN-co-VAc) kopolimeri sentezleri 3 saatte metanolle sonlandırıldı. Nanokapsüller ve kopolimer kimyasal kompozisyonu, yüzey morfolojisi, partikül büyüklüğü, sıcaklık ve mekanik özellikleri ve ayrıca iletkenliğiyle ilgili olarak FTIR-ATR (Fourier Dönüşümlü Infrared Spektrofotometre), UV-görünür spektrofotometre, XRD (X-ışın saçınım), SEM (Taramalı Elektron Mikroskobu), TEM (Geçirimli Elektron Mikroskobu), AFM (Atomik Kuvvet Mikroskobu), TGA (Sıcaklık Kütle Analizör), DSC (Diffransiyel Taramalı Kalorimetri), DMA (Dinamik Mekaniksel Analizör) ve Parstat Elektrokimyasal Analizör cihazlarıyla karakterize edildi. Nanokapsüllerin ve kopolimerin sentezlenmesinden sonra DMF/THF (1: 1) 'de çözülerek elektroçkim yöntemiyle nanofiber üretmek için kullanıldı. Etanolde yıkanarak ve ardından vakum etüvde kurutularak elde edilen nanokapsüller veya P(AN-co-VAc)/ Fe_2O_3 tozları başlangıç olarak polimerizasyonu kanıtlamak amacıyla FTIR-ATR 'de analiz edildi. Daha sonra, emülsiyon ortamından ve DMF'de çözülerek hazırlanan örneklerle UV-görünür spektrofotometre ile polimerlerin davranışları incelendi. Toz polimerlerin kristallinitesini ve Fe_2O_3 'ün polimerler içerisindeki varlığını anlamak için XRD ile karakterize edildi. Ubbelohde viskozimetresi kullanılarak DMF içerisinde %4'lük olarak hazırlanan numuneler 30°C'de viskozite ölçümleri gerçekleştirilmiştir. P(AN-co-VAc) kopolimerinin ve Fe_2O_3 nanokapsüllerinin özgül ve gerçek viskozite sonuçları elde edilmiş olup bu sonuçlarla da örneklerin molekül ağırlığı hakkında fikir sağlanmıştır ve ayrıca partikül büyüklüklerini ve çekirdek-kabuk yapısını göstermek için SEM ve TEM cihazlarından yararlanıldı. SEM'den partikül çapları için gaussian eğrilerinden elde edilen sonuçlar, TEM'den elde edilen görüntülerden partikül büyüklüğüne yönelik yapılan hesaplamalar, elektroçkim yöntemiyle üretilen nanofiberlerin SEM görüntüleri ile kopolimer ve Fe_2O_3 'lü nanokapsüllerin nanofiber çapları ve Atomik Kuvvet Mikroskobu'dan nanofiberlerin pürüzlülükleri hakkında bilgi edinebilmek için 25 pm^2 alanda ölçüm yapılarak değerler elde edilmiştir. P(AN-co-VAc), P(AN-co-VAc)/ Fe_2O_3 (20), P(AN-co-VAc)/ Fe_2O_3 (30), ve P(AN-co-VAc)/ Fe_2O_3 (40) 'ın SEM (Partikül Çapları) (nm) sırasıyla; 48.85 ± 21.31 , 20.59 ± 9.32 , 25.10 ± 2.72 , 30.67 ± 11.47 . Ayrıca, sentezlenen nanokapsüllerden elde edilmiş fiberlerin çapları (SEM) ve fiberlerin pürüzlülük (AFM) değerleri ise sırasıyla şu şekildedir: P(AN-co-VAc) [98 nm ve 110 nm], P(AN-co-VAc)/ Fe_2O_3 (20) [368 nm ve 773 nm], P(AN-co-VAc)/ Fe_2O_3 (30) [232 nm ve 276 nm], P(AN-co-VAc)/ Fe_2O_3 (40) [138 nm ve 464 nm]'dir.

DSC ile yapılan analiz ile de yapıdaki Fe_2O_3 miktarının artışına bağlı olarak camsı geçiş sıcaklıkları incelenmiştir. Örneklerin T_g sıralamasında en düşük P(AN-co-VAc) kopolimere ait olup kabuk-çekirdek yapısındaki nanokapsüllerde ise P(AN-co-VAc)/ Fe_2O_3 'in 20, 40 ve 30 şeklinde ki azalan sıralaması gözlenmektedir. Bu da bize 20 mg Fe_2O_3 içeren örnekteki nanopartiküllerin yapıya daha fazla dahil olduğunu göstermektedir. DMA cihazı ile ölçüm yapabilmek için her bir polimerden ince filmler hazırlanmıştır. İnce film hazırlamak için P(AN-co-VAc) ve Fe_2O_3 (20), (30) ve (40) türevlerinin

DMF içerisinde %4 'lük çözeltileri hazırlanıp bir gece akum etüvünde kurumaya bırakılmıştır. Bu filmler cihaza uygun boyutlarda kesilerek ölçüm için hazır hale getirilmiştir. Çekme gerilmesine karşılık uzama grafiğinden filmlerin elastik modülüsleri hesaplanmıştır. DMA'dan elde edilen young modulus (elastik modülüs) sonuçlarına göre en yüksek esnek örnek P(AN-co-VAc) ait ve sıra olarak Fe₂O₃ (30) ve Fe₂O₃ (40) nanokapsülleri şeklinde devam eder. Bu yüzden, stress-strain grafiklerinin altındaki alan olarak tanımlanan tokluk sonuçları da şu şekildedir: çok uzama nedeniyle en yüksek tokluk değeri Fe₂O₃ (20) aittir ve sıralama da P(AN-co-VAc), Fe₂O₃ (30) ve Fe₂O₃ (40) nanokapsülleri şeklinde devam eder. DMA cihazı ile yapılan diğer bir analiz ise frekansa bağlı sıcaklık artışına dayanan testlerdir. Bu testler sabit frekansta sıcaklığın artışıyla depolama ve kaybetme modülüs değerlerinin elde edilip bu iki değerlerin de birbirine oranlanmasından elde edilen tan delta grafiklerinin en üst tepesindeki değerlerin numunelerin termal özellikleri hakkında sonuçlar vermesidir. Bu sonuçlar malzemelerin camı geçiş sıcaklıkları hakkındadır. Sonuçlar DSC'den elde edilen sonuçlarla da paralellik göstermektedir. P(AN-co-VAc), Fe₂O₃ (20), Fe₂O₃ (30) ve Fe₂O₃ (40) nanokapsüller'den elde edilmiş nanofiberlerin SEM cihazı ile çaplarıyla ilgili olarak ve Parstat cihazı ile de empedans özellikleri detaylı incelenmiştir. Bu inceleme sırasında Nyquist, faz açısı, faz genliği ve admitans grafikleri elde edilmiştir. Nyquist grafiği ile nanofiberlerin dirençleri, faz açısı grafikleri ile kapasitansı ve admitans grafikleri ile de iletkenlikleri hakkında bilgi edinilmiştir. Nanofiberlerin faz açısı grafiklerinden Fe₂O₃ miktarı arttıkça kapasitansın nanofiber çaplarıyla orantılı olarak azaldığı görülmüştür. Admitans grafiklerinin maksimum noktasından tespit edilen değerler $Y=1/Z$ formülünde yerine konularak nanofiberlerin iletkenliklerini hesaplanmıştır. Burdan elde edilen değerlerde en yüksek iletkenliğin P(AN-co-VAc)/Fe₂O₃@PEDOT ait olduğunu ve sıralamanın Fe₂O₃ (30), Fe₂O₃ (40), Fe₂O₃ (20) ve P(AN-co-VAc) olarak devam ettiğini göstermiştir. Nanofiberlerin elektrokimyasal sonuçlarının, modelleme yapılarak R (Q(R(CR))) olan eşdeğer bir devreye uyduğu ortaya çıkmıştır.

Tezin ikinci amacını etanolle yıkanmış ve 60°C 'de vakum etüvünde kurutulmuş P(AN-co-VAc)/Fe₂O₃'den P(AN-co-VAc)/Fe₂O₃@PEDOT sentezlenmesi oluşturmaktadır. Sentez için P(AN-co-VAc)/Fe₂O₃ çekirdek, PEDOT ise kabuk olarak kullanıldı. Çünkü, demir oksit nanopartikülleri polimerizasyon sırasında birbirlerine uyguladıkları manyetik alandan kaynaklı topaklanma sebebiyle doğrudan iletken polimerlerle uygulanabilirliği kolay olmamaktadır. P(AN-co-VAc)/Fe₂O₃@PEDOT çekirdek-kabuk nanokapsülleri elde edildikten sonra polimerizasyonun başarılı gerçekleşip gerçekleşmediği FTIR-ATR ölçümleri ile kontrol edildi. Daha sonra, iletkenlik özelliklerini incelemek için P(AN-co-VAc)/Fe₂O₃@PEDOT dönerli kaplama yöntemiye ITO cam üzerine kaplandı. P(AN-co-VAc)/Fe₂O₃@PEDOT'ın admitans ölçümleri bize gösterdi ki iletkenliği P(AN-co-VAc)/Fe₂O₃'den on kat daha fazladır. Aynı şekilde, bu sonuçlar R (Q(R(QR))) olan bir eşdeğer devre modeline uyduğugörüldü.

1. INTRODUCTION

Inorganic nanoparticles assembled with composite polymers have attracted great interest of many researchers in recent years [1]. Nanoparticles have received tremendous attention of modern materials science due to their potential technological importance, which results from their unique physical properties. These properties stem from their reduced dimensions: for example, the cubic spinel structured maghemite ($\gamma\text{-Fe}_2\text{O}_3$) is technologically significant. So, It has widely used for information storage [2], in color imaging [3], in magnetic refrigeration [4], in bioprocessing [5], in medical diagnosis [6], in controlled drug delivery [7], and as ferrofluids [8]. Pure magnetic particles might not be useful in applications. Since they have some following limitations: (i) they tend to form large aggregates, (ii) their original structure may become changed due to unstable resulting in the variation of magnetic properties, (iii) they may conduct rapid biodegradation as they are exposed to the biological system. Thus, a suitable coating such as capsule with polymers is a very necessary to remove limitations [9]. In order to encapsulate such magnetite particles in the monomeric phase, reaction conditions must be such that all the magnetite particles are transferred uniformly into the resulting particles, or the magnetite particles must provide the only site for precipitation of polymers [1]. For the formation of nanocapsule structure, nano-emulsion polymerization technique known as generally miniemulsion is widely used. To remain a long term stability, it is considerable to involve chemically link between polymer chains and particle surfaces. Magnetic polymeric nanospheres prepared by nano-emulsion polymerization in the presence of iron oxide particles have been studied by Liu et al. [10]. Core-shell SiO_2 /polystyrene nanocomposite particles as well as particles with other morphologies has been reported by Zhang et al. [11]. In lithium-ion batteries to fabricate high-performance anode materials, iron oxides (mainly Fe_2O_3 and Fe_3O_4) nanoparticles have usually been regarded as very appealing candidates due to their much higher capacity than that of conventional graphite (372 mA h g^{-1}). The principle is based on the lithium storage capacity of iron oxides delivered through the reversible conversion reaction between lithium ions and metal oxide

forming metal nanocrystals dispersed in a Li_2O matrix [12]. Removal of contamination of heavy-metal ions such as Pb(II) , Cr(VI) , As(V) , Cu(II) , Zn(II) , Cd(II) , and Hg(II) from water which affects the health of human beings and ecological environment is a serious problem in the worldwide that has to be solved. A variety of nanostructured materials, such as self-assembled 3D flower like Fe_2O_3 (Zhong et al. 2006), $\text{Fe@Fe}_2\text{O}_3$ core–Shell nanowires (Ai et al. 2008), porous hematite hollow microspheres (Li et al. 2010), ceria hollow nanospheres (Cao et al. 2010), and iron oxide/carbon nanotube composites (Gupta et al. 2011), have been successfully developed for removal of Cr(VI) from wastewater [13]. Moreover, polymer materials that possess magnificent optical properties, high flexibility and toughness can facilitate processability and improve the brittleness of inorganic materials [1].

Electrospinning is a simple and cost-effective process to prepare micro- or nanofibers through electrostatic forces, and over thirty different polymers have been electrospun to prepare fibers with diameters below $1\mu\text{m}$ [14]. The nanofibers have a remarkably large surface-to-volume ratio and have many fascinating properties, such as high surface energy, high surface reactivity, and high thermal and electrical conductivity [15].

Multi-functional micro and nano structures of conducting polymers are major focus of research and development due to their unique properties and technological applications in electrical, optical, and magnetic materials and devices [14]. Among the different families of conducting polymers, poly(3,4-ethylenedioxythiophene) (PEDOT) has been studied widely because of its great thermal and environmental stability, low band gap, high conductivity, and high transparency [16]. PEDOT was developed at Bayer AG in the late 1980s [17] and it is extensively used in the electrochromics, light emitting diodes, solar cells and antistatic film coating [14]. The rigid and linear conformation of PEDOT contributes charge transport and crystallization [18] resulting in favorable properties such as, high charge/discharge capacities, fast response times and high sensing capabilities [19-23]. PEDOT is polymerized oxidatively, either with appropriate oxidants (chemically) or with an electrochemical method.

Spin coating is a technique that utilize centrifugal forces created by a spinning substrate to spread a coating solution evenly over a surface, usually with attendant

solvent evaporation to form a very uniform gel or polymer coating [24]. This technology combined with nanosphere lithography (NSL) becomes more widespread to produce masks [25]. 2D colloidal-crystal films comprised of PS nanospheres [26,27] or silica particles [28,29] fabricated by spin-coating have been reported.

In this study, we firstly propose the synthesis P(AN-co-VAc) nanostructure combined as core-shell structure with Fe_2O_3 nanoparticles by miniemulsion polymerization. Because, nanomaterials assembled with composite polymers have attracted great interest for widely usage in electromagnetic shielding, electrochromic coatings, and corrosion resistance due to their electrical conductivity, processability, magnetic, mechanical and environmental sensitivity [30]. AN and VAc monomers were chosen because AN provides the copolymer with good processability and thermal stability[31] and VAc provides strong adhesion and mechanical stability to the materials [31]. During polymerization, Triton X-100 was used as surfactant, PVP as stabilizer [32] and capping agent [33]. It is considerable to involve chemically a link between polymer chains and particle surfaces in order to remain a long term stability. So, it is necessary of surface modification on produced nanoparticles by polymeric surfactants or other modifiers. Adding polymeric molecules having charged or ionizable sites into colloidal dispersion particles results in the attachment of the polymer to the particles. Because of the length of the polymeric chain the motion of the colloid-polymer particle is hindered, thus promoting contact with other particles. Interaction with similar particles forms "bridges." This results in particle agglomeration and eventual flocculation. The flocculation depends on a number of factors such as: the amount of polymer attached to the surface, solvent quality and whether the polymer is chemically or physically attached to the surface.

First of all, Fe_2O_3 and PVP were dispersed after formation of micelles with stirring Triton X-100 within distilled water. Due to hydrophilic surfaces of Fe_2O_3 and PVP, they entered into micelles as core. Because, -OH group of Triton X-100 was inward and other tail of the surfactant called as hydrophobic was outward. As a result, P (AN-co-VAc) copolymer was formed as shell on the hydrophobic tails of Triton X-100 after adding acrylonitrile and vinyl acetate monomers.

In order to characterize these nanocapsule structures, Fourier Transform Infrared - Attenuated Total Reflectance (FTIR-ATR), UV-visible spectrophotometers were used and XRD to determine crystallinity were used. Electrospun nanofibers were fabricated to examine conductivity properties of the nanocapsule composites, using Parstat Electrochemical Analyser via EIS. Thermal stabilities were checked by Differential Scanning Calorimeter (DSC) and Thermalgravimetric Analyser (TGA). Mechanical properties were examined by Dynamic Mechanical Analyser (DMA). To determine the particle size and fiber diameters of the Fe_2O_3 coated with P(AN-co-VAc), Scanning Electron Microscope (SEM) and Transmission Electron Microscope were used. To show morphological properties of the nanofibers, Atomic Force Microscope (AFM) as well as Scanning Electron Microscope (SEM) was used.

In the second part of the study, P(AN-co-VAc)- Fe_2O_3 coated with PEDOT was synthesised via oxidative polymerization. PEDOT was used as shell and P(AN-co-VAc)- Fe_2O_3 as core. Since conducting polymers could not be directly deposited onto the surface of magnetic particles due to flocculation and the hydrophilic surfaces of magnetic particles [34]. After that, the prepared capsule was coated onto ITO-glass by spin coating to represent the effect upon conductivity of the Fe_2O_3 coated with P(AN-co-VAc) assembled with PEDOT.

2. THEORETICAL PART

2.1 Acrylonitrile, Polyacrylonitrile and Poly (acrylonitrile-co-vinyl acetate)

The first synthesis of acrylonitrile (AN) was made in 1893 by Moureu [35], by the dehydration of ethylene cyanhydrine (1-cyanoethanol) or acrylamide (Figure 2.1). Ethylene cyanhydrine was used as starting material for the industrial processes of AN production, but since 1960 practically the entire AN production has been based on catalytic ammonoxidation of propene [36].

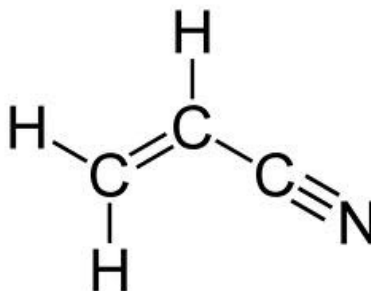


Figure 2.1 : General formula of acrylonitrile.

In comparison to the other vinyl polymerization reactions, AN has different characteristic properties. AN is soluble in most organic solvents and in water. On the other hand, solubility of PAN differs from its monomer. It is insoluble in most common organic solvents, in water, and also in its monomer. Thus, the polymerization reaction heterogeneously occurs even at low conversions and monomer concentrations, and the borders between emulsion and suspension polymerization are not well defined. Heterogeneous AN polymerization displays autoacceleration when a sufficient amount of a surfactant is not used. Thereby, there is obviously no consensus among the authors reporting on AN polymerization as far as use of solution polymerization, dispersion polymerization, and precipitation polymerization is concerned, especially in aqueous systems [37].

Polyacrylonitrile (PAN) is a commercially crucial polymer. Because PAN contributes good processability, electrochemical and thermal stability to the copolymer [38]. Polyacrylonitrile (PAN) and its copolymers are the most promising

materials generally used in textile applications. It also possess unique and well-known properties including chemical resistance, compatibility with certain polar substances, low gas permeability [39], hardness and rigidity which result from the interaction of adjacent cyanide groups increases the resistance of interior rotation of the main chain and thus decreases the flexibility of the polymer chain [38].

PAN is usually prepared by radical polymerization without control over molecular dimension and structure [40]. PAN usually exhibits polar character due to strong interchain interactions through nitrile groups and so it decomposes before melting [41-42]. Some exothermic reactions such as cyclization of nitrile groups takes place of melting, which results in formation of ladder like structure during the heat treatments of homo and copolymers of acrylonitrile. In addition, PAN has a magnitude of the dipole moments of the CN lead to strong intrachain and interchain interactions through secondary bonding. Thus, combination of a number of flexible comonomers such as vinyl acetate which provides strong adhesion and excellent mechanical stability to the copolymer [31] weakens the dipolar interactions of CN, so that decreases melting point or increases decomposition temperatures of the PAN based copolymers [43]. As a consequence, it is important to consider the effect of comonomer on the thermal behaviour of PAN based copolymers [44].

2.2 Triton X-100

TRITON X-100 is an octylphenol ethoxylate consisting of nine to 10 moles of ethylene oxide and supplied as a 100-percent active product. It has a number of properties, which are such as a high-purity, water-soluble, liquid, and nonionic surfactant, which has come to acknowledged as the performance standard among similar products. The nonionic amphiphile is used in heavy-duty industrial products/gentle detergents and is one of the important emulsifiers used in the production of emulsion polymers and stabilizers in polymer latex [45]. Tritons are also recognized for pigment wetting and stabilization in coatings. TRITON X-100 provides good surface activity by the lowering of the surface tension of water and the interfacial tensions between water and mineral oil (Figure 2.2).

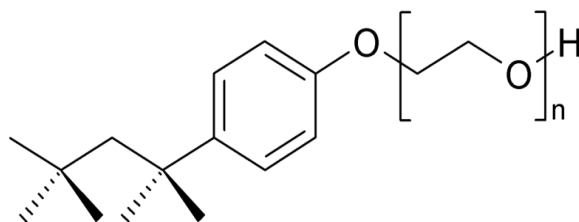


Figure 2.2: General formula of Triton X.

TX-100 is freely soluble in a number of nonaqueous solvents and can generate microemulsion without the use of cosurfactant [46,47]. Reverse micelles of TX-100 in nonpolar solvents and in polar–nonpolar solvent systems have been reported [48–51] and used as a surfactant to synthesize of nanoparticles of TiO_2 [52] and copper [53].

Small angle neutron scattering (SANS) studies by Goyal et al. [54–56] represented that TX-100 micelles were spherical or oblate ellipsoids (with an axial ratio around two) over a wide range of concentration and temperature and so the effect of temperature on inter-micellar interactions has been reported. At higher temperature, as well as decreasing in the hydration a decrease in screening of van der Waal's interactions emerges so the interaction potential between non-ionic micelles becomes more attractive with an increase in temperature.

2.3 γ - Fe_2O_3 Nanoparticles

Fe_2O_3 has four phases: α - Fe_2O_3 (hematite), β - Fe_2O_3 , γ - Fe_2O_3 (maghemite), and ξ - Fe_2O_3 [57]. Among them, α - Fe_2O_3 has the corundum structure whereas the others have the cubic structure [58]. γ - Fe_2O_3 (maghemite) which is a technologically important magnetic material possess a wide range of applications in the production of permanent magnetic materials [59], magnetic refrigeration, information storage, controlled drug delivery, bioprocessing and ferrofluids [60, 61]. At nanoscale, these composite materials have attracted great interest for widely usage as electromagnetic shielding, biosensors, electrochromism, and corrosion resistance due to their excellent electrical conductivity, processability, magnetic, mechanical, and environmental sensitivity, as well [62, 63]. On the other hand, pure maghemite transforms into hematite (α - Fe_2O_3) at a rather low temperature: $\sim 380^\circ C$. Because of this reason, the processing of γ - Fe_2O_3 magnetic nanocomposites has often been carried out at very low temperatures using water soluble polymers [64, 65].

Unfortunately, it is very difficult to synthesize a single phase nanocrystalline γ -Fe₂O₃ via both conventional and chemistry-based processing routes, due to the fact that the nanocrystallites tend to aggregate and coarsen at the calcination temperatures [66]. To prevent the formation of unwanted crystallite coarsening and particle aggregation and to stabilize the maghemite phase, several attempts have been conducted to disperse the maghemite phase in a variety of matrix materials such as silica [67, 68], porous glass [69] and polymers [70, 71].

2.4 Emulsion Polymerization

Emulsion polymerization is a unique chemical process widely used to produce waterborne resins with various colloidal and physicochemical properties. This heterogeneous free radical polymerization process includes emulsification of the relatively hydrophobic monomer in water by an oil-in-water emulsifier, followed by the initiation reaction with either a water soluble initiator (e.g. sodium persulfate (NaPS)) or an oil-soluble initiator (e.g. azobisisobutyronitrile (AIBN)) [72]. Typical monomers used in emulsion polymerization compose of butadiene, styrene, acrylonitrile, vinyl acetate, and vinyl chloride.

Emulsion polymerization is a rather complex process because nucleation, growth and stabilization of polymer particles are controlled by the free radical polymerization mechanisms in combination with various colloidal phenomena. Perhaps, the most important feature of emulsion polymerization is the segregation of free radicals among the discrete monomer-swollen polymer particles. This will greatly reduce the probability of bimolecular termination of free radicals and, thereby, result in a faster polymerization rate and polymer with a higher molecular weight. In bulk or solution polymerization, these advantageous properties of emulsion polymerization cannot be achieved simultaneously. Although the nucleation period is quite short, generation of particle nuclei during the early stage of the polymerization plays a crucial role in determining the final latex particle size and particle size distribution and it has also a crucial influence on the quality of latex products.

Miniemulsion, microemulsion and conventional emulsion polymerizations show quite different particle nucleation and growth mechanisms and kinetics [72]. Emulsions with droplet size in the nanometric scale (typically in the range 20–200

nm) are often referred to in the literature as miniemulsions [73], nano-emulsions [74, 75], ultrafine emulsions [74], submicron emulsions [76], etc.

The reaction system is characterized by the emulsified monomer droplets (ca. 1–10 μm in diameter, 10^{12} – 10^{14} dm^{-3}) dispersed in the continuous aqueous phase with the aid of an oil-in-water surfactant at the very beginning of polymerization. Monomer swollen micelles (ca. 5–10 nm in diameter, 10^{19} – 10^{21} dm^{-3} in number) may also exist in the reaction system provided that the concentration of surfactant in the aqueous phase is above its critical micelle concentration (CMC). Only a small fraction of the relatively hydrophobic monomer is present in the micelles (if present) or dissolved in the aqueous phase. Most of the monomer molecules dwell in the giant monomer reservoirs (i.e. monomer droplets). The polymerization is initiated by the addition of initiator. According to the micelle nucleation model, proposed by Harkins [77–80] and Smith and Ewart [81–83] and modified by Gardon [84, 85], submicron latex particles (ca. 0.05–1 μm in diameter, 10^{16} – 10^{18} dm^{-3} in number) are generated via the capture of free radicals by micelles, which exhibit an extremely large oil–water interfacial area. Monomer droplets are not generally effective in competing with micelles in capturing free radicals generated in the aqueous phase because of their relatively small surface area. However, monomer droplets may become the predominant particle nucleation loci if the droplet size is reduced to the submicron range. This technique is termed the miniemulsion polymerization [86–90] and innovative miniemulsion polymerization technology continues to progress in recent years [89].

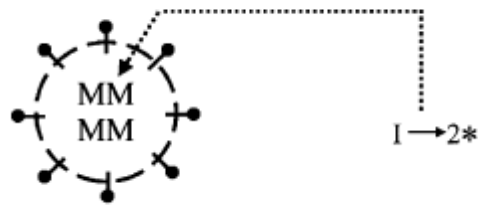
Waterborne free radicals first polymerize with monomer molecules dissolved in the continuous aqueous phase. This would cause the increased hydrophobicity of oligomeric radicals. When a critical chain length is achieved, these oligomeric radicals become so hydrophobic that they show a strong tendency to enter the monomer-swollen micelles and then continue to propagate by reacting with those monomer molecules therein. As a consequence, monomer-swollen micelles are successfully transformed into particle nuclei. These embryo particles continue to grow by acquiring the reactant species from monomer droplets and monomer-swollen micelles. In order to maintain adequate colloidal stability of the growing particle nuclei, micelles that do not contribute to particle nucleation disrupt to supply the increasing demand for surfactant. In addition, the surfactant molecules

adsorbed on monomer droplets may desorb out of the droplet surface, diffuse across the continuous aqueous phase and then adsorb on the expanding particle surface. The particle nucleation stage (Interval I) ends immediately after the completion of micelles.

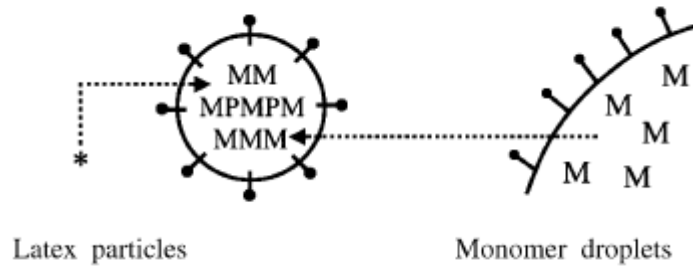
After the particle nucleation process is completed, the number of latex particles (i.e. reaction loci) per unit volume of water remains relatively constant toward the end of polymerization. The propagation reaction of free radicals with monomer molecules takes place primarily in monomer-swollen particles. Monomer droplets only serve as reservoirs to supply the growing particles with monomer and surfactant species. The majority of monomer is consumed in this particle growth stage ranging from ca. 10–20 to 60% monomer conversion. The particle growth stage (Interval II) ends as monomer droplets disappear in the polymerization system.

Emulsion polymerization continues from Interval II to III when all the monomer droplets disappear. In Interval III, latex particles become monomer-starved and the concentration of monomer in the reaction loci proceeds decreasing toward the end of polymerization, thereby, the steady polymerization rate observed in Interval II cannot be maintained any more and the polymerization rate decreases during Interval III. On the other hand, the polymerization rate may increase rapidly with increasing monomer conversion. This is attributed to the greatly reduced bimolecular termination reaction between two polymeric radicals within the very viscous particle provided that polymerization is carried out at a temperature below the glass transition temperature of the monomer-starved polymer solution. This phenomenon is termed the gel effect [91, 93]. To minimize residual monomer in latex products is essential for the successful product development due to the potential hazard to end-users. Schematic representations of the micelle nucleation model and the rate of polymerization as a function of monomer conversion are shown in Figure 2.3 and 2.4, respectively.

Interval I : Nucleation of monomer-swollen micelles



Interval II : Growth of latex particles



Interval III : Consumption of residual monomer

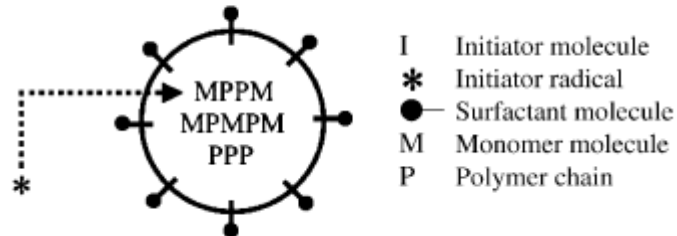


Figure 2.3 : A schematic representation of the micelle nucleation model.

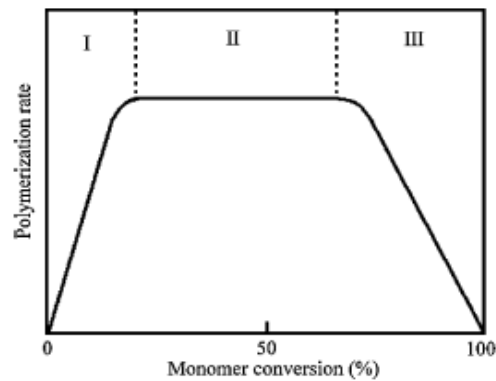


Figure 2.4 : Typical rate of polymerization as a function of the monomer conversion.

2.4.1 The generation of nanocapsule (core-shell) by in-situ miniemulsion polymerization

Nanoparticles can be divided into two main groups: nanospheres, which have a homogeneous structure in the whole particle, and nanocapsules, which exhibit a typical core-shell structure.

Several methods are usually used to produce such a core-shell structure on a nanometric scale. In general, nanocapsule is obtained with generation of core using preformed polymer and the generation of polymer nanocapsules. Mainly, lipophilic and hydrophilic cores of the nanocapsules are distinguished, requiring the nanocapsule to be dispersed respectively in water and in oil. Because of being an unsuitable system the aqueous-core nanocapsule dispersed in oil, the aqueous dispersion medium is usually chosen [93]

Polymer synthesis is performed at droplet interface by utilizing ‘in situ’ interfacial polymerization method. After the generation of nano-emulsion, this process may become independent from the method chosen in which involves both low and high-energy to produce nano-emulsions. Therefore, as regards choice of monomers and the chemical reactions during polymerization, the nano-emulsion template can constitute the starting point of the process. After the formulations of nanocapsules, the monomer is included in the dispersed nano-emulsion droplets via interfacial polymerization. With the formulation of polymeric nanospheres, the hydrophobe is now composed of a monomer, an initiator and oil, dispersed in water by sonication, which includes core structure to fabricate nano-emulsions. Polymerization is initiated via the temperature, then the monomer precipitates in oil and there is gradually segregation towards the water/oil interface, so constituting nanocapsules. In fact, this phenomenon has given rise to the theory of droplets composed of binary mixture [94], and the polymer/oil system can adopt several configurations (i.e. the polymer can engulf the oil totally, partially or not at all). Nanocapsule generation requires the polymer to totally engulf the oil core after its segregation. Such segregating behavior is governed by the respective interfacial tensions between the three immiscible species [93]

2.5 Nanofiber

Nano-scaled materials have recently drawn amazing extensive attention due to their many advantages, extraordinary high surface area per unit mass (for instance, nanofibers with ~ 100 nm diameter have a specific surface of $\sim 1000\text{m}^2/\text{g}$), showing Figure 2.5, coupled with remarkable high porosity, excellent structural mechanical properties, high axial strength combined with extreme flexibility, low basis weight, and cost effectiveness, among others [94].

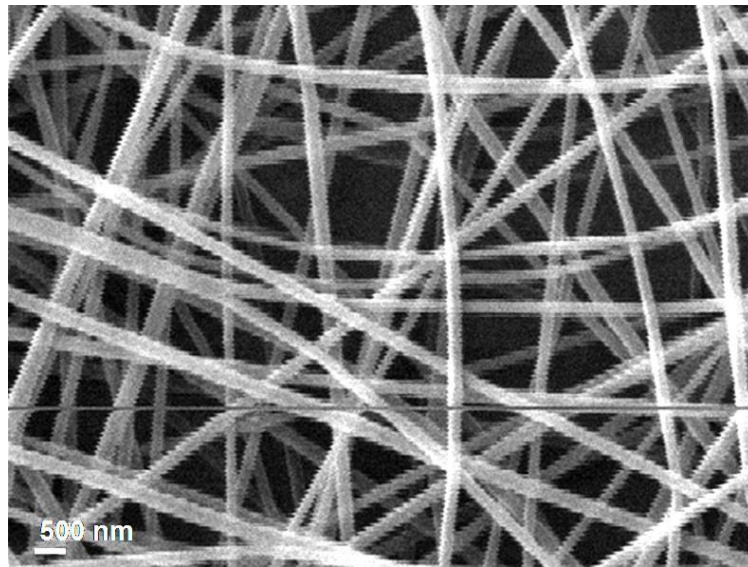


Figure 2.5 : SEM image of nanofibers from previous studies [95].

Interesting aspect of using nanofibers is that it is feasible to modify not only their morphology and their (internal bulk) content but also their surface structure to carry various functionalities [96, 97]. Nanofibers can be easily post-synthetically functionalized (for example by chemical or physical vapour deposition). Furthermore, it allows even to control secondary structures of nanofibers in order to prepare nanofibers with core/shell structures, nanofibers with hollow interiors and nanofibers with porous structures.

2.6 Electrospinning

Electrospinning is a simple and versatile method for generating ultrathin fibers from a rich variety of materials that include polymers, composites and ceramics [98–107]. Studies on electrically driven liquid jets were initially started in 19th century, and electrospinning of polymer fibers was first patented by Formhals in

1934 [108]. This nonmechanical, electrostatic technique involves the use of a high voltage electrostatic field to charge the surface of a polymer solution droplet and thus to induce the ejection of a liquid jet through a spinneret.

In a typical process, an electrical potential is applied between a droplet of a polymer solution held at the end of a capillary tube and a grounded target. When the applied electric field overcomes the surface tension of the droplet, a charged jet of polymer solution is ejected. The route of the charged jet is controlled by the electric field. The jet exhibits bending instabilities caused by repulsive forces between the charges carried with the jet. The jet extends through spiralling loops; as the loops increase in diameter the jet grows longer and thinner until it solidifies or collects on the target [94].

Choice of the polymer solutions, co-processing of polymer mixtures, chemical cross-linking of the formed nanofibers, etc. can provide a variety of pathways for controlling the chemical composition of electrospun nanofibers with a wide range of properties (such as strength, weight, elasticity, porosity, charged surface area, etc.). The electrospinning technique also provides the capacity to lace together a variety of types of nanoparticles or nanofillers to be encapsulated into an electrospun nanofiber matrix. Carbon nanotubes, ceramic nanoparticles, etc. may be dispersed in polymer solutions, which are then electrospun to form composites in the form of continuous nanofibers and nanofibrous assemblies [94].

2.6.1 Electrospinning process

Electrospinning basically comprises of three components to fabricate nanofibers: a high voltage supplier, a capillary tube with a pipette or needle of small diameter, and a metal collecting screen (Figure 2.6). In the electrospinning process a high voltage is used to emerge an electrically charged jet of polymer solution or melt out of the pipette.

Before reaching the metal collector on which are covered with aluminium foil, the solution jet evaporates, and is collected as an interconnected web of small fibers [109]. One electrode is placed into the spinning solution/melt and the other attached to the collector. Most of the polymers are dissolved in some solvents before electrospinning, and when it completely dissolves, forms polymer solution.

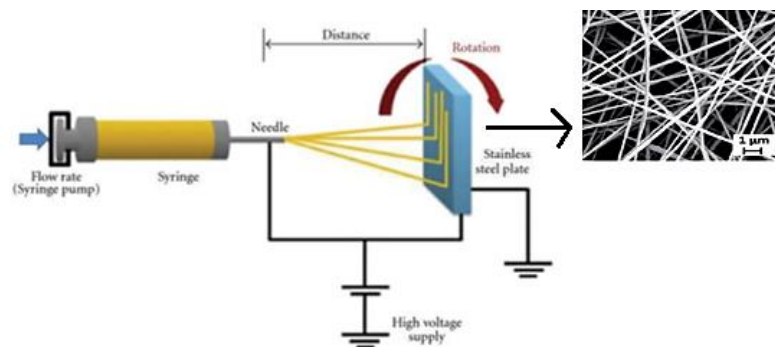


Figure 2.6 : Schematic diagram of an electrospinning apparatus.

The polymer fluid is then introduced into the capillary tube for electrospinning [110].

In the electrospinning process, a polymer solution held by its surface tension at the end of a capillary tube is subjected to an electric field and an electric charge is induced on the liquid surface due to this electric field. When the electric field applied reaches a critical value, the repulsive electrical forces overcome the surface tension forces. Eventually, a charged jet of the solution is ejected from the tip of the Taylor cone and an unstable and a rapid whipping of the jet occurs in the space between the capillary tip and collector which leads to evaporation of the solvent, leaving a polymer behind [111-113].

2.6.2 Effects of parameters on electrospinning

There are a number of parameters and processing variables that affect the electrospinning process: (i) system parameters such as molecular weight, molecular weight distribution and architecture (branched, linear, etc.) of the polymer, and polymer solution properties (viscosity, conductivity, dielectric constant, and surface tension, charge carried by the spinning jet) and (ii) process parameters such as electric potential, flow rate and concentration, distance between the capillary and collection screen, ambient parameters (temperature, humidity and air velocity in the chamber) and finally motion of the target screen [94].

2.6.3 Solution parameters

2.6.3.1 Viscosity

Solution viscosity plays an important role in determining the fiber size and morphology during spinning of polymeric fibers. It has been found that viscosity

low enough does not allow continuous fiber formation and prevents polymer motion induced by the electric field, as well [109]. However, very high viscosity not provide easily forming nanofibers with the ejection of jets from polymer solution, and thus solution must have condition of optimal viscosity for electrospinning to [114]. At very high viscosity polymer solutions usually exhibit longer stress relaxation times, which could prevent the fracturing of the ejected jets during electrospinning. An increase in solution viscosity or concentration gives rise to a larger and more uniform fiber diameter [115]. For solution of low viscosities, surface tension is the dominant factor and just beads or beaded fibers are formed while above a critical concentration, a continuous fibrous structure is obtained and its morphology is affected by the concentration of the solution [116].

2.6.3.2 Surface tension

Surface tension, more likely to be a function of solvent compositions of the solution plays a critical role in the electrospinning process and by reducing the surface tension of a nanofiber solution; fibers can be obtained without beads. Different solvents may contribute different surface tensions. Generally, the high surface tension of a solution inhibits the electrospinning process because of instability of the jets and the generation of sprayed droplets [117]. Basically, surface tension determines the upper and lower boundaries of the electrospinning window if all other variables are held constant [118-120].

2.6.3.2 Concentration

There should be an optimum solution concentration for the electrospinning process, as at low concentrations beads are formed instead of fibers and at high concentrations the formation of continuous fibers are prohibited because of the inability to maintain the flow of the solution at the tip of the needle resulting in the formation of larger fibers [121]. Researchers have attempted to find a relationship between solution concentration and fiber diameter and they found a power law relationship, that increasing the concentration of solution, increases the fiber diameter with gelatin electrospinning [122-123]

2.6.3.4 Molecular weight

Molecular weight of the polymer has a significant effect on rheological and electrical properties such as viscosity, surface tension, conductivity and dielectric

strength [124]. This is the other important solution parameter that affects the morphology of electrospun fiber and generally high molecular weight polymer solutions have been used in electrospinning as they provide the desired viscosity for the fiber generation. It has been observed that too low a molecular weight solution tends to form beads rather than fibers and a high molecular weight solution gives fibers with larger average diameters. Molecular weight of the polymer reflects the number of entanglements of polymer chains in a solution, thus solution viscosity. Chain entanglement plays an important role in the processing of electrospinning. It has been observed that high molecular weights are not always essential for the electrospinning process if sufficient intermolecular interactions can provide a substitute for the interchain connectivity obtained through chain entanglements, and using this principle, researchers have prepared oligomer-sized phospholipids from lecithin solutions into nonwoven membranes through electrospinning [125-126].

2.6.3.5 Conductivity/surface charge density

Polymers are mostly nonconductive, with a few exceptions of dielectric materials, and the charged ions in the polymer solution are highly influential in jet formation. Solution conductivity is mainly determined by the polymer type, solvent used, and the availability of ionisable salts. It has been found that with the increase of electrical conductivity of the solution, there is a significant decrease in the diameter of the electrospun nanofibers whereas with low conductivity of the solution, there results insufficient elongation of a jet by electrical force to produce uniform fiber, and beads may also be observed. Researchers have showed that highly conductive solutions are extremely unstable in the presence of strong electric fields, which results in a dramatic bending instability as well as a broad diameter distribution [127]. Generally, electrospun nanofibers with the smallest fiber diameter can be obtained with the highest electrical conductivity and it has been found that there is drop in the size of the fibers is due to the increased electrical conductivity. It was observed that the jet radius varied inversely with the cube root of the electrical conductivity of the solution [128-136].

2.6.4 Processing parameters

Another important parameter that affects the electrospinning process is the distinct external factors which involve the voltage supplied, the flow-rate, type of collector, and distance between the needle tip [137] exerting on the electrospinning jet.

2.6.4.1 Applied voltage

The high voltage will induce the necessary charges on the solution and together with the external electric field, will initiate the electrospinning process when the electrostatic force in the solution overcomes the surface tension of the solution. Generally, both high negative or positive voltage of more than 6kV is able to result in the solution drop at the tip of the needle to distort into the shape of a Taylor Cone during jet initiation [138]. Depending on the feed rate of the solution, a higher voltage may be required so that the Taylor Cone is stable. The columbic repulsive force in the jet will then stretch the viscoelastic solution. If the applied voltage is higher, the greater amount of charges will cause the jet to accelerate faster and more volume of solution will be drawn from the tip of the needle. This may result in a smaller and less stable Taylor Cone [139]. When the drawing of the solution to the collection plate is faster than the supply from the source, the Taylor Cone may recede into the needle [140]. Applied voltage has also effects on the morphology and the resultant fibers. Increase in the applied voltage results with a decrease in the fiber diameter. High voltage causes higher bead formation, but increased jet stretching leads to fewer amounts of beads [141]. Because of the weaker electrostatic force, flight time may become longer at lower voltage. Longer flight time lets the jet to elongate and stretch stronger and longer resulting with reduced fiber diameter. Wang et al. measured both jet diameter and fiber diameter and investigated the effect of voltage difference [142]. They found out that not only jet diameter but also fiber diameter decreased slightly. Furthermore, better chain orientation within electrospun fibers was observed by an increase in the applied voltage. [143].

2.6.4.2 Flow rate

The flow rate of the polymer from the syringe is a significant process parameter since it influences the jet velocity and the material transfer rate. A lower feed rate is more desirable as the solvent will get enough time for evaporation [144]. There should always be a minimum flow rate of the spinning solution. It has been observed that the fiber diameter and the pore diameter increases with an increase in the polymer flow rate in the case of polystyrene (PS) fibers and by changing the flow rate, the morphological structure can be slightly changed. Some studies have

systematically researched the relationship between solution feed or flow rate on fiber morphology and size [145-146].

If the flow rate is at the same rate which the solution is carried away by the electrospinning jet, there must be a corresponding increased in charges connected with the flow rate is increased. Thus, there is a corresponding increase in the stretching of the solution which counters the increased diameter because of increased volume. Due to the greater volume of solution drawn from the needle tip, the jet will takes a longer time to dry. Therefore, the solvents in the deposited fibers could not have enough time to evaporate in the given same flight time. The residual solvents may cause the fibers to fuse together where they make contact forming webs. As a results, a lower flow rate is more desirable as the solvent will have more time for evaporation [147].

2.6.4.3 Distance

The distance (the distance from the terminus of the capillary tip to the surface of the collector) defines the strength of the electric field as well as the time available for evaporation of the solvent before the nanofibers reach the collector surface. Increasing the distance, assuming other parameters constant, usually reduces fiber diameters [148]. Reducing the distance does not affect size and shape of the fibers, but, inhomogeneously distributed beads can be formed [149]. These beads can be due to increase in the electric field strength. If the distance between the tip and the collector is longer, solution jet finds more time for the evaporation of the solvent and jet can be stretched sufficiently before it lands to the collecting media. Increasing the working distance enhances the density of the fibers whereas decreasing the number of beads [150]. Jet diameter dependence on the working distance is studied [151].

2.6.4.4 Effect of collector

In the electrospinning process, usually conductive material is used to cover collecting media. Aluminium foil is one of the most common conductive materials that are used for collection of fibers onto it.

One important aspect of the electrospinning process is the type of collector used. In this process, a collector serves as a conductive substrate where the nanofibers are collected. Generally, aluminium foil is used as a collector but due to difficulty in

transferring of collected fibers and with the need for aligned fibers for various applications, other collectors such as, conductive paper, conductive cloth, wire mesh [152], pin [153], parallel or grided bar [154], rotating rod, rotating wheel [155], liquid non solvent such as methanol coagulation bath [156] and others are also common types of collectors nowadays. With less conductive area, there was generation of beaded fibers because of the less surface area. In another study they compared wire screen with aluminium foil and wire screen without aluminium foil in the same conductive area and found that pure wire screen is a better collector for fiber collection because with the use of wire screen the transfer of fibers to other substrates became easy. The fiber alignment is determined by the type of the target/collector and its rotation speed [157].

3. EXPERIMENTAL PART

3.1 Materials

Acrylonitrile ($\geq 99\%$), vinyl acetate ($\geq 99\%$) and 3, 4-ethylenedioxythiophene (97%) were purchased by Sigma Aldrich. Ammonium persulfate (APS) was provided by the Aksa Acrylic Factory of Turkey. Iron (III) oxide Fe_2O_3 nanoparticles (<50 nm particle size) and Triton X-100 as non-ionic surfactant were obtained from Sigma Aldrich. Polyvinyl pyrrolidone as stabilizer (K30) and tetraethylammonium tetrfluoroborate ($\geq 99\%$) as electrolyte salt were bought by Fluka Chemika. N, N dimethylformamide (DMF, $\geq 99\%$), dicloromethane ($\geq 99\%$) and tetrahydrofuran (THF, $\geq 99\%$) were all Merck reagents. Ethanol and methanol being of analytical grade were also purchased by Merck. The water used in the experiment was double distilled.

3.2 Synthesis of P(AN-co-VAc) and P(AN-co-VAc)/ Fe_2O_3 Core-Shell nanocapsules

P(AN-co-VAc)/ Fe_2O_3 core-shell nanocapsule structures were synthesized by in-situ miniemulsion polymerization. In the procedure, 0.77 ml of Triton X-100 was added to 60 ml of doubly distilled water inside the three-neck flask in order to form micelles. After stirring for two hours, Fe_2O_3 nanoparticles were added to the flask with PVP (poly vinyl pyrrolidone) together in ratio of 1:10, respectively. (Figure 3.1)

Fe_2O_3 particles were derived in amounts of 20, 30 and 40 mg and modified by PVP using as stabilizer and capping agent. The amounts of PVP varied from 200, 300 and 400 mg to remain the ratio between PVP and Fe_2O_3 particles. The solution was mixed in total of about two hours with waiting in an ultrasonic bath half-hourly for 5 min. After all of them, AN and VAc monomers were added into the beaker in ratios of 80 % and 20 %, respectively. The polymerization was initiated with 0.115 g of APS (dissolved in 5 ml doubly distilled water) and carried out at 70°C for about 3 h. The stirring rate was maintained at 200 RPM (Figure 3.3).

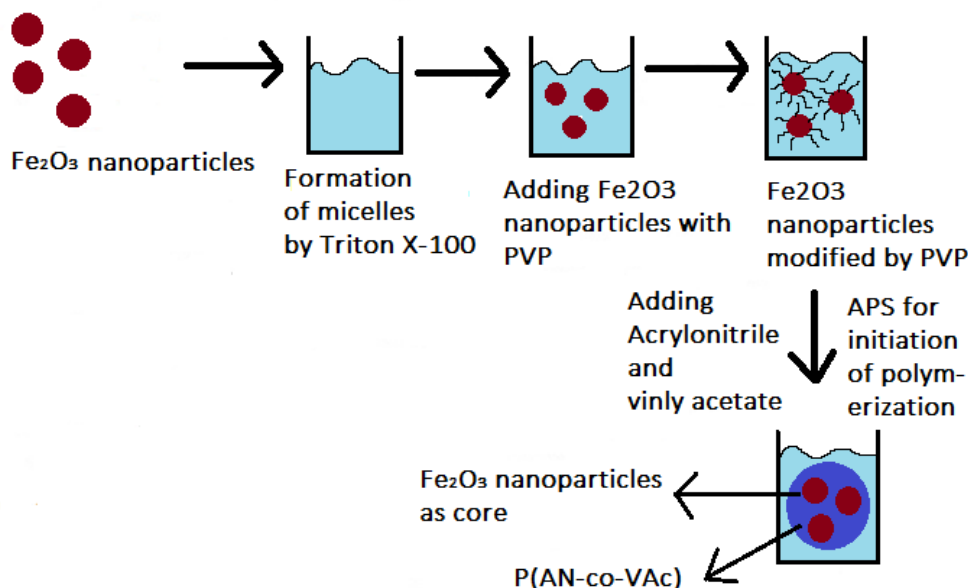


Figure 3.1 : A schematic representation of the polymerization.

The red Fe_2O_3 coated with $\text{P}(\text{AN-co-VAc})$ nanocapsules were washed with alternating doubly distilled water and anhydrous ethanol 3-4 times. Then, the solutions were filtered with filtration micro paper and dried under vacuum at 60°C for 24 h (Figure 3.4).

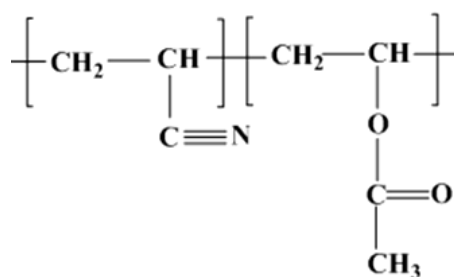


Figure 3.2 : $\text{P}(\text{AN-co-VAc})$ structure.

$\text{P}(\text{AN-co-VAc})$ copolymer (Figure 3.2) was also synthesized by miniemulsion polymerization because of comparison with Fe_2O_3 coated with $\text{P}(\text{AN-co-VAc})$ nanocapsules. As mentioned the above procedure, 0.77 ml of Triton X-100 was used as surfactant in the three-neck flask with 60 ml of doubly distilled water. After formation of micelles, AN and VAc in the above same ratios were supplemented into the beaker. The reaction was initiated with adding 0.115 g of APS (dissolved in 5 ml doubly distilled water) and performed at 70°C for about 2.5 h. The white $\text{P}(\text{AN-co-VAc})$ was washed, filtered and dried with the same procedure, above.



Figure 3.3 : Experimental setup for synthesis of P (AN-co-VAc)/Fe₂O₃.



Figure 3.4 : Pellets of precipitated with EtOH and dried P (AN-co-VAc), P(AN-co-VAc)/Fe₂O₃ (20), P (AN-co-VAc)/Fe₂O₃ (30), P (AN-co-VAc)/Fe₂O₃ (40) powders after polymerization.

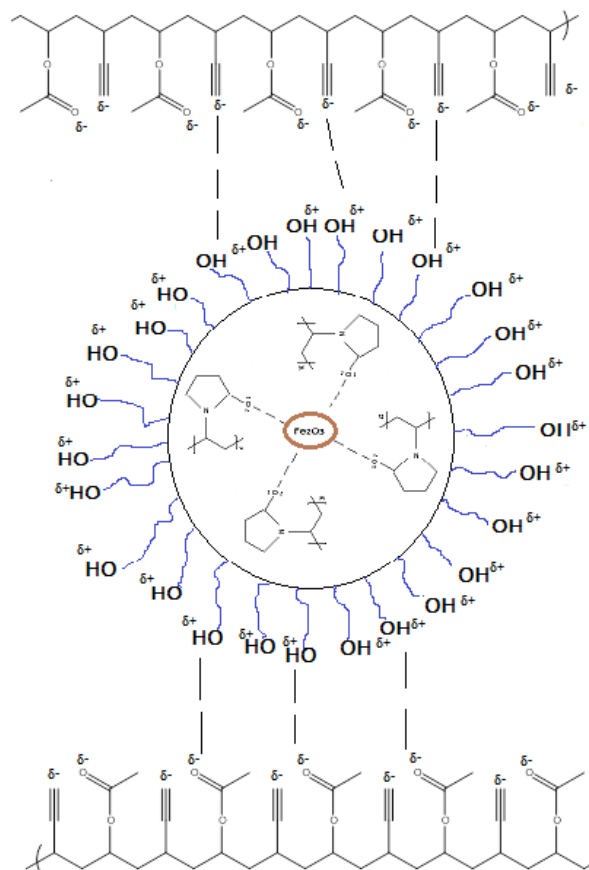


Figure 3.5 : Formation of the nanocapsules.

In Figure 3.5, it seems that how the comonomers were interacted with Triton X-100 and also formation of the structure between Fe_2O_3 nanoparticles and PVP. The CN groups of AN, and C=O groups of VAc showed an interaction with non-ionic OH groups of Triton X-100 during polymerization. Before initiating reaction, firstly the van der Waals intermolecular forces were emerged because of the interaction between oxygen atoms of C=O groups of PVP using as stabilizer and Fe-O in order to keep the nanoparticles together.

3.3 Synthesis of P(AN-co-VAc)/ Fe_2O_3 @PEDOT core-shell nanocapsule

P(AN-co-VAc)/ Fe_2O_3 @PEDOT core-shell nanocapsules was synthesised by chemical oxidative polymerization coating PEDOT as the shell of P (AN-co-VAc)/ Fe_2O_3 . First of all, 0.25 g Triton X-100 using as surfactant was dispersed with adding 0.005 g of dried P (AN-co-VAc)/ Fe_2O_3 in a three-neck flask including 25 ml of distilled water for about 3 hours. The suspension was carried out by ultrasound treatment for 10 min. After that, 75 μl of EDOT was added into the dispersal and

then stirred for an hour at a constant rate of 200 RPM. Finally, 0.34 g of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and 3.78 mg of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were dissolved in a beaker involving 5ml of distilled water and 0.1 ml of HNO_3 added into the solution. The suspension was carried out by ultrasound treatment for 10 min and was transferred into the three-neck flask. Afterward, the polymerization was conducted for 12 h at 25 ° C. The obtained black P (AN-co-VAc)/ Fe_2O_3 @PEDOT core-shell nanocapsule was centrifuged at a constant stirring rate of 3000 RPM and then separated from distilled water. (Figure 3.6)



Figure 3.6 : P (AN-co-VAc)/ Fe_2O_3 @PEDOT.

3.4 Preparation of Electrospinning Solutions

Three series of P (AN-co-VAc)/ Fe_2O_3 core-shell nanocapsule solutions were dissolved in DMF/THF (1:1 v/v) at room temperature. In addition to DMF, THF was used because through reducing surface tension with the use of its solutions can easily transform to nanofibers. For each solutions were stirred at room temperature with the speed of 300 rpm at least 2 hour and exposed to ultrasonic at ~30min. The electrospinning conditions are shown in the Table 3.1. The electrospinning apparatus consists of a syringe pump (NE-500 model, New Era Pump Systems, Inc., USA) with feeding rate from 5.5 $\mu\text{L}/\text{h}$ to 400 mL/h , high voltage DC power supplier generating positive DC voltage up to 50 kV DC power supply (ES50 model, Gamma High Voltage Inc., USA) and a grounded collector which is covered with aluminum foil. Solution was loaded into a syringe having 12 mm diameter and positive electrode was clipped onto the dispensing needle having 0.8 mm outer diameter. The feeding rate of the polymer solution was controlled by syringe pump.

Table 3.1: Electrospinning parameters for the copolymer and various nanocapsules.

Electrospinning Parameters	
Solution concentration	% 6
Applied voltage	15KV
Tip-to-collector distance	15cm
Feed rate	0,6 ml/h

3.5 Electrospinning Process Setup

The metal collector was covered with an aluminum foil. The process was conducted in a plexiglass box for experimenter's safety. All experiments were carried out under atmospheric pressure and at room temperature. The positive electrode wire was hooked at the metal part of the needle and negative part of the electrode was attached to the metal collector. 5 to 60 minutes of operation time was sufficient for the deposition of fibers on aluminum foil. A horizontal setup was chosen for electrospinning process. A picture that was captured during electrospinning is illustrated in Figure 3.7.



Figure 3.7 : A representative view of electrospinning devices.

3.6 Characterization P(AN-co-VAc), P(AN-co-VAc)/Fe₂O₃ and P(AN-co-VAc)/Fe₂O₃@PEDOT

The structure of P(AN-co-VAc), P(AN-co-VAc)/Fe₂O₃ and P(AN-co-VAc)/Fe₂O₃@PEDOT were characterized as powder form by means of FTIR-ATR reflectance spectrophotometer (Perkin Elmer, Spectrum One, with a Universal ATR attachment with a diamond and ZnSe crystal), showing in Figure 3.8.



Figure 3.8 : Perkin Elmer FTIR-ATR spectrophotometer.

The effect of the Fe_2O_3 on the resulting nanocapsules were also analysed by UV-Visible (Perkin Elmer, Lambda 45) spectrophotometric analysis displaying in Figure 3.9. First of all, P(AN-co-VAc) and P (AN-co-VAc)/ Fe_2O_3 samples obtained from emulsion mediums were examined, then powder forms dissolved in DMF of P(AN-co-VAc) and P (AN-co-VAc)/ Fe_2O_3 obtained from precipitating with EtOH and drying at 60 °C of samples in emulsion medium were analysed.



Figure 3.9 : Perkin Elmer UV Visible Spectrophotometer.

X-ray powder diffraction (XRD) analysis was performed to determine crystallinity of P(AN-co-VAc) and P(AN-co-VAc)/ Fe_2O_3 by using D/Max-3C automatic X-ray diffractometer (Philips Panalytical X'Pert Pro). A scan rate of 0.08°/s was applied to record the pattern in the 2θ range of 20-80. (Figure 3.10)



Figure 3.10 : Philips Panalytical X'Pert Pro (XRD).

The morphology of the core-shell nanocapsules was observed by Scanning Electron Microscope (FEI - Quanta FEG 250) and by transmission electron microscopy. Besides, electrospun nanofibers were characterized as morphological by Scanning Electron Microscope (FEI - Quanta FEG 250) and by Atomic Force Microscope (Nanosurf EasyScan2 STM). The samples for the SEM measurements were prepared by coating of gold (Ion Sputter Metal Coating Device, MCM-100). (Figure 3.11)



Figure 3.11 : Scanning Electron Microscope (FEI - Quanta FEG 250) on the left, Atomic Force Microscope (Nanosurf EasyScan2 STM) on the right.

Thermogravimetric analyses were performed by Perkin Elmer Q 600 instrument. The measurements were carried out at a heating rate of 10 °C/min under high-purity N₂ atmosphere. The DSC measurements were conducted on TA Q 1000 DSC instrument. The measurements of the nanocapsules were operated with 3 cycles. First cycle was heating from 25 °C to 250 °C, second cycle was cooling from 250 °C to 25 °C, and third cycle was heating from 25 °C to 250 °C at a heating rate of 10 °C/min under N₂ atmosphere. Third cycles were considered for DSC analysis. (Figure 3.12)



Figure 3.12 : TA Q 1000 DSC on the left, Perkin Elmer Q 600 TGA on the right.

Electrochemical measurements of samples (EIS with supplied Power Sine software package) were obtained in 0.1 M C₈H₂₀BF₄N /DCM by a Princeton Applied

Research (PAR) Parstat 2263 potentiostat (Oak Ridge, USA). (Figure 3.13) The impedance measurements were scanned in the frequency range 10 mHz–100 kHz with applied AC signal amplitude of 10 mV using Power Sine.



Figure 3.13: Parstat 2263 Electrochemical Analyser.

Mechanical properties of molded films obtained by polymer core-shell nanocapsules were measured by using a TA Q800 Dynamic Mechanical Analyser, DMA. Mechanical measurements were operated by DMA controlled-force test method. (Figure 3.14)



Figure 3.14: TA Q800 Dynamic Mechanical Analyser.

4. RESULTS AND DISCUSSION

4.1. FTIR-ATR Spectrophotometric Characterizations of P(AN-co-VAc), P(AN-co-VAc)/Fe₂O₃ core-shell nanocapsules and P(AN-VAc)/Fe₂O₃@PEDOT Nanocapsules

Figure 4.1 shows the FTIR-ATR spectra of P(AN-co-VAc), P(AN-co-VAc)/Fe₂O₃ (20, 30 and 40) nanocapsules and P(AN-co-VAc)/Fe₂O₃@PEDOT core-shell structured nanocapsules. The characteristic absorption peaks at 2248 cm⁻¹ and 1442 cm⁻¹ corresponds to the CN stretching and CH bending of polyacrylonitrile, respectively. The absorption peaks at 1726 cm⁻¹, 1227 cm⁻¹, and 1034 cm⁻¹ are ascribed to the C=O stretching, C-O-C stretching and C-O stretching vibration peaks, respectively for PVAc. The major absorption bands for P (AN-co-VAc) are the CH bending (1453 cm⁻¹), C=O stretching (1737 cm⁻¹), CN stretching (2243 cm⁻¹), and CH stretching (2940 cm⁻¹) vibration bands [159-162].

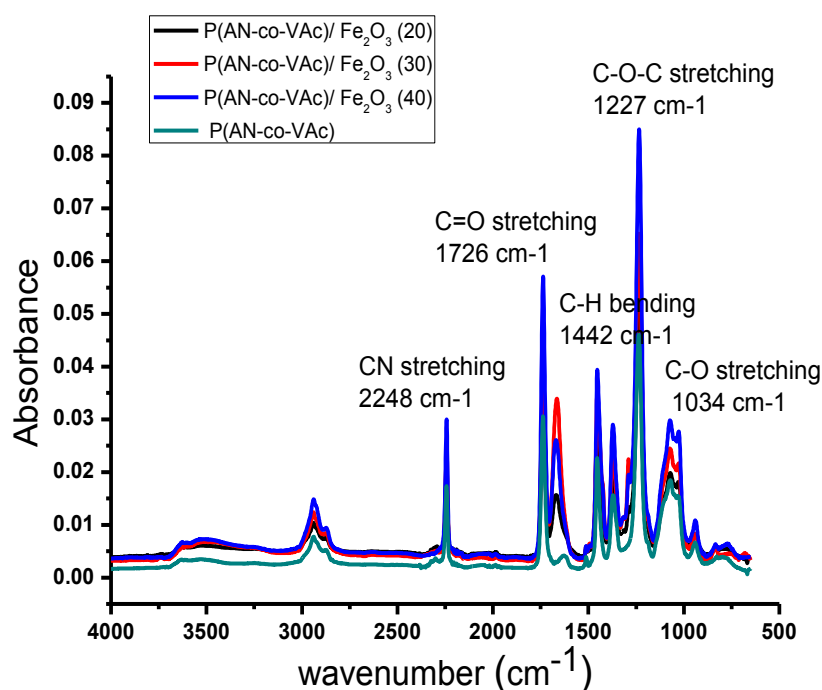


Figure 4.1 : FTIR-ATR spectra of powder forms of P(AN-co-VAc) copolymer and P(AN-co-VAc)/Fe₂O₃ core-shell nanocapsules.

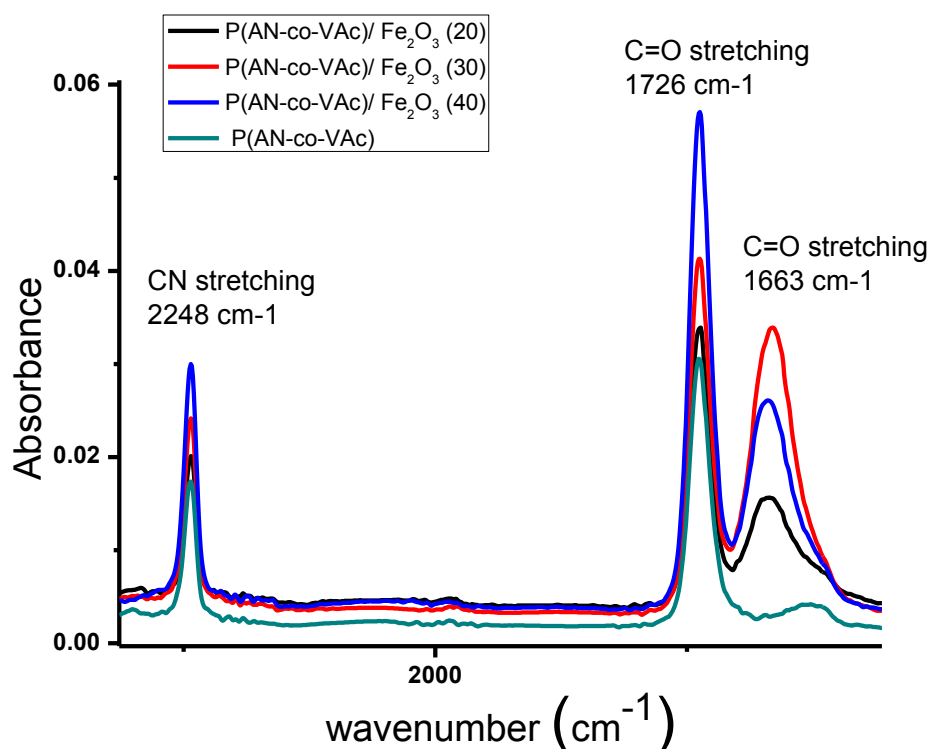


Figure 4.1 (continued) : FTIR-ATR spectra of powder forms of P(AN-co-VAc) Copolymer and P(AN-co-VAc)/Fe₂O₃ core-shell Nanocapsules.

The absorption peaks at 2926 cm⁻¹ and 1361 cm⁻¹ are caused by the cyclic CH₂ groups and stretching vibration of CH and CH₂ that belongs to poly vinyl pyrrolidone (PVP, M_w=30000). The peak at 1663 cm⁻¹ is attributed to the C=O stretching of PVP [163-167]. Decreasing of the peak at 1662 cm⁻¹ confirms the presence of interaction between PVP and Fe₂O₃. Some researches have offered that a blue shift of the amide group in PVP can be based on the change of p- π conjugation resulting from dissociation of PVP chains due to the incorporation of other species [168]. It is possible that the interaction between the complexes and PVP leads to the dissociation of aggregated of PVP chains, resulting in the blue shift of the C=O vibration band. [168] In addition, the peak belonging to the carbonyl group of PVP is shifted from 1667 cm⁻¹ to 1663 cm⁻¹ and 1661 cm⁻¹. Because PVP is modified on the surface of the Fe₂O₃ nanocrystals via coordination interaction through its carbonyl group. [163] Thus, it can be aligned that the highest interaction is 20, the lowest is also 30 for Fe₂O₃.

The chemical composition of P(AN-co-VAc)/Fe₂O₃@PEDOT was characterized by FTIR-ATR spectrum showing in Figure 4.2. The vibrations of the C–S bond in PEDOT chains can be seen at 980, 836 and 680 cm⁻¹. The band around 933 cm⁻¹ is also due to the ethylenedioxy ring deformation mode. The vibration peaks at 1147 and 1040 cm⁻¹ are ascribed from C-O-C bond stretching in the ethylene dioxy group. The absorption peaks at 1225, 1350, 1468 and 1546 cm⁻¹ correspond to the stretching of the thiophene ring.

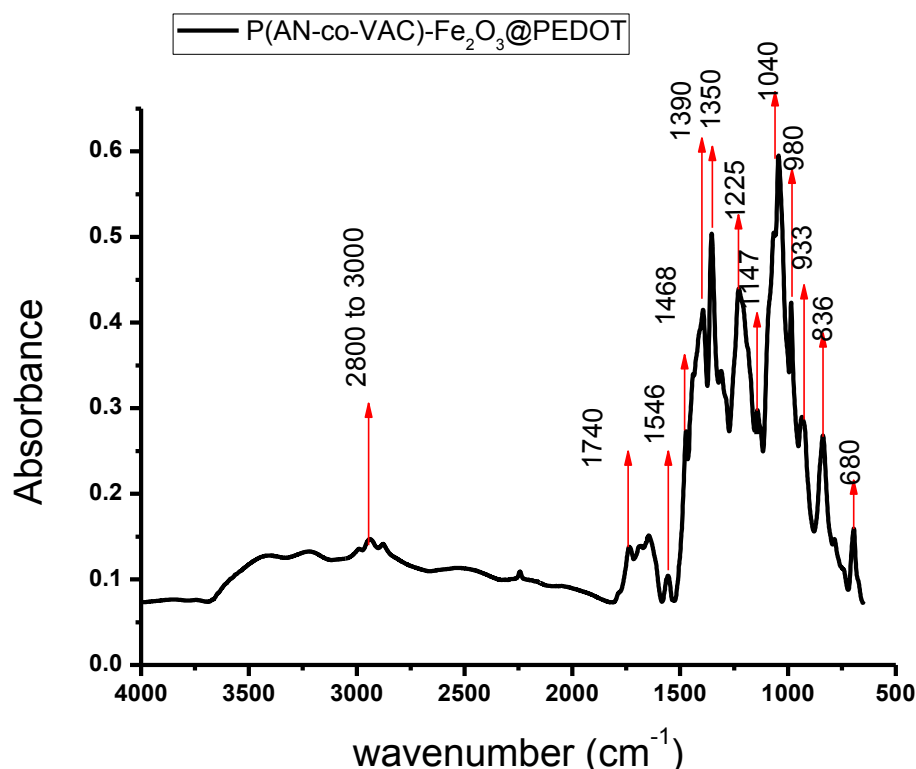


Figure 4.2 : FTIR-ATR spectra of powder form of P(AN-co-VAc)-Fe₂O₃@PEDOT Core-shell nanostructure.

The characteristic peak at 1,740 cm⁻¹ is usually associated with the doped state of PEDOT. The small peaks ranging from 2800 to 3000 cm⁻¹ is attributed to aliphatic O-H stretching of the distilled water [169-172]. The results confirmed that the existence of PEDOT in the coating of P(AN-co-VAc)/Fe₂O₃ as core-shell with in-situ polymerization.

4.2 UV-Visible spectrophotometric analyses of P(AN-co-VAc), P(AN-co-VAc)/Fe₂O₃ Core-Shell Nanocapsules

The core-shell nanocapsules containing different amounts of Fe₂O₃ was followed with UV-Visible spectroscopy by taking samples from emulsion medium and P(AN-co-VAc)/Fe₂O₃ core-shell nanocapsules precipitated after being dispersed by ethanol in which is dissolved by N,N-dimethylformamide (DMF) solution.

Figure 4.3 consists of an onset of two absorption maxima at 398 and 245 nm for Fe₂O₃ in visible range between 200 and 800 nm wavelengths. The γ -Fe₂O₃ showed two broad adsorption bands in 290-670 nm and 210-284 nm wavelength. The high-energy absorption band associated with ligand to metal charge transfer (LMCT) assigns to isolated tetrahedral coordination of Fe³⁺ [173]. These two bands have been corresponded to electronic transition of O²⁻ to the *t*_{2g} and *e*_g orbitals of Fe³⁺ in the iron oxide [173]. To examine the interaction between PVP and Fe₂O₃, their Uv-Vis spectrum was checked separately and also after by mixing at 70 °C to create polymerization conditions. It displays an absorption band between 390-400 nm [174]. However, the absorption bands of the nanocapsules coating P (AN-co-VAc) copolymer were quite different according to others.

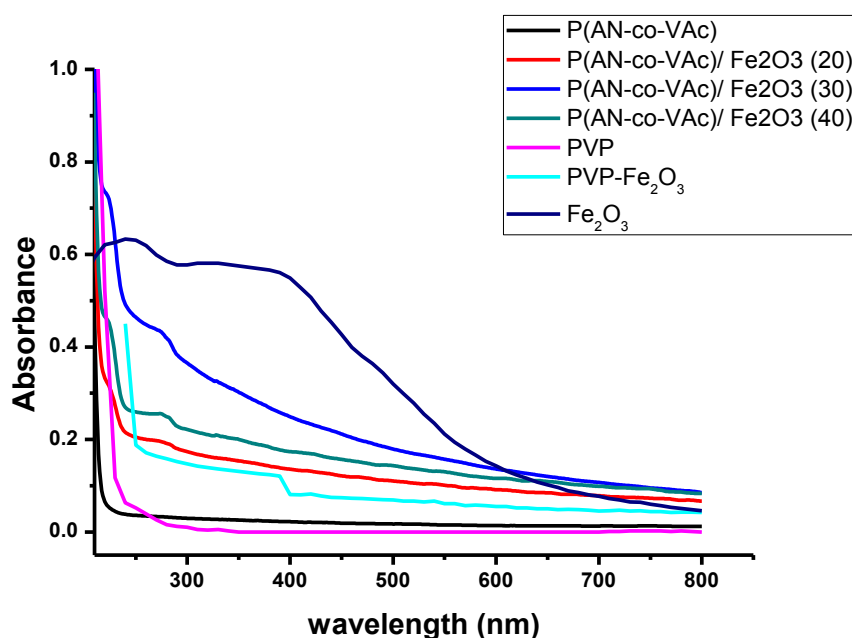


Figure 4.3 : UV-Vis Spectrum of P(AN-co-VAc), P(AN-co-VAc)/Fe₂O₃, PVP and Fe₂O₃ nanoparticle.

In the spectrum, the broad bands showing between 290 to 253 nm were attributed to γ -Fe₂O₃ in the nanocapsules. Moreover, band range from 290 nm to 600 nm proved the presence of γ -Fe₂O₃ nanoparticles. Absorbance values were in the following order of 30, 40 and 20 mg samples because of interaction between PVP and Fe₂O₃. Besides, maxima redshift was observed due to increase in particle size [175].

Dissolved core-shell nanocapsules in DMF were also analysed by UV-visible spectrophotometer. The concentration of the nanocapsules was 0.0002 v %. UV-Vis spectroscopy of Fe₂O₃ exhibited an absorbance maxima at about 342 nm in Figure 4. 4 [176]. The narrow bands corresponding to P (AN-co-VAc)/Fe₂O₃ were located between 270 to 285 nm and displayed in the following order of 20, 40 and 30 mg samples, respectively. Because of dissolution of copolymer structure being responsible of shell in DMF Fe₂O₃ nanoparticles emerged. Hence, 20 mg sample indicated in the highest peak due to interaction between PVP and Fe₂O₃ as understanding from FTIR-ATR spectrophotometer.

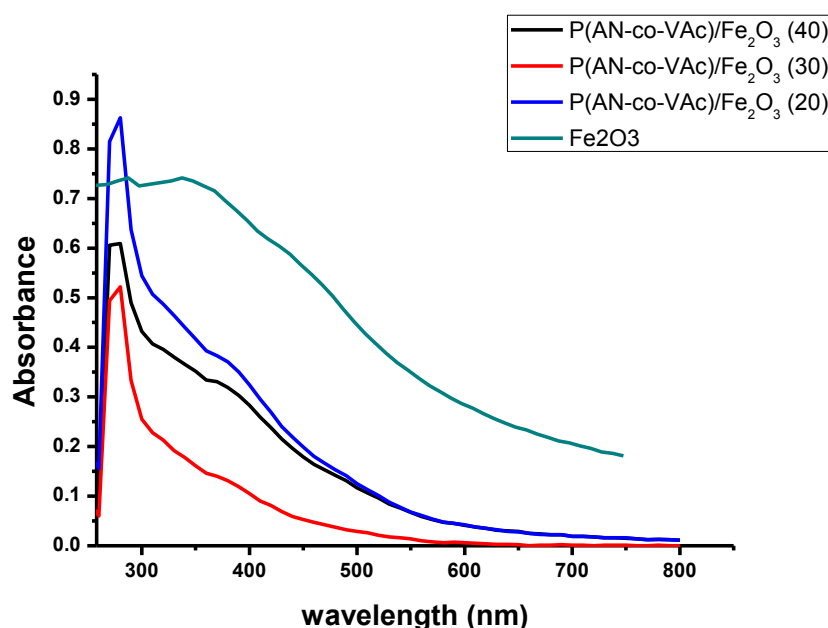


Figure 4.4 : UV-Visible Spectrum of P(AN-co-VAc), P(AN-co-VAc)/Fe₂O₃ and Fe₂O₃ dissolved in DMF.

Figure 4.5 presents the relation between the absorbance ratios of characteristic PVP peak (C=O stretching) to PAN peak (CN stretching) in FTIR-ATR spectrum and absorbance values of P(AN-co-VAc)/Fe₂O₃ samples obtained from emulsion medium calculated by UV-visible spectrophotometer at 276 nm corresponding to Fe₂O₃ amount fractions (mg). The ratio of the absorbance of C=O stretching band at

1663 cm^{-1} to the total absorbance of CN stretching band at 2248 cm^{-1} and C=O stretching band at 1663 cm^{-1} was obtained from FTIR–ATR. It is deduced that P(AN-co-VAc)/ Fe_2O_3 samples have interactions between PVP and Fe_2O_3 in range of 20, 40, and 30 (mg), respectively. Absorbance values measured from UV-visible spectra also proved the interaction.

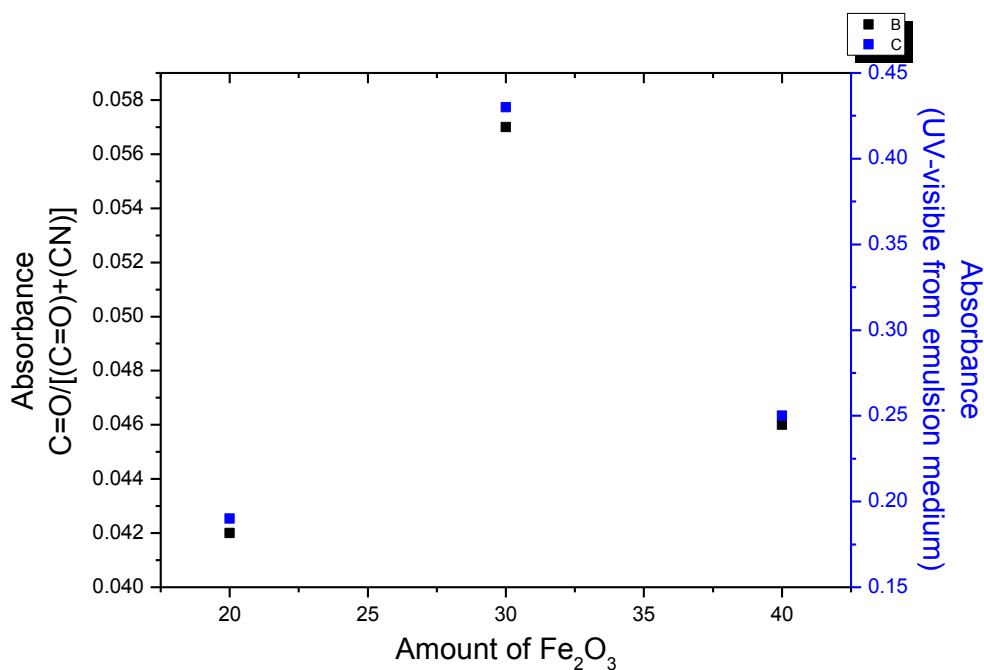


Figure 4. 5 : Correlation between FTIR-ATR absorbance ratio of CO str. (1663 cm^{-1})/[CN str. (2248 cm^{-1})/ CO str. (1663 cm^{-1})], UV-Vis absorbance values at 276 nm and Amount of Fe_2O_3 .

Figure 4.6 shows the relationships between the absorbance ratios of certain functional groups corresponding to CN stretching (2248 cm^{-1}) of PAN and C=O stretching (1726 cm^{-1}) of PVAc obtained from FTIR-ATR and absorbance values of P(AN-co-VAc)/ Fe_2O_3 samples dissolving in the same ratio in DMF at 276 nm. This graph gives an idea in term of the molecular weight of P(AN-co-VAc) and P(AN-co-VAc)/ Fe_2O_3 core-shell nanocapsules and the maximal and the minimum Mw belongs to Fe_2O_3 (20) and Fe_2O_3 (40) samples, respectively. Moreover, after P(AN-co-VAc)/ Fe_2O_3 samples dissolved in DMF, the emergence of the amount of Fe_2O_3 nanoparticles arranged as Fe_2O_3 (20), Fe_2O_3 (40), and Fe_2O_3 (30), respectively, as seeing in the graph. The result indicated that the highest amount of

Fe_2O_3 nanoparticles which joined into the core-shell structure is Fe_2O_3 (20) and the lowest one is Fe_2O_3 (30), as well.

Figure 4.7 shows us photographs of the separation process of P(AN-co-VAc)/ Fe_2O_3 core-shell nanocapsules with external magnetic field.

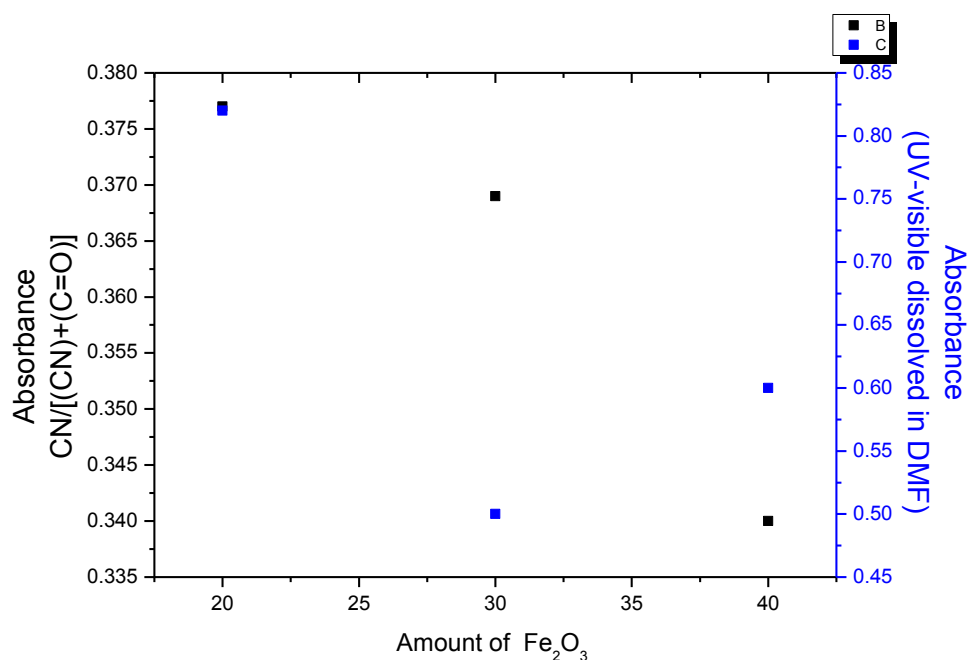


Figure 4.6 : Correlation between FTIR-ATR absorbance ratio of CN str. (2248 cm^{-1}) / [CN str. (2248 cm^{-1}) / CO str. (1726 cm^{-1})], UV-Vis absorbance values at 276 nm and Amount of Fe_2O_3

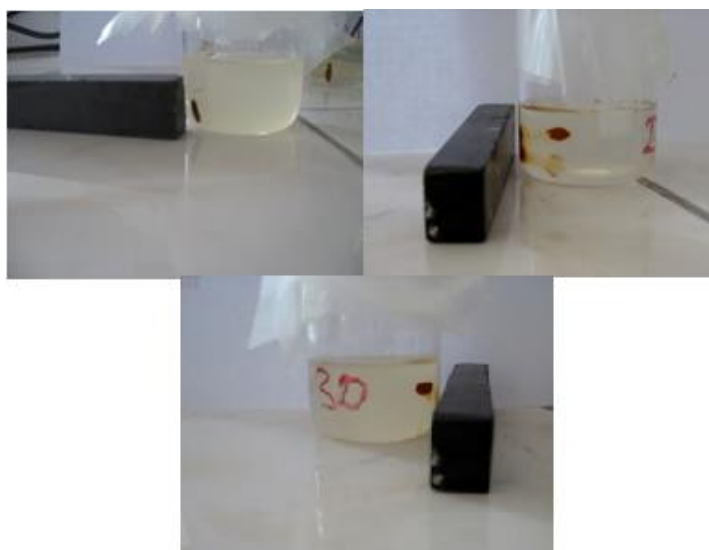


Figure 4.7 : Photographs of the separation process of P(AN-co-VAc)/ Fe_2O_3 core-shell nanocapsules with external magnetic field.

4.3 Xrd (X-ray diffraction) of P(AN-co-VAc) Copolymer and P(AN-co-VAc)/Fe₂O₃ core-shell nanocapsules

The crystalline structures of the P(AN-co-VAc) and P(AN-co-VAc) nanocapsules containing Fe₂O₃ in different ratios were investigated by XRD. Figure 4.8 presents that the diffraction peaks of Fe₂O₃ nanoparticles are at 2θ of 30.22°, 37.06°, 44.9°, 58°, 64.5°, correspond to the spinel structure of Fe₂O₃ as termed by cubic with tetragonal supercell [177]. These peaks are attributed to the diffraction of the (220), (311), (400), (422), (511) and (440) faces of the crystals, respectively [178-180]. However, the XRD patterns of P(AN-co-VAc)/Fe₂O₃ core-shell structured nanocapsules displayed that the crystalline structure of different amounts of Fe₂O₃ nanoparticle was retained because of coating these particles with copolymer structure. Thus, the broad diffraction peak in the range of 2θ between 20° and 30° can be ascribed to the amorphous polymer of nanocapsules. The XRD results proved that Fe₂O₃ nanoparticles were successfully coated with polymer.

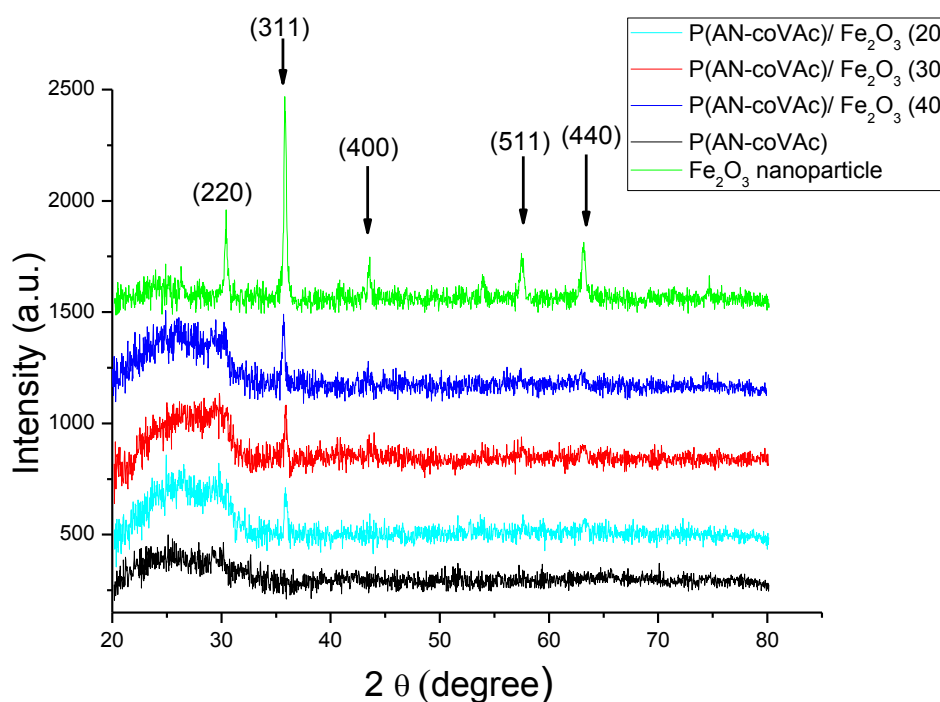


Figure 4.8 : X-ray diffraction (XRD) of P(AN-co-VAc) Copolymer and P(AN-co-VAc)/Fe₂O₃ core-shell nanocapsules.

4.4 Particle Size Distribution of P(AN-co-VAc) Copolymer and P(AN-co-VAc)/Fe₂O₃ core-shell nanocapsules

Latex form of P(AN-co-VAc) and P(AN-co-VAc)/Fe₂O₃ core-shell nanocapsules were used to investigate the particles' morphology and determine particle size by utilizing Scanning Electron Microscopy. Afterwards, effect of Fe₂O₃ addition in the composite synthesis was analysed with distribution of Gaussian curve. The results show that particle size increases as the amount of Fe₂O₃ in the composite rises. However, P(AN-co-VAc) displays the highest particle size (Figure 4.9). Since oligomeric radicals during polymerization become so hydrophobic that they tend to enter the monomer-swollen micelles when a critical chain length is achieved. Then, the radicals proceed to propagate by reacting with the monomer molecules therein. As a result, P(AN-co-VAc) emerged much more radicals reacting inside monomer micelles in comparison of other core-shell composites and so had the greatest size.

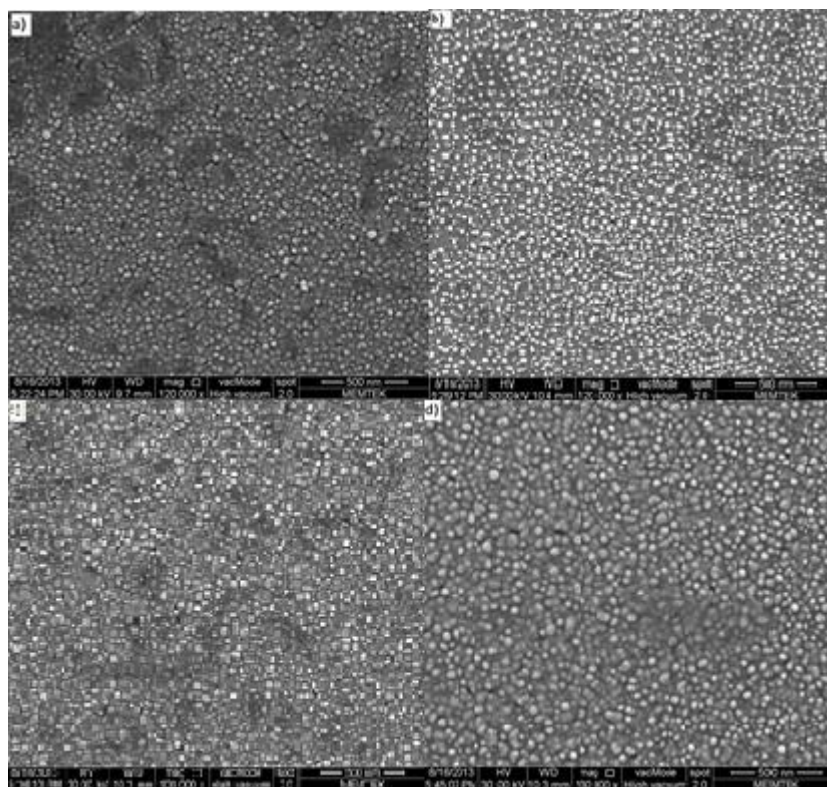


Figure 4.9 : SEM images of latex particles of P(AN-co-VAc)/Fe₂O₃ (20) (a), P(AN-co-VAc)/Fe₂O₃ (30) (b), P(AN-co-VAc)/Fe₂O₃ (40) (c), P(AN-co-VAc) (d).

Results obtained from gaussian curves indicate that particle sizes are 20.59 ± 9.32 for (a), 25.10 ± 2.72 for (b), 30.67 ± 11.47 for (c) and 48.85 ± 21.31 for (d).

4.5 Morphology of P(AN-co-VAc) Copolymer and P(AN-co-VAc)/Fe₂O₃ core-shell nanocapsules

The process of electrospinning P(AN-co-VAc) and P(AN-co-VAc)/Fe₂O₃ nanofibers are so stable and appropriate and facilitate production of non-bead nanofiber mats for several hours. Morphologic properties of these polymers were shown in SEM and AFM images in Figure 4.11, and Figure 4.12 for AFM. The average diameter of electrospun fibers of different concentrations is determined by using Imagej program to randomly measure the diameters of 50 individual fibers shown in SEM images with x 60 000 magnification that was given in Figure 4.11.

Amount of the initially added Fe₂O₃ varies as 20, 30 and 40 mg (Figure 4. 10). The average diameters of the nanofibers are reduced from 368 to 98 nm as showing Gaussian curves of the nanofibers with the increase of the initially added Fe₂O₃ amounts (Table 4.1).

Table 4.1: Avg. Diameter of Electrospun Nanofibers (20, 30 and 40 w content).

1.1.1 Sample	Average Diameter (nm)
P(AN-co-VAc)	98 ± 1.02
P(AN-co-VAc)-Fe ₂ O ₃ (20)	368 ± 80
P(AN-co-VAc)-Fe ₂ O ₃ (30)	232 ± 74
P(AN-co-VAc)-Fe ₂ O ₃ (40)	138 ± 31

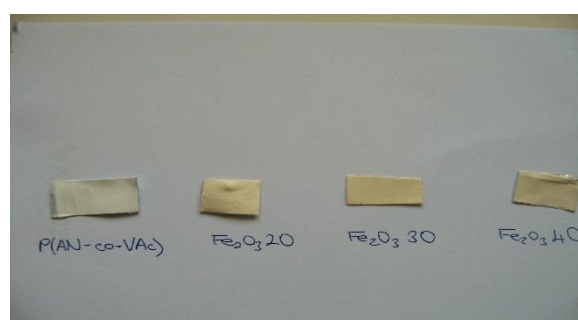


Figure 4.10 : Images of the nanofibers.

Our method showed that it is possible to obtain nanocapsules via miniemulsion polymerization exhibited that Fe₂O₃ was homogeneously distributed in copolymer composition and successfully inclusion into the copolymer structure. Furthermore, it was realized forming thicker nanofibers and especially decreasing of beads as

increasing of Fe_2O_3 amounts in the nanocapsules in comparrison of P(AN-co-VAc) (Figure 4.10).

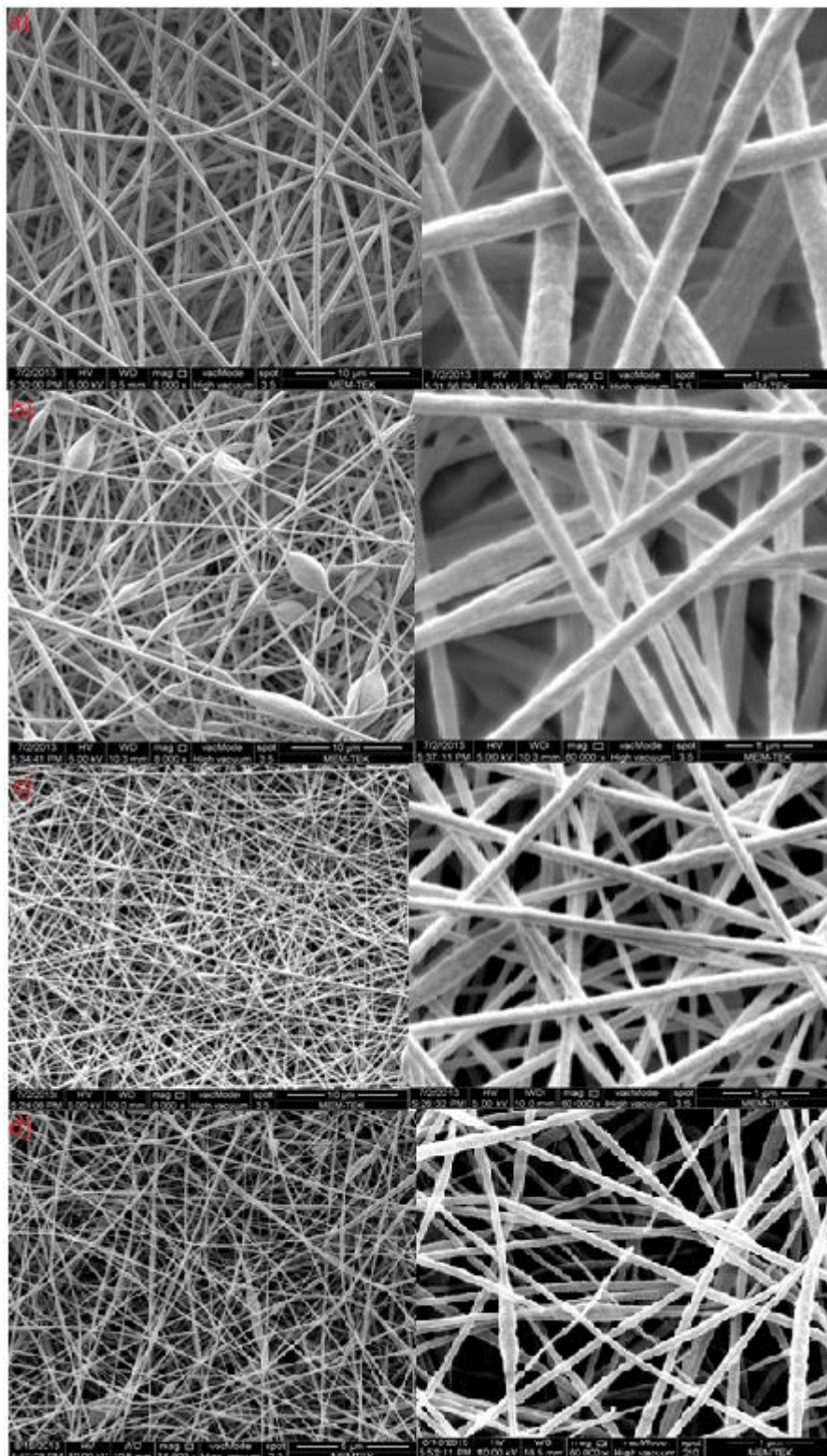


Figure 4.11 : SEM images (10 μm and 1 μm) of nanofibers of P(AN-co-VAc)/ Fe_2O_3 (20), P(AN-co-VAc)/ Fe_2O_3 (30), P(AN-co-VAc)/ Fe_2O_3 (40), SEM image (5 μm and 1 μm) of nanofiber of P(AN-co-VAc).

Surface morphologies of the nanofibers were also investigated by atomic force microscope. During scanning of the nanofibers, surface features deflect the tip and thus the cantilever. A topographic image of the surface can be obtained by measuring the deflection of the cantilever. Therefore, the effect of microroughness upon the nanofibers comprising of Fe_2O_3 nanoparticles has been examined by using atomic force microscopy (AFM) to characterize the surface roughness. Root mean square (RMS) roughness values were calculated via Nanosurf Easy-scan software by electing image are 4.738 pm^2 . The values were resulted in 773.5 nm for (a), 276.13 nm for (b) and 464.11 nm for (c).

Figure 4.13 belongs to TEM (Transmission Electron Microscopy) results of P(AN-co-VAc)/ Fe_2O_3 in which comprises of derivation of 20, 30 and 40 mg Fe_2O_3 nanoparticles diluted and dispersed in water. The Fe_2O_3 nanoparticles modified by polyvinylpyrrolidone (PVP) are shaped like irregular capsules, and their average sizes ranged as 133 nm, 80 nm, and 115 nm that the values correspond to samples with 20,30 and 40 mg Fe_2O_3 .

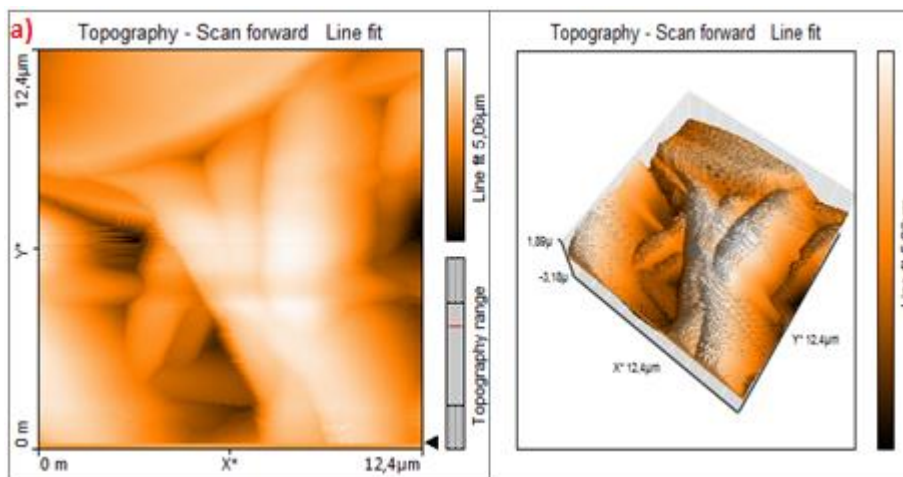


Figure 4.12 : AFM images of nanofibers of P(AN-co-VAc)/ Fe_2O_3 (20) (a), P(AN-co-VAc)/ Fe_2O_3 (30) (b), P(AN-co-VAc)/ Fe_2O_3 (40) (c)

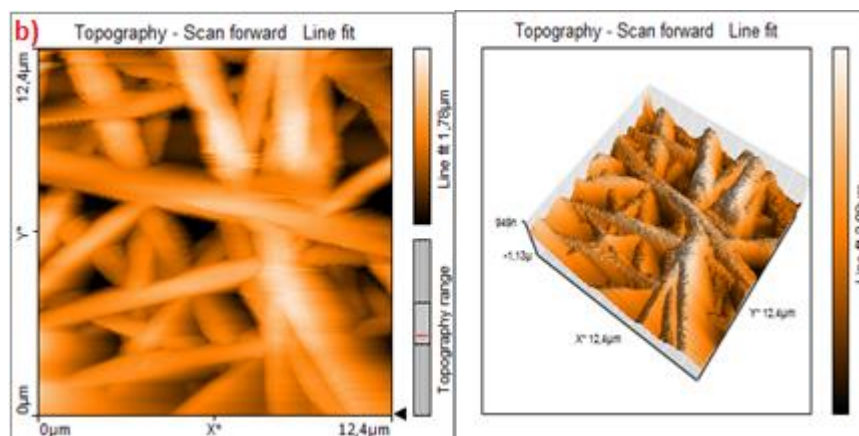


Figure 4.12 (continued) : AFM images of nanofibers of P(AN-co-VAc)/Fe₂O₃ (20) (a), P(AN-co-VAc)/Fe₂O₃ (30) (b), P(AN-co-VAc)/Fe₂O₃ (40) (c)

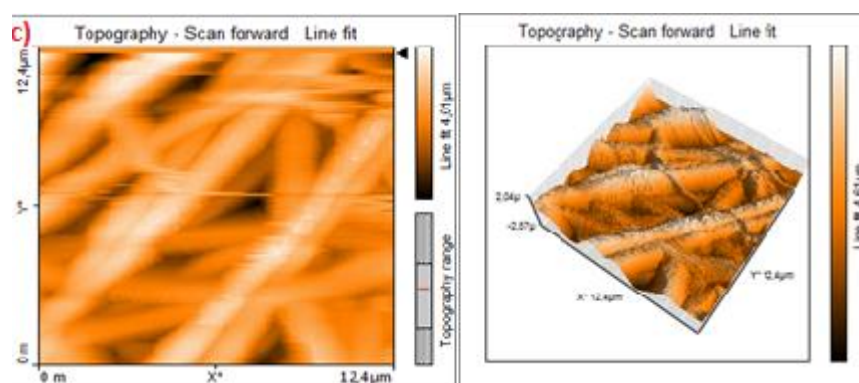


Figure 4.12 (continued) : AFM images of nanofibers of P(AN-co-VAc)/Fe₂O₃ (20) (a), P(AN-co-VAc)/Fe₂O₃ (30) (b), P(AN-co-VAc)/Fe₂O₃ (40) (c)

The diameters are in agreement of spectroscopic results obtained by FTIR-ATR. Because it can easily determined the amount of Fe₂O₃ nanoparticles inside polymers. The particles show good dispersion and have no obvious aggregation. Moreover, images of TEM prove that the Fe₂O₃ nanoparticles were fully encapsulated by the P(AN-co-VAc) polymer layer and so it was obtained as core-shell nanocapsules.

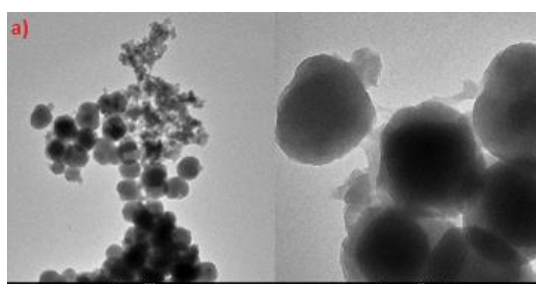


Figure 4.13 : TEM images of P(AN-co-VAc)/Fe₂O₃ (20) (a), P(AN-co-VAc)/Fe₂O₃(30) (b), P(AN-co-VAc)/Fe₂O₃ (40) (c)

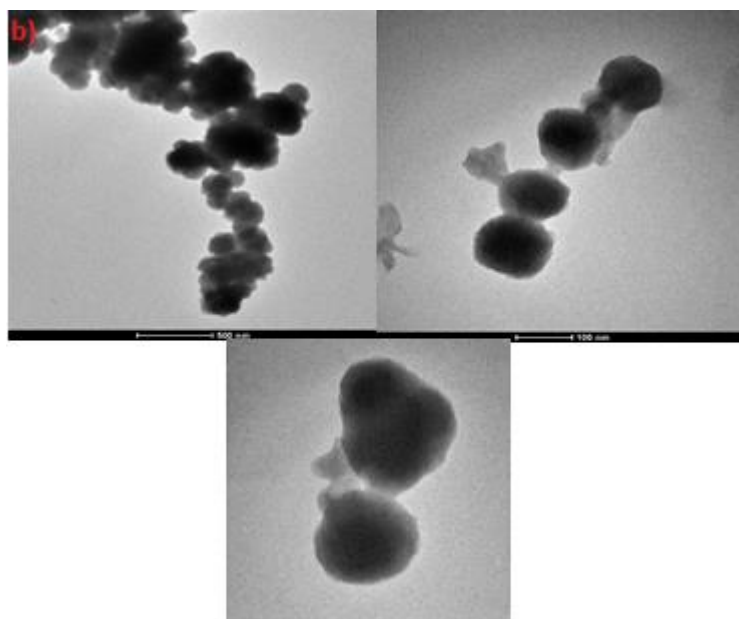


Figure 4.13 (continued) : TEM image of TEM images of P(AN-co-VAc)/Fe₂O₃ (20) (a), P(AN-co-VAc)/Fe₂O₃(30) (b), P(AN-co-VAc)/Fe₂O₃ (40) (c)

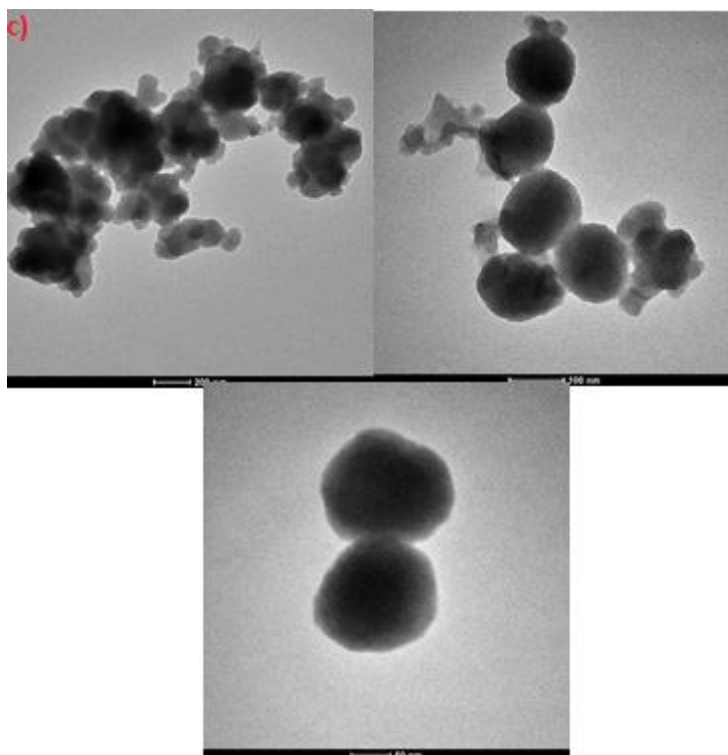


Figure 4.13 (continued) : TEM image of TEM images of P(AN-co-VAc)/Fe₂O₃ (20) (a), P(AN-co-VAc)/Fe₂O₃(30) (b), P(AN-co-VAc)/Fe₂O₃ (40) (c)

4.6 Properties of P(AN-co-VAc) Copolymer and P(AN-co-VAc)/Fe₂O₃ core-shell nanocapsules

4.6.1 Thermal Gravimetric Analysis of P(AN-co-VAc) Copolymer and P(AN-co-VAc)/Fe₂O₃ core-shell nanocapsules

P(AN-co-VAc) and P(AN-co-VAc) consisting of 20, 30, and 40 mg Fe₂O₃ nanoparticles were analysed by TGA to determine thermal stability of copolymer and the nanocapsules. TGA curves are shown in Figure 4.14. The homopolymer of AN of the main thermal degradation temperature were defined as 276 °C [158]. The first weight loss step of P(AN-co-VAc) and P(AN-co-VAc)/Fe₂O₃ below ~305 °C resulted from elimination of residuals and the loss of absorption water. Because of adding the content (20 %) of VAc [158] and using Triton X-100 as surfactant, the decomposition temperature increased up to 305 °C. After that, the weight loss of approximately 30 % of the copolymer and the nanocapsules appeared at ~345°C. As reaching the temperature at 475 °C, the mass loss of the P(AN-co-VAc) and the P(AN-co-VAc) coated with Fe₂O₃ nanoparticles was approximately 60 %. The indicated weight loss in the temperature range from 305 to 475 °C was caused by the thermal degradation of the P(AN-co-VAc) polymers and hydroxyl from the Fe₂O₃ nanoparticles [182]. At ~800 °C, as looking weight loss of P(AN-co-VAc) and P(AN-co-VAc)/Fe₂O₃ the maximal loss seems in nanocapsule comprising of 20 mg Fe₂O₃ and minimal loss in P(AN-co-VAc).

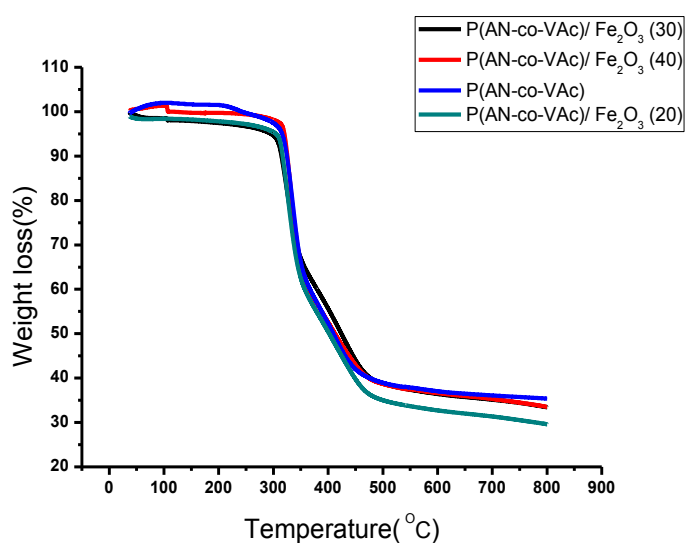


Figure 4.14 : TGA graph of P(AN-co-VAc)/Fe₂O₃ (20), P(AN-co-VAc)/Fe₂O₃ (30), P(AN-co-VAc)/Fe₂O₃ (40), and P(AN-co-VAc).

4.6.2 Differential scanning calorimetry measurement (DSC) of P(AN-co-VAc) and P(AN-co-VAc)/Fe₂O₃ core-shell nanocapsules

The free radically obtained PAN shows a glass transition temperature of 105 °C and a melting point around 317 °C. PAN tends to decompose before its melting point reaches. It is well known that the melting and glass transition points of semi-crystalline polymers can be reduced through incorporating comonomer units [158]. T_g values of the P(AN-co-VAc) and P(AN-co-VAc)/Fe₂O₃ involving 20, 30 and 40 mg nanoparticles were determined as 100.60 °C, 105.56 °C, 103.54 °C, and 104.19 °C, respectively. (Figure 4.15) It is appeared that the presence of the the Fe₂O₃ nanoparticles in the copolymers exhibits tendency to increase in the T_g values due to the decrease in chain flexibility. However, the highest T_g value corresponds to the composite containing 20 mg Fe₂O₃ nanoparticle since the sample having much more interaction than other samples because of the highest molecular weight. These results correspond with FTIR-ATR and UV-visible spectrophotometers.

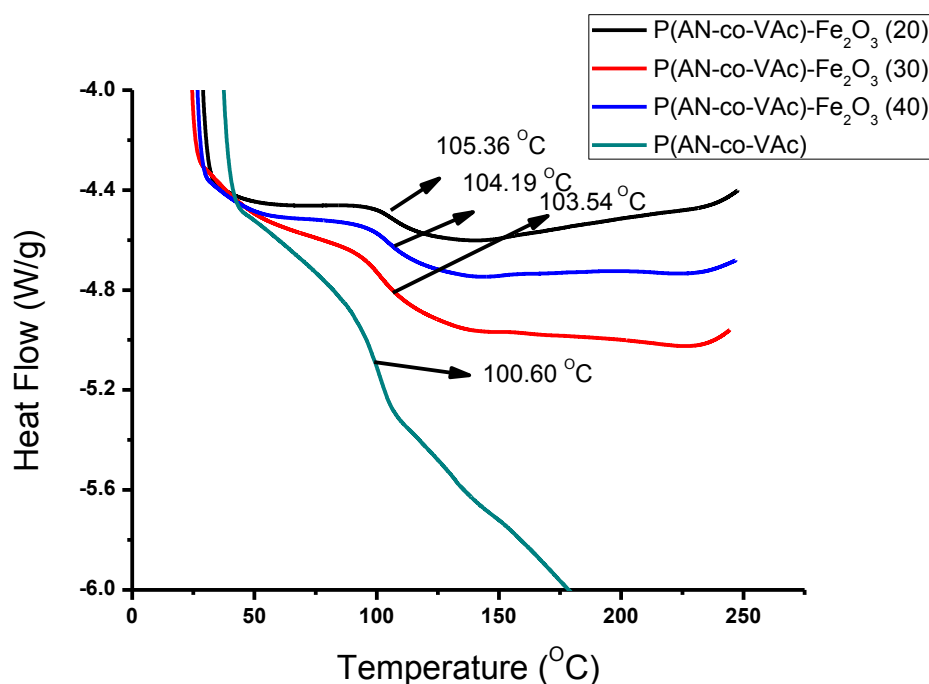


Figure 4.15 : DSC graph of P(AN-co-VAc)/Fe₂O₃ (20), P(AN-co-VAc)/Fe₂O₃ (30), P(AN-co-VAc)/Fe₂O₃ (40), and P(AN-co-VAc).

4.6.4 Dynamic Mechanical Analysis of P(AN-co-VAc) and P(AN-co-VAc)/Fe₂O₃ core-shell nanocapsules

DMA (Dynamic Mechanical Analysis) determines storage modulus, loss modulus, and damping coefficient as a function of temperature, frequency, or time [183]. To

understand mechanical properties of polymer and nanocapsules, stress vs. strain graphs of the samples are evaluated by utilizing DMA.

The slope of the stress-strain curve in the elastic deformation region is the modulus of elasticity, which is known as Young's modulus (elastic modulus). It shows the stiffness of the material-resistance to elastic strain. Young's modulus measurements of the copolymer and the three nanocapsules were defined by using Controlled Force mode in DMA. Table 4.16 represents mechanical properties of four specimens. The elastic modulus measurements of the polymer and nanocapsules are reported in Table 4.2.

Table 4.2: Elastic modulus of P(AN-co-VAc)/Fe₂O₃ (20), P(AN-co-VAc)/Fe₂O₃ (30), P(AN-co-VAc)/Fe₂O₃ (40), and P(AN-co-VAc).

Sample	Elastic Modulus (Young's Modulus) (MP
P(AN-co-VAc)	933
P(AN-co-VAc)/Fe ₂ O ₃ (2	234
P(AN-co-VAc)/Fe ₂ O ₃ (3	249
P(AN-co-VAc)/Fe ₂ O ₃ (4	454

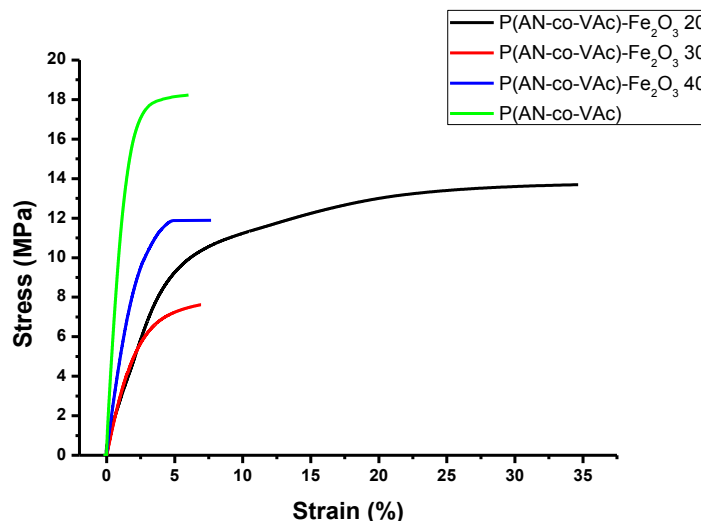


Figure 4.16 : Stress-strain curve of P(AN-co-VAc)/Fe₂O₃ (20), P(AN-co-VAc)/Fe₂O₃ (30), P(AN-co-VAc)/Fe₂O₃ (40), and P(AN-co-VAc).

As examining the results of elastic modulus, the highest belongs to P(AN-co-VAc) so that the copolymer is brittle. Elastic modulus of others is in the range of P(AN-co-VAc)/Fe₂O₃ (20), P(AN-co-VAc)/Fe₂O₃ (30), and P(AN-co-VAc)/Fe₂O₃ (40), respectively. Thus, the samples exhibit brittle property except for P(AN-co-VAc)-

Fe₂O₃ (20). Because it has the highest $\epsilon_{\max}$, which is described as the maximal strain, among the samples. Therefore, the nanocapsule has ductile property. Ductility is more commonly defined as the ability of a material to deform easily upon the application of a tensile force, or as the ability of a material to withstand plastic deformation without rupture. Ductility may also be thought of in terms of bendability and crushability. Ductile materials show large deformation before fracture. The lack of ductility is often termed brittleness. A material is brittle if, when subjected to stress, it breaks without significant deformation (strain). Brittle materials absorb relatively little energy prior to fracture, even those of high strength. Elastic modulus (Young's modulus) is also a measure of rigidity. If a material has a very high elastic modulus, it is meant to be a rigid material which means that, cannot elongate too much with increasing stress. Thus, the steepest slope belonged to P(AN-co-VAc) indicating that it was the most rigid one among the others whereas P(AN-co-VAc)/Fe₂O₃ (20) had the lowest rigidity. The other specimens were in between, as well.

Toughness, which is known as the area under a stress-strain curve, represents the total strain energy, which can be absorbed by the material before it breaks, per unit volume in the material induced by the applied stress. The highest toughness value belonged to P(AN-co-VAc)/Fe₂O₃ (20) because of higher molecular weight than others. Thus, the sample absorbed the greater energy and displayed ductility as well as the maximal impact resistance. Other samples showed brittleness according to obtained toughness values. All of values were indicated in Table 4.3.

Table 4.3 : Toughness of P(AN-co-VAc)/Fe₂O₃ (20), P(AN-co-VAc)/Fe₂O₃ (30), P(AN-co-VAc)/Fe₂O₃ (40), and P(AN-co-VAc).

Sample	Toughness (N/mm ²)
P(AN-co-VAc)	91.60
P(AN-co-VAc)/Fe ₂ O ₃ (20)	147.52
P(AN-co-VAc)/Fe ₂ O ₃ (30)	39.41
P(AN-co-VAc)/Fe ₂ O ₃ (40)	91.60

4.6.5 Determination of T_g values of P(AN-co-VAc) and P(AN-co-VAc)/Fe₂O₃ core-shell nanocapsules by DMA

The DMA provides the full information about glass transition (T_g) and viscoelastic properties of polymeric materials that should be obtained over a wide range of both temperatures and frequencies measurements. The useful information is a short time maybe obtained by measuring the modulus and damping (tan delta) over a wide temperature range while keeping the frequency constant. Under tension/compression deformations the measured viscous component is referred to as the loss modulus (E''), while the measured elastic component is referred to the storage modulus (E'). The ratio of the loss modulus to the storage modulus is referred to the loss tangent (E''/E'), or tan delta [184].

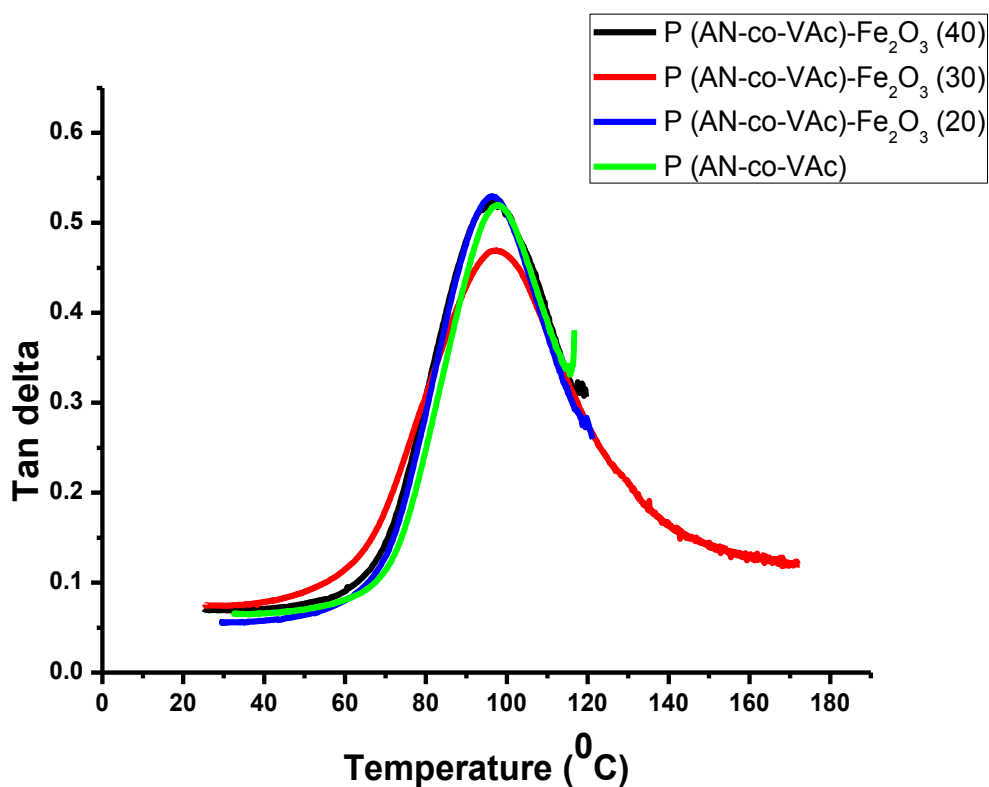


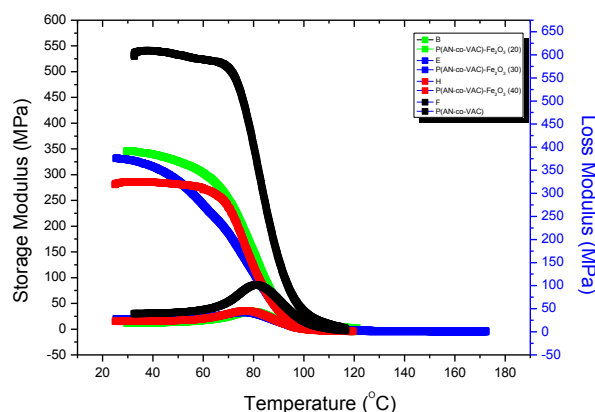
Figure 4.17 : Tan delta curves of P(AN-co-VAc)/Fe₂O₃ (20), P(AN-co-VAc)/Fe₂O₃ (30), P(AN-co-VAc)/Fe₂O₃ (40), and P(AN-co-VAc).

T_g of the nanocapsules was obtained from the temperature corresponding to the maximum of the tan delta curves determined with multifrequency – strain test method using DMA instrument (Figure 4.17). T_g values were represented in Table 4.4.

Table 4.4: Tan delta values of the samples.

Sample	Tan Delta
P(AN-co-VAc)	98.12
P(AN-co-VAc)/Fe ₂ O ₃ (20)	96.36
P (AN-co-VAc)/Fe ₂ O ₃ (30)	97.40
P (AN-co-VAc)/Fe ₂ O ₃ (40)	96.68

Figure 4.18 displays storage and loss modulus vs. temperature of the copolymer and nanocapsules. The storage modulus decreases slowly as the temperature increases. Near the glass transitions the modulus decreases dramatically. The modulus takes another drop at still higher temperatures due to the increasing role of viscous flow. At low and high temperatures, damping (tan delta) is low. At low temperatures, chain segments are completely frozen in structure and material has nearly perfect elasticity. By examining the storage modulus curves, it can be decided that the material has either crystalline or amorphous structure. If the curve was sufficiently broad during the reduction, the material would become semi-crystalline. If the curve was however sharp enough, the sample would have amorphous structure. Therefore, crystallinity of the nanocapsules were in range of 30, 20 and 40, respectively. The copolymer was amorphous in comparison to others. Crystalline polymers show much more complex dynamic behaviors than do amorphous polymers. The mechanical properties are strongly depending upon the degree of crystallinity, the size of crystallites and the melting point of the crystallites. Crystalline polymers always have a glass transition and generally at least one or two secondary transitions. The greater the crystallinity, the higher is the modulus.

**Figure 4.18 :** Storage Modulus and Loss Modulus versus Temperature of the film Samples.

4.6.6 Electrochemical Impedance Spectroscopy (EIS) of P(AN-co-VAc), P(AN-co-VAc)/Fe₂O₃ core-shell nanocapsules and P(AN-co-VAc)/Fe₂O₃@PEDOT core-shell structure

The electrical properties of the nanofibers in which includes P(AN-co-VAc), and P(AN-co-VAc)/Fe₂O₃ nanocapsules upon ITO-PET (Indium thin oxide-polyethylene terephthalate) were determined by Electrochemical Impedance Spectroscopy. To examine electrochemical properties of core-shell structure with PEDOT, P(AN-co-VAc)/Fe₂O₃ (40) was chosen as core and PEDOT as shell. After that, the core-shell capsule structure was used to coat upon ITO-glass by spin coating method in order to evaluate impedance values. The conductivity in ferrites generally exists because of hopping of electrons between ions of the same element occurring in different valence states, distributed over crystallographically equivalent lattice sites. In this case electron hopping between Fe²⁺ and Fe³⁺ causes the impedance response for electrochemical systems [185]. The Nyquist, Bode Magnitude and Bode Phase and admittance plots of the fibers were given in the frequency range 0.01 Hz–100 kHz. From the Nyquist plots, CPE (constant-phase element), which also termed as the low-frequency redox capacitance, values were obtained at 0.01 Hz of low frequency. The impedance in EIS often exists a distribution of reactivity that is mainly represented in equivalent electrical circuits as a constant-phase element (CPE) [186]. CPE can be expressed associated simple Faradaic (4.1) reaction without diffusion

$$Z(\omega) = R_s + \frac{R_{ct}}{1 + (j\omega)^n Q R_{ct}} \quad (4.1)$$

where R_s is defined as the sum of resistances because of the presence of the electrolyte on the nanofiber, and in solution. R_{ct} is the charge-transfer resistance. The CPE parameters n and Q are independent of frequency [186]. This equation can be simplified as $Z_{CPE} = A^{-1} (j\omega)^{-n}$ [187] wherein ω ($\omega = 2\pi f$) is the angular frequency, A is fitted parameter and the exponent n ($0 \leq n \leq 1$) arises from the slope of the $\log Z$ versus $\log f$ plot. When $n=1$, the CPE describes an ideal capacitor with $C = A$ so that presents the capacity of the interface, while $n=0$ the CPE describes an ideal resistor with $R=1/A$. When $n < 1$, the system displays behaviour that

corresponding to surface heterogeneity [186] or to continuously distributed time constants for charge-transfer reactions [186]. However, the n value of CPE ($0.70 < n < 1$) is known for description of the inhomogeneity of the polymer film [187]. The CPE of the nanofibers and PEDOT core-shell capsule measured by EIS was represented in Figure 4.19.

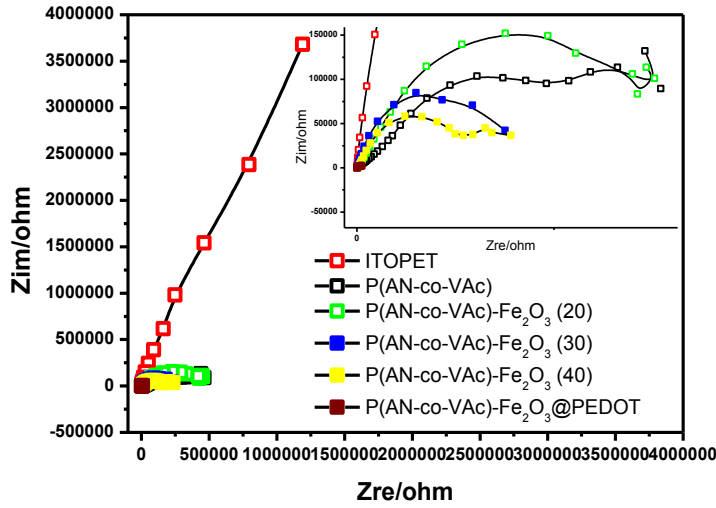


Figure 4.19 : Nyquist plot of P(AN-co-VAc)/Fe₂O₃ (20), P(AN-co-VAc)/Fe₂O₃ (30), P(AN-co-VAc)/Fe₂O₃(40),P(AN-co-VAc)andP(AN-co-VAc)/Fe₂O₃@PEDOT.

As depending on admittance results obtained from the maximum points in the admittance plot, the lowest value belonged to the nanocapsule with Fe₂O₃ (20) and the highest to Fe₂O₃ (40)@PEDOT, in Table 4.5.

Table 4.5: EIS results of P(AN-co-VAc)/Fe₂O₃ (20), P(AN-co-VAc)/Fe₂O₃ (30), P(AN-co-VAc)/Fe₂O₃ (40), P(AN-co-VAc) and P(AN-co-VAc)/Fe₂O₃@PEDOT.

	C_{sp} [$\Omega \cdot s^{-1}$]	C_{dl} [μF]	Bode Phase	Admittance (mS)
P(AN-co-VAc)	1.77×10^{-4}	1.63	16.8°	9.51×10^{-5}
P(AN-co-VAc)/ Fe ₂ O ₃ (20)	2.34×10^{-4}	6.84	14.5°	1.06×10^{-4}
P(AN-co-VAc)/ Fe ₂ O ₃ (40)	4.30×10^{-4}	9.26	8.92°	2.60×10^{-4}
P(AN-co-VAc)/ Fe ₂ O ₃ (30)	3.80×10^{-4}	27.5	10.43°	3.54×10^{-4}
P(AN-co-VAc)/ Fe ₂ O ₃ (40)@PEDOT	6.35×10^{-3}	314	17.31°	2.8×10^{-3}

The Bode magnitude plots for the nanocapsules and PEDOT core-shell capsule were displayed in Figure 4.20. C_{dl} (double layer capacitance) is essentially calculated with $1/|Z_{im}|$ at 1 Hz. Fe_2O_3 (30) had higher conductivity compared to other nanocapsules, however Fe_2O_3 (40)@PEDOT was the highest in all of them. The Bode graphs show a decreasing of Z by corresponding with admittance values, causing an increasing of double layer capacitance [187]. Bode phase angles which approached the minimum frequency at 0.01 Hz were $\sim 8.92^\circ$ for Fe_2O_3 (40), $\sim 10.43^\circ$ for Fe_2O_3 (30), $\sim 14.5^\circ$ for Fe_2O_3 (20), $\sim 16.8^\circ$ for the copolymer and $\sim 17.31^\circ$.

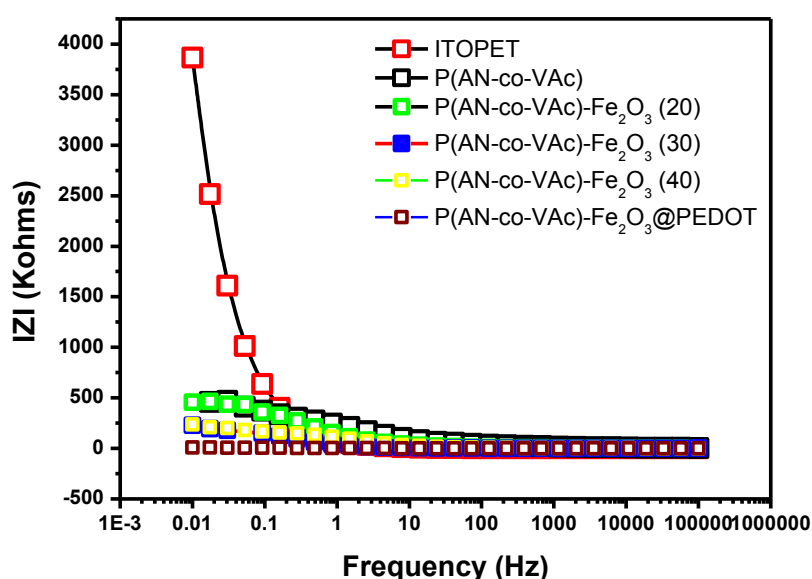


Figure 4.20: Bode Magnitude plot of P(AN-co-VAc)/ Fe_2O_3 (20), P(AN-co-VAc)/ Fe_2O_3 (30), P(AN-co-VAc)/ Fe_2O_3 (40), P(AN-co-VAc) and P(AN-co-VAc)/ Fe_2O_3 @PEDOT.

for core-shell structure with PEDOT, in Figure 4.21. That indicates the presence of Fe_2O_3 nanoparticles in the nanocapsule. The Bode phase peaks of the fibers in the frequency range of 0.01 Hz–100 000 Hz appeared that the nanofibers cannot be used as a capacitor.

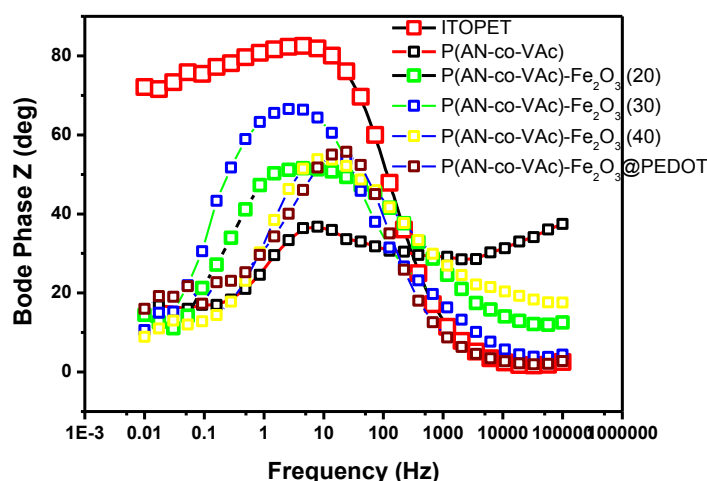


Figure 4.21: Bode Phase plot of P(AN-co-VAc)/Fe₂O₃ (20), P(AN-co-VAc)/Fe₂O₃ (30), P(AN-co-VAc)/Fe₂O₃ (40), P(AN-co-VAc) and P(AN-co-VAc)/Fe₂O₃@PEDOT.

In addition, when examining admittance plot of the samples the maximum point presented the values of the conductivity and the range revealed as the highest Fe₂O₃ (40)@PEDOT, Fe₂O₃ (30), Fe₂O₃ (40) and the lowest Fe₂O₃ (20), in Figure 4.22.

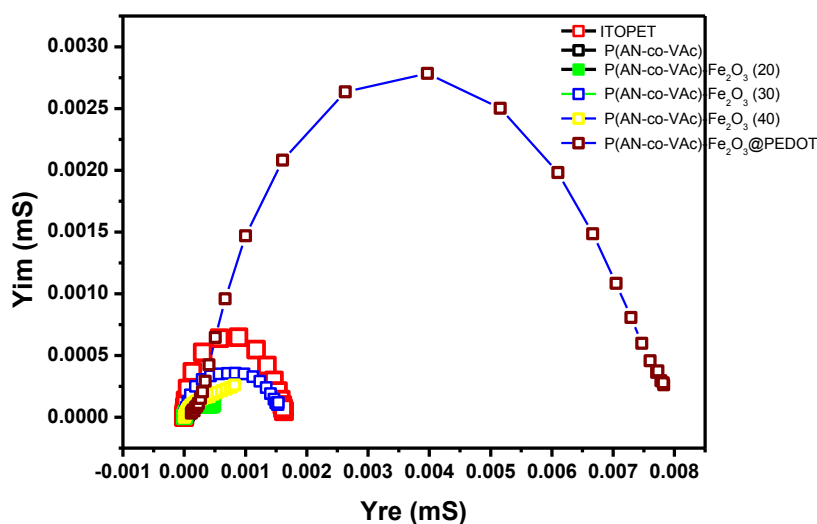


Figure 4.22 : Admittance plot of P(AN-co-VAc)/Fe₂O₃ (20), P(AN-co-VAc)/Fe₂O₃ (30), P(AN-co-VAc)/Fe₂O₃ (40), P(AN-co-VAc) and P(AN-co-VAc)/Fe₂O₃@PEDOT.

In Figure 4.23, a plot to nanofiber diameter and bode phase versus amount of Fe₂O₃, it indicates that nanofiber diameter as well as bode phase decreased with an

increase in amount of Fe_2O_3 . Therefore, capacitance which is proportional to nanofiber diameter were reduced.

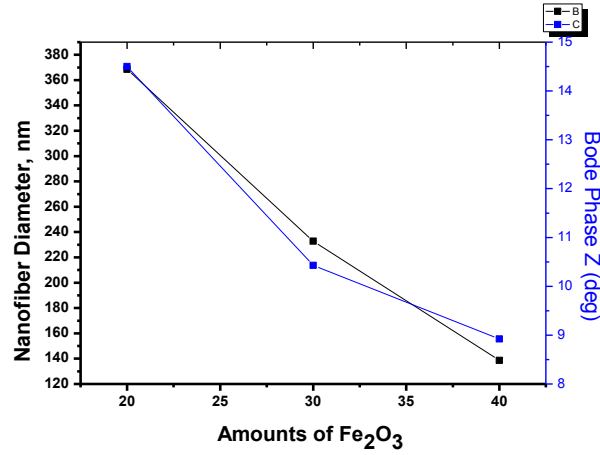


Figure 4.23 : Relationship between nanofiber diameter, bode phase and Fe_2O_3 Amounts.

4.6.7 Modelling

To create the simulation of the impedance behaviour of nanofibers of copolymer and core-shell nanocapsules, experimentally obtained the EIS data was fitted with an equivalent electrical circuit and shown in Figure 4.25. The proposed model was constructed using components in series. The first component was the solution resistance of the electrolyte, R_s . The second one was the parallel combination of the constant phase element, Q , and the charge transfer resistance between the nanofiber electrode and the electrolyte interface, R_{ct} . The series connection to R_{ct} was made up using double layer capacitance (CPE) parallel to R_p where R_p is pore resistance of the nanofibers. All results and graphs belonging to the nanofibers of copolymer and core-shell nanocapsules are represented in Table 4.7 and Figure 4.26.

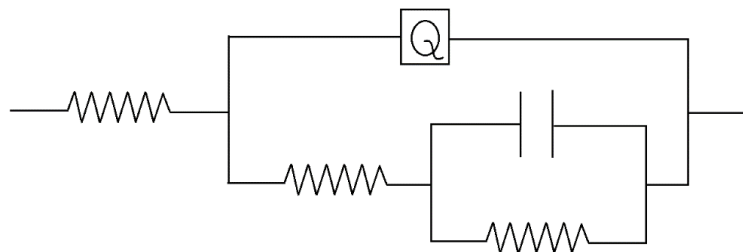


Figure 4.24 : Equivalent electrical circuit model of $\text{P(AN-co-VAc)/Fe}_2\text{O}_3$ (20), $\text{P(AN-co-VAc)/Fe}_2\text{O}_3$ (30), $\text{P(AN-co-VAc)/Fe}_2\text{O}_3$ (40), and $\text{P(AN-co-VAc) [R(Q(R(CR)))]$.

The impedance results between a solid electrode and electrolyte interface often generate a frequency dispersion that cannot be described by simple elements such as resistances, capacitances, inductances or convective diffusion (e.g., Warburg) impedance. The frequency dispersion is chiefly referred to a “capacitance dispersion” expressed in terms of a constant-phase element (CPE) [189].

Table 4.6: Content of Fe_2O_3 dependence of parameters calculated from the equivalent circuit model for the electrospun nanofibers.

	P(AN-co-VAc)	P(AN-co-VAc) $\text{Fe}_2\text{O}_3(20)$	P(AN-co-VAc) $\text{Fe}_2\text{O}_3(40)$	P(AN-co-VAc) $\text{Fe}_2\text{O}_3(30)$
R_s [Ω]	1.595E-3	2080	996.2	654.8
CPE [Y_0/Ss^n]	1.528E-6	1.802E-6	2.062E-6	4.819E-6
n	0.3836	0.6073	0.5654	0.7302
R_{ct} [Ω]	1.301E5	2.771E4	8046	2278
C_{nfb} [μF]	5.014E-8	7.869E-8	1.617E-7	1.211E-6
R_{nfb} [Ω]	5.395E5	5.28E5	2.126E5	2.341E5
Chi Squared (χ^2)	4.016E-3	6.688E-3	7.681E-3	2.234E-3

a)

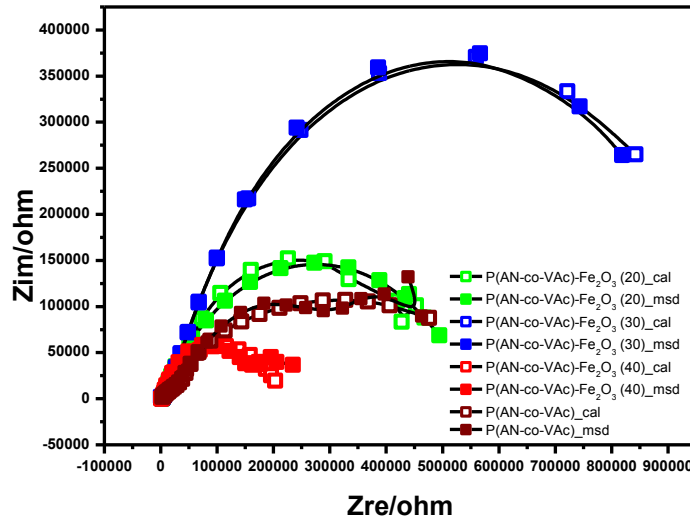


Figure 4.25 : (a) Nyquist, (b) Bode Magnitude, (c) Bode Phase, and (d) admittance plots indicating that measured and calculated datas well fitted to each other with the model

b)

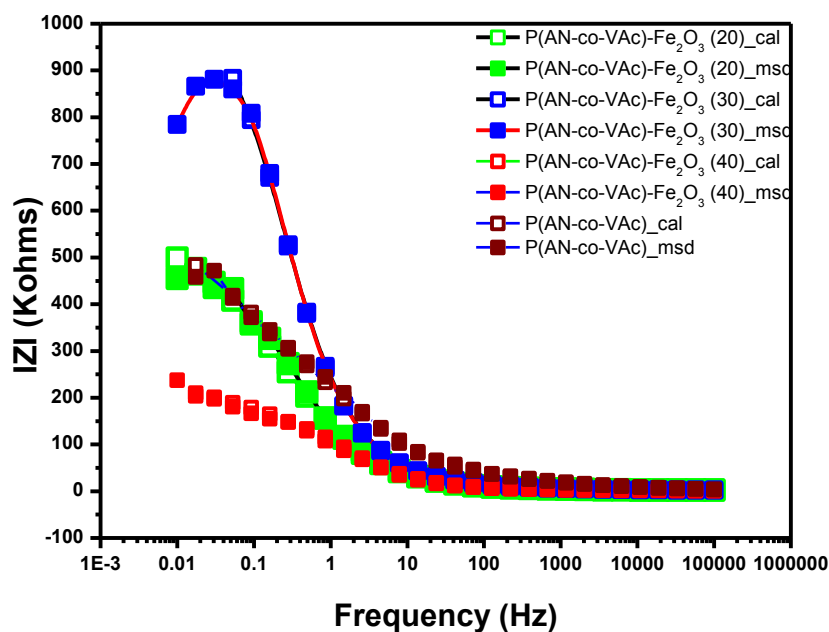


Figure 4.25 (continued) : (a) Nyquist ,(b) Bode Magnitude, (c) Bode Phase, and (d) admittance plots indicating that measured and calculated datas well fitted to each other with the model.

c)

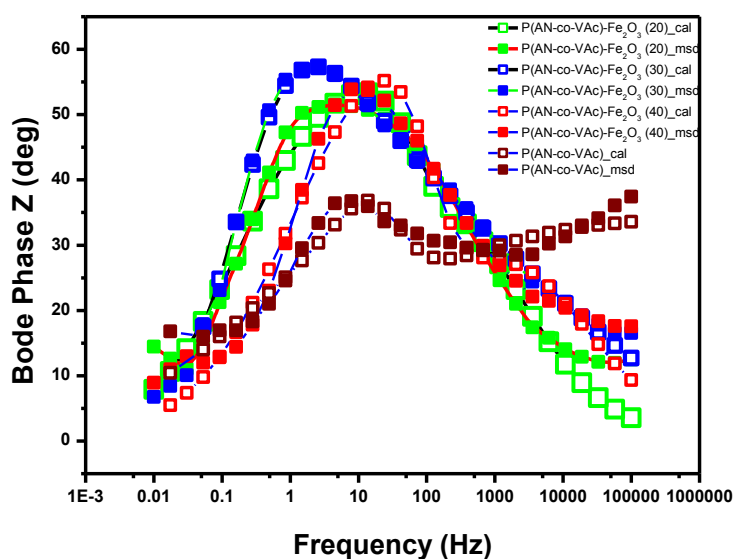


Figure 4.25(continued) : (a) Nyquist ,(b) Bode Magnitude, (c) Bode Phase, and (d) admittance plots indicating that measured and calculated datas well fitted to each other with the model

d)

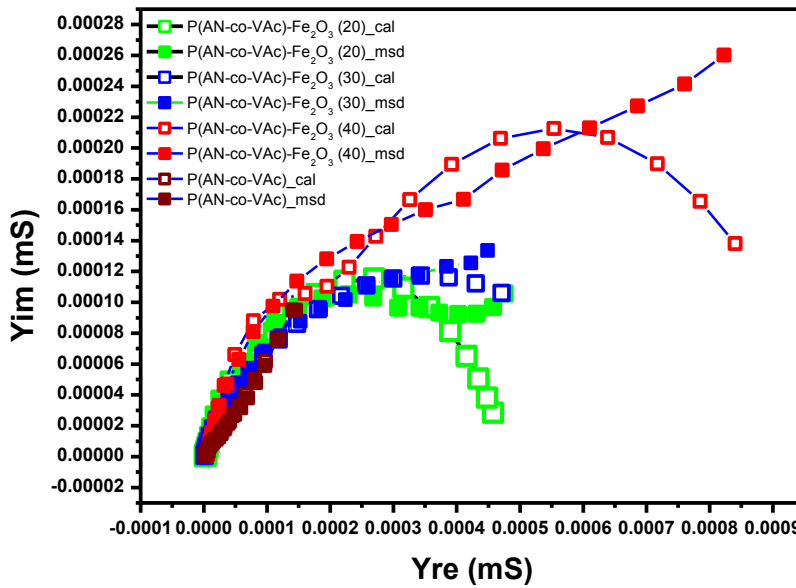


Figure 4.25 (continued) : (a) Nyquist, (b) Bode Magnitude, (c) Bode Phase, and (d) admittance plots indicating that measured and calculated data well fitted to each other with the model

As examining in Table 4.7, R_s was decreased with compatibly increasing conductivity of the nanocapsules due to the different size of particles and pore structure of obtained composite from each electrolyte solution. CPE was also utilized to fit the experimental data into the equivalent circuit. The presence of CPE can be ascribed to the nanofiber roughness or to the inhomogeneity in the conductance or the dielectric constant. The n ($0.70 < n < 1$) value arisen from the slope of the $\log Z$ versus $\log f$ plot is used for indication of the inhomogeneity of the nanofibers. When the n values compare to each other, Fe_2O_3 (20) and Fe_2O_3 (40) have low inhomogeneity according to Fe_2O_3 (30) because of being able to have core-shell structure, core as Fe_2O_3 nanoparticle and P(AN-co-VAc) as shell. As R_{ct} was detected, it can be seen that these results were in agreement with the C_{nfb} values of the nanocapsules. Because R_{ct} decreased whereas increasing C_{nfb} . Actually, a good agreement was exhibited with the best fitting electrical equivalent circuit model between the experimental results and the calculated parameters which chi-squared (χ^2) values minimized. χ^2 is the function defined as the sum of the squares of the residuals.

Another electrical equivalent circuit was produced for core-shell structure as coating of the nanocapsule with PEDOT. As seen parameters in Table 4.8, obtained model is $R(Q(R(QR)))$, in Figure 4.27. The first component was the solution resistance of the electrolyte, R_s . The second one was the parallel combination of the former constant phase element, Q which is corresponded to PEDOT, and the charge transfer resistance between the polymer electrode and the electrolyte interface, R_{ct}

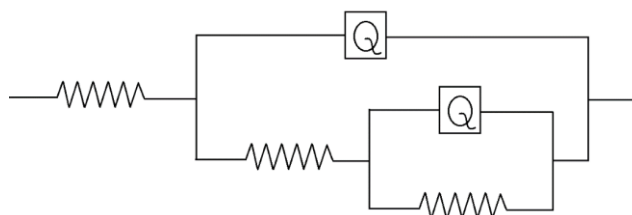


Figure 4.26 : Equivalent electrical circuit model of P(AN-co-VAc)/Fe₂O₃-(40)@PEDOT, $R(Q(R(QR)))$.

The series connection to R_{ct} was that latter constant phase element (Q) which is attributed to the nanocapsule and R_p which is parallel to latter constant phase element is pore resistance of the core-shell with PEDOT. With the coating of PEDOT, R_s dramatically decreased and the former of CPE which belongs to PEDOT increased in comparison of other nanocapsules.

Table 4.8 : Content of P(AN-co-VAc)/Fe₂O₃@PEDOT dependence of parameters calculated from the equivalent circuit model for film coating on ITO-glass.

P(AN-co-VAc) Fe ₂ O ₃ (40)@PEDOT	
R_s [Ω]	130.7
CPE [$\Omega \cdot s^{-1}$]	2.689E-5
n	0.8451
R_{ct} [Ω]	2590
CPE [$\Omega \cdot s^{-1}$]	0.000307
n	0.3747
R_p [Ω]	1.654E4
Chi Squared (χ^2)	1.395E-03

a)

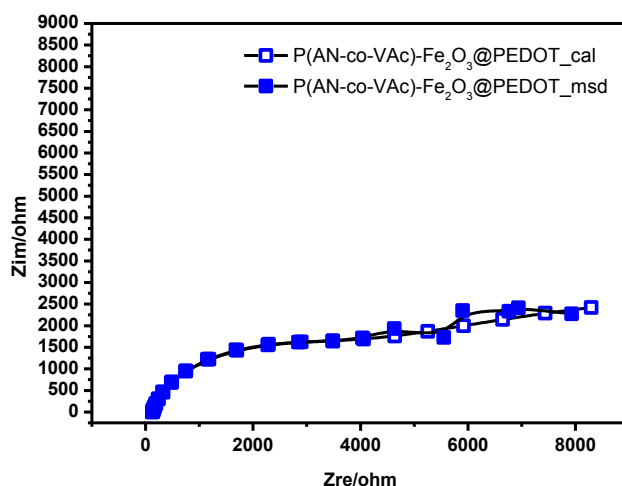


Figure 4.27 : (a) Nyquist ,(b) Bode Magnitude, (c) Bode Phase, and (d) admittance plots indicating that measured and calculated datas well fitted to each other with the model

b)

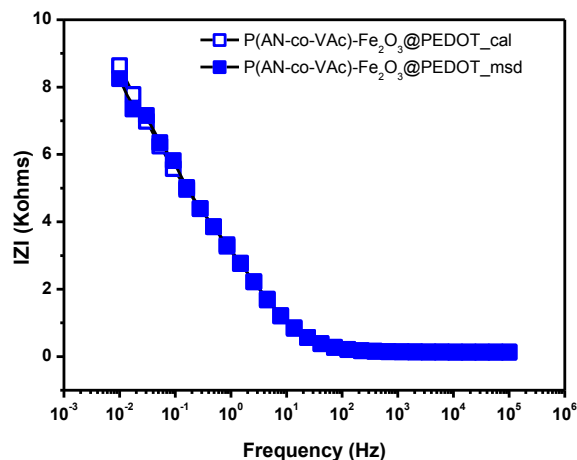


Figure 4.27 (continued): (a) Nyquist ,(b) Bode Magnitude, (c) Bode Phase, and (d) admittance plots indicating that measured and calculated datas well fitted to each other with the model

The first n value represented that coating inhomogeneity of PEDOT as shell was successful due to being ($0.70 < n < 1$). The latter of CPE increased because of referring to core-shell. The latter n value of the modelling decreased. Because it belongs to all of core-shell structure. Figure 4.28 indicates that calculated datas and measured datas were well fitted with the chosen model.

c)

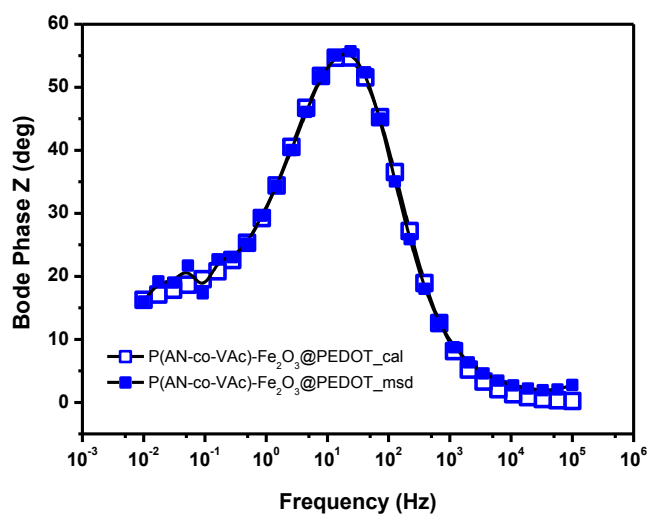


Figure 4.27 (continued) : (a) Nyquist ,(b) Bode Magnitude, (c) Bode Phase, and (d) admittance plots indicating that measured and calculated datas well fitted to each other with the model

d)

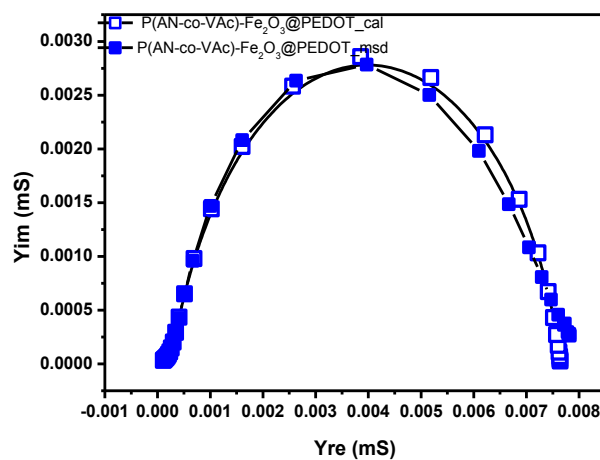


Figure 4.27 (continued) : (a) Nyquist ,(b) Bode Magnitude, (c) Bode Phase, and (d) admittance plots indicating that measured and calculated datas well fitted to each other with the model

5. CONCLUSION

The first objective of this thesis was to obtain P(AN-co-VAc)/Fe₂O₃ core-shell structure by using miniemulsion polymerization. Because conducting polymers are not processable to synthesis nanocomposite microsphere and nanocapsule structures with nanoparticles themselves. In addition, conducting polymers such as PPy can not easily deposited onto surfaces of magnetic nanoparticles because of flocculation and the hydrophilic surfaces of the magnetic nanoparticles [34]. Thus, the second part of the thesis constituted to synthesis P(AN-co-VAc)/Fe₂O₃@PEDOT. Obtained P(AN-co-VAc)/Fe₂O₃ nanocapsules which were characterized by FTIR-ATR and UV-Visible spectrophotometers. By using FTIR-ATR, it was revealed the interaction between PVP (poly vinyl pyrrolidone) and Fe₂O₃ nanoparticles. UV- vis spectra proved the presence of different content of Fe₂O₃ nanoparticles within P(AN-co-VAc). XRD represented the morphology of Fe₂O₃ nanoparticles and the crystallinity of P(AN-co-VAc)/Fe₂O₃. To determine thermal properties of P(AN-co-VAc)/Fe₂O₃, powder P(AN-co-VAc)/Fe₂O₃ nanocapsules were exposed to Differential Scanning Calorimetry (DSC) and Thermal Gravimetric Analysis (TGA) in order to display *T_g* values and thermal stabilities of the nanocapsules. In addition, the size and core structure of Fe₂O₃ nanoparticles inside powder P(AN-co-VAc)/Fe₂O₃ was proven by using Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM). The nanofibers of P(AN-co-VAc)/Fe₂O₃ dissolved in THF/ DMF (1:1) were fabricated by electrospinning method. Afterwards, the nanofibers of P(AN-co-VAc)/Fe₂O₃ which had synthesized by miniemulsion polymerization was generated appropriately to ideal targets which are the diameters of the fibers be consistent and controllable, the fiber surface be defect-free and continuous single nanofibers be collectable [109]. The nanofibers were characterized via SEM to display both the presence of nanofibers and determination of fiber diameters. Films obtained by dissolving in DMF of P(AN-co-VAc)/Fe₂O₃ were performed via Dynamic Mechanical Analysis (DMA) to examine mechanical properties. To measure conductivity properties of the nanofibers, electrochemical impedance spectroscopy was used by utilizing copper

electrode as counter, platinum as reference and nanofiber covered on ITO-PET as working electrodes in the medium of dichlorometane. So, the nanofibers of P(AN-co-VAc)/Fe₂O₃ were analysed in detail with the graphs of nyquist, bode phase, bode magnitude and admittance. As based on these results, appropriate modelling was easily fixed. Modelling and EIS results were compatible with each other. After synthesised P(AN-co-VAc)/Fe₂O₃@PEDOT, this was covered onto ITO glass by spin coating and then performed electrical properties in the same conditions. And modelling for P(AN-co-VAc)/Fe₂O₃@PEDOT was performed, as well. According to results of modelling and experimental results of EIS, best fits were obtained.

REFERENCES

- [1] **Mahdavian, A.R., Sehri, Y., Salehi-Mobarakeh, H.** (2008). Nanocomposite particles with core-shell morphology II. An investigation into the affecting parameters on preparation of Fe₃O₄-poly (butyl acrylate-styrene) particles via miniemulsion polymerization *Eur Polym J*, **44**, 22, 2482–2488.
- [2] **Audram, R. G., & Huguenard,** (1981), *A. P. U. S. Patent* **4**, **302**, 523.
- [3] **Ziolo,** (1984). *R. F. U.S. Patent*, 4474866.
- [4] **McMichael, R. D., Shull, R. D., Swartzendruber, L. J., Bennett, L. H., Watson, R. E.** (1992). Magnetocaloric effect in superparamagnets. *J. Magn. Mater.* , **29**, 111.
- [5] **Pope, N. M., Alsop, R. C., Chang, Y.A., Sonith, A. K.** (1994) *J. Biomed.Mater. Res.* , **28**, 449.
- [6] **Marchessault, R.H., Richard, S., Rioux, P.** (1992). In situ synthesis of ferrities in Ignocellulosics. *Carbohydrate Res.*, **224**, 133.
- [7] **Bhatnagar, S.P., Rosensweig, R.E.** (1995). Magnetic fluids bibliography. *J. Magn. Mater.* , **149**, 199.
- [8] **Rosensweig, R. E.,** *Ferrohydrodynamics*, (1985). MIT Press: Cambridge, MA,
- [9] **Santra, S., Tapeç, R., Theodoropoulou, N., Dobson, J., Hebard, A., & Tan, W.** (2001). Synthesis and characterization of silica-coated iron oxidenanoparticles in microemulsion: the effect of nonionic surfactants. *Langmuir*, **17(10)**, 2900-2906.
- [10] **Liu, X., Guan, Y., Liu, Z. M.,** (2004). *Langmuir*, **20**, 102782-10282.
- [11] **Zhang, S.W., Zhou, S.-X., Weng Y.M., Wu L.M.,** (2005), *Langmuir*, **21**, 2124- 2128.
- [12] **Zhang, J., Huang, T., Liu, Z., & Yu, A.** (2013). Mesoporous Fe₂O₃ nanoparticles as high performance anode materials for lithium-ion batteries *Electrochemistry Communications*, **29**, 17-20.
- [13] **Ren, T., He, P., Niu, W., Wu, Y., Ai, L., & Gou, X.** (2013). Synthesis of α -nanofibers for applications in removal and recovery of Cr (VI) from wastewater. *Environmental Science and Pollution Research*, **20(1)**, 155-162.
- [14] **Xu, Q., Li, Y., Feng, W., & Yuan, X.** (2010). Fabrication and electrochemical properties of polyvinyl alcohol/poly (3, 4-ethylenedioxythiophene) ultrafine fibers via electrospinning of EDOT monomers with subsequent in situ polymerization. *Synthetic Metals*, **160(1)**, 88-93.
- [15] **Cetiner, S., Kalaoglu, F., Karakas, H., & Sarac, A. S.** (2011). Characterization of conductive poly (acrylonitrile-co-vinyl acetate) composites: Matrix polymerization of pyrrole derivatives. *Fibers and Polymers*, **12(2)**, 151-158.
- [16] **Kirchmeyer, S., & Reuter, K.** (2005). Scientific importance, properties and growing applications of poly (3, 4-ethylenedioxythiophene). *J. Mater. Chem.*, **15(21)**, 2077-2088.

- [17] Jonas, F., Heywang, G., Schmidtberg, W., Heinze, J., Dietrich, M., Bayer, A. G. (1988), *Eur Patent*, 339-340.
- [18] Feng, Z. Q., Wu, J., Cho, W., Leach, M. K., Franz, E. W., Naim, Y. I. & Martin, D. C. (2013). Highly aligned poly (3, 4-ethylene dioxothiophene)(PEDOT) nano-and microscale fibers and tubes. *Polymer*, **54**(2), 702-708.
- [19] Aleshin, A. N. (2006). Polymer nanofibers and nanotubes: Charge transport and device applications. *Advanced materials*, **18**(1), 17-27.
- [20] Law, M., Goldberger, J., & Yang, P. (2004). Semiconductor nanowires and nanotubes. *Annu. Rev. Mater. Res.*, **34**, 83-122.
- [21] Cho, S., Lee, S.B., (2008). Fast electrochemistry of conductive polymer nanotubes: synthesis, mechanism, and application *Acc Chem Res*, **41**, 699- 707.
- [22] Li, N.C., Martin, C.R., Scrosati B. (2000). A High - Rate, High - Capacity, Nanostructured Tin Oxide Electrode. *Electrochem. Solid-State Lett.* **3**, 316.
- [23] Cassagneau, T., Caruso, F. (2002). Conjugated polymer inverse opals for potentiometric biosensing. *Adv Mater*, **14**, 1837-1841.
- [24] Lin, M. C., & Chen, C. K. (2012). Finite amplitude long-wave instability of a thin viscoelastic fluid during spin coating. *Applied Mathematical Modelling*, **36**(6), 2536-2549.
- [25] Chena, J., Donga, P., Dia, D., Wanga, C., Wanga H., Wanga J., Wua X. (2013). *App. Surf. Sci.* , **270**, 6– 15.
- [26] Ellinas, K., Smyrnakis, A., Malainou, A., Tserepi, A., & Gogolides, E. (2011). “Mesh-assisted” colloidal lithography and plasma etching: A route to large-area, uniform, ordered nano-pillar and nanopost fabrication on versatile substrates. *Microelectronic Engineering*, **88**(8), 2547-2551.
- [27] Nandiyantoo, A.B.D., Ogia, T., Iskandarb, F., Okuyamaa, K. (2011). *Chemical Engineering Journal*, **167**, 409–415.
- [28] Jiang, P., & McFarland, M. J. (2005). Wafer-scale periodic nanohole arrays from two-dimensional nonclose-packed colloidal crystals. *Journal of the American Chemical Society*, **127**(11), 3710-3711.
- [29] Kim, B.J., Mastro, M.A., Jung, H.J., Kim, H.Y., Holm, R.T., Hite, J., Eddy, J.R. Bang, J. Kim, J. (2008). Controllable fabrication of 2D colloidal-crystal films with polystyrene nanospheres of various diameters by spin-coating. *Thin solid films*, **516**, 7744–7747.
- [30] Chen, H., Wang, W., Li, G., Li, C., & Zhang, Y. (2011). Synthesis of P (St-MAA)-Fe₃O₄/PPy core-shell composite microspheres with conductivity and superparamagnetic behaviors. *Synthetic Metals*, **161**(17), 1921-1927.
- [31] Liao, Y. H., Zhou, D. Y., Rao, M. M., Li, W. S., Cai, Z. P., Liang, Y., & Tan, C. L. (2009). Self-supported poly (methyl methacrylate-acrylonitrile-vinyl acetate)-based gel electrolyte for lithium ion battery. *Journal of Power Sources*, **189**(1), 139-144.
- [32] Sharma, M. Kumar, S. & Pandey, O. P. (2008). Photophysical and morphological studies of organically passivated core-shell ZnS nanoparticles, *Digest Journal of Nanomaterials and Biostructures*, **3**(4), 189-197.

- [33] Feng, X. Liu, Y. Lu, C. Hou, W. & Zhu, J. J. (2006). One-step synthesis of AgCl/polyaniline core-shell composites with enhanced electroactivity. *Nanotechnology*, **17**(14), 3578.
- [34] Chen, H. , Wang, W. , Li, G. Li, C. , & Zhang, Y. (2012). Synthesis of P (St-MAA)-Fe₃O₄/PPy core-shell composite microspheres with conductivity and superparamagnetic behaviors. *Synthetic Metals*, **16**(18), 1921-1927.
- [35] Ueda, W. , Morooka, Y. , Sasaki, Y. (1992). *Petrotech*, **15**, 346.
- [36] Monjol, P. , Champetier, G. (1972). *Bull. Soc. Chim.* , **4**, 1302.
- [37] Quingling, C. , Xin, C. Liansheng M. Wencai, C. (1999). Recent advances IR and D of commercial catalysts for acrylonitrile synthesis, styrene production and toluene disproportionation processes. *Catal. Today*, **51**,141.
- [38] Hu, G. Chen, H.Z. Yuan, F. Yang, L.G. Wang, M. Fu, R.J. (2007). Novel porous polymer electrolyte based on polyacrylonitrile. *Materials chemistry and physics, Mater. Chem. Phys.* , **104**, 284.
- [39] Peng, F. M. Mark, H. F. Bikales, N. M. Overberger, C. G. Menges, G. Kroschwitz, J. I. (1995), *Eds. ; Wiley: New York*, **1**, 426.
- [40] Nuyken, O. , Lattermann G. Kricheldorf, H. R. (1992). In *Handbook of Polymer Synthesis* Ed; Marcel Dekker: New York, **1**, 223.
- [41] Chae, D. W. , & Kim, B. C. (2006). *J.Applied Polymer Science*, **99**(4), 1854-1858.
- [42] Landfester, K. Antinietti, M. (2010). Preparation of polymer particles in nonaqueous direct and inverse miniemulsions, *Macromol. Rapid Commun*, **21**, 820-824.
- [43] Bhanu, V. A. Rangarajan, P. Wiles, K. Bortner, M. Sankarpandian, M. Godshall, D.& McGrath, J.E. (2002). *Polymer*, **43**(18), 4841-4850.
- [44] Han, N. Zhang, X. & Wang, X. C. (2010). Various comonomers in acrylonitrile based copolymers: effects on thermal behaviour. *Iranian Polymer Journal*, **19**(4), 243-253.
- [45] Dharaiya, N. & Bahadur, P. (2012). Phenol induced growth in Triton X-100 micelles: Effect of pH and phenols' hydrophobicity. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **410**, 81-90.
- [46] Kumar, C. & Balasubramanian, D. (1980). Spectroscopic studies on the microemulsions and lamellar phases of the system Triton X-100: hexanol water in cyclohexane. *Journal of Colloid and Interface Science*, **74**(1), 64-70.
- [47] Kumar, C. & Balasubramanian, D. (1980). Structural features of water-in-oil microemulsions. *The Journal of Physical Chemistry*, **84**(15), 1895-1899.
- [48] Zhu, D.M. Feng, K.I. Schelly, Z.A. (1992), *J. Phys. Chem.***96**, 2382–2385.
- [49] Zhu, D. M. & Schelly, Z. A. (1992). *Langmuir*, **8**(1), 48-50.
- [50] Kumar, C. & Balasubramanian, D. (1979). Studies on the triton X-100: alcohol: water reverse micelles in cyclohexane. *Journal of Colloid and Interface Science*, **69**(2), 271-279.
- [51] Qi, L. & Ma, J. (1998). Investigation of the microenvironment in nonionic reverse micelles using methyl orange and methylene blue as absorption probes. *Journal of colloid and interface science*, **197**(1), 36-42.
- [52] Chhabra, V. Pillai, V. Mishra, B. K. Morrone, A. & Shah, D. O. (1995).

- Synthesis, characterization, and properties of microemulsion-mediated nanophase TiO₂ particles. *Langmuir*, **11**(9), 3307-3311.
- [53] **Qi, L. Ma, J. Shen, J.** (1997). *J. Colloid Interface Sci.*, **186**, 98–500.
- [54] **Rao, K. S. Goyal, P. S. Dasannacharya, B. A. Kelkar, V. K. & Manohar, C.** (1991). Small angle neutron scattering from micellar solutions of triton X-100. *Pramana*, **37**(4), 311-319.
- [55] **Goyal, P. S. Menon, S. V. G. Dasannacharya, B. A. & Thiyagarajan, P.** (1995). SANS study of micellar structure and interactions in Triton X-100 solutions, *Physica B: Condensed Matter*, **213**, 610-612.
- [56] **Goyal, P. S. & Aswal, V. K.** (2001). Micellar structure and inter-micelle in micellar solutions: results of small angle neutron scattering studies. *CURRENT SCIENCE- BANGALORE*, **80**(8), 972-979.
- [57] **Cornell, R. M. & Schwertmann, U.** (2003). *The iron oxides: structure, properties, reactions, occurrences and uses*. John Wiley & Sons.
- [58] **Kovalenko, M. V. Bodnarchuk, M. I. Lechner, R. T. Hesser, G. Schäffler, Heiss, W.** (2007). Fatty acid salts as stabilizers in size-and shape controlled nanocrystal synthesis: the case of inverse spinel iron oxide. *Journal of the American Chemical Society*, **129**(20), 6352-6353.
- [59] **Saravanan, P. Hsu, J. H. Sivaprahasam, D. & Kamat, S. V.** (2013). Structural and magnetic properties of $\gamma\text{-Fe}_2\text{O}_3$ nanostructured compacts processed by spark plasma sintering. *Journal of Magnetism and Magnetic Materials*, **346**, 175-177.
- [60] **Sugimoto, M.** (1999). The past, present, and future of ferrites. *Journal of the American Ceramic Society*, **82**(2), 269-280.
- [61] **Bate, G.** (1999). *J. Magn. Mater.* **100**, 413–424.
- [62] **Alivisatos, A. P. Johnsson, K. P. Peng, X. Wilson, T. E. Loweth, C. J. Bruchez, M. P. & Schultz, P. G.** (1996). Organization of 'nanocrystal molecules' using DNA.
- [63] **Colvin, V. L. Schlamp, M. C. & Alivisatos, A. P.** (1994). Light-emitting diodes made from cadmium selenide nanocrystals and a semiconducting polymer. *Nature*, **370** (6488), 354-357.
- [64] **Yallapu, M. M. Othman, S. F. Curtis, E. T. Gupta, B. K. Jaggi, M. & Chauhan, S. C.** (2011). Multi-functional magnetic nanoparticles for magnetic resonance imaging and cancer therapy. *Biomaterials*, **32**(7), 1890-1905.
- [65] **Mahmoudi, M. Milani, A. S. & Stroeve, P.** (2010). Synthesis, surface architecture and biological response of superparamagnetic iron oxide nanoparticles for application in drug delivery: a review. *International Journal of Biomedical Nanoscience and Nanotechnology*, **1**(2), 164-201.
- [66] **Sharrock M. P.** (1989), Measurement and interpretation of magnetic time effects in recording media. *IEEE Trans. Magn.*, **25**, 4374–4389.
- [67] **Ennas, G. Musinu, A. Piccaluga, G. Zedda, D. Gatteschi, D. Sangregorio, C. & Spano, G.** (1998). Characterization of iron oxide nanoparticles in an Fe₂O₃-SiO₂ composite prepared by a sol-gel method. *Chemistry of materials*, **10**(2), 495-502.
- [68] **Monte, F.D. Morales, M.P. Levy, D. Fernandez, A. Ocana, M. Roig, A. Molins, E. Ogrady, K.** (1997), *Langmuir*, **13**, 3627– 3634.

- [69] **Borelli, M. F. Morse, D. L. Schreurs, J. W. H.** (1983), *J. Appl. Phys.* , **54**, 3344.
- [70] **Ziolo, R.F. Giannelis E.P. Weinstein B.A. Ohoro M.P. Gangul B.N. Mehrotra, V. Russell M.W. Huffman D.R.** (1992), *Science*, **257**, 219–222.
- [71] **Nguyen, M. T. & Diaz, A. F.** (1994). A novel method for the preparation of magnetic nanoparticles in a polypyrrole powder. *Advanced Materials*, **6(11)**, 858-860.
- [72] **Chern, C. S.** (2006). Emulsion polymerization mechanisms and kinetics. *Progress in Polymer Science*, **31(5)**, 443-486.
- [73] **El-Aasser, M. S. Sudol, E. D** (2004). Miniemulsion: overview of research and application. *JCT. Res.* , **1**, 21–31.
- [74] **Nakajima, H.** (1997), Microemulsions in cosmetics, in: **C. Solans, H. Kunieda (Eds.)**, Industrial applications of microemulsions, **Marcel Dekker**, New York, 175– 197.
- [75] **Sonneville-Aubrun, O. Simonnet, J. T. & L'alloret, F.** (2004). Nanoemulsions: a new vehicle for skincare products. *Advances I Colloid and Interface Science*, **108**, 145-149.
- [76] **Amselem, S. Friedman, D. S. Benita (Ed.)** (1998). *Submicron emulsions in drug targeting and delivery*, Harwood Academic Publishers, London, 153–173.
- [77] **Harkins, WD.** (1945), *J. Chem Phys.* **13**, 381–382.
- [78] **Harkins, WD.** (1946), *J. Chem Phys.* **14**, 47–48.
- [79] **Harkins, WD.** (1947), *J. Am. Chem. Soc.* **69**, 1428–44.
- [80] **Smith, WV. Ewart, RH.** (1948), *J. Chem. Phys.* , **16**, 592–599.
- [81] **Smith, WV.** (1948), *JACS*, **70**, 3695–3702.
- [82] **Smith, WV.** (1949), *JACS*, **71**, 4077–4082.
- [83] **Gardon, JL.** (1968), *J. Polym. Sci. A. 1*, **6**, 623–641.
- [84] **Gardon, JL.** (1968), *J. Polym. Sci. A. 1*, **6**, 643–64.
- [85] **El-Aasser, M.S. Miller, CM.** (1997). Preparation of latexes using miniemulsions. *Dordrecht: Kluwer*, 109–26.
- [86] **Sudol, E.D. El-Aasser, M.S.** (1997), Miniemulsion polymerization, Lovell PA, El-Aasser MS, Emulsion polymerization and emulsion polymers, *Chichester: Wiley*, 699–722.
- [87] **Capek, I. Chern, C.S.** (2001), Radical polymerization in direct mini-emulsionsystems. In *New Polymerization Techniques and Synthetic Methodologies* *Adv. Polym. Sci.* , **155**, 101–165.
- [88] **Antonietti, M. Landfester, K.** (2002), *Prog. Polym. Sci.* , **27**, 689–757.
- [89] **Asua, J.M.** (2002). Emulsion polymerization: from fundamental mechanisms to process developments. *Prog. Polym. Sci.* , **27**, 1283–1346.
- [90] **Friis, N. Hamielec, AE.** (1976), *ACS symposium series no.* **24**, 82–91.
- [91] **Russell, G. T. Gilbert, R. G. & Napper, D. H.** (1992). Chain-length-dependent termination rate processes in free-radical polymerizations *Macromolecules*, **25(9)**, 2459-2469.
- [92] **Anton, N. Benoit, J. P. & Saulnier, P.** (2008). Design and production of nanoparticles formulated from nano-emulsion templates—a review. *Journal of Controlled Release*, **128(3)**, 185-199.
- [93] **Torza, S. Mason, S.G.** (1970), *J. Colloid Interface Sci.* , **33**, 6783.

- [94] **Chronakis, I. S.** (2005). Novel nanocomposites and nanoceramics based on polymer nanofibers using electrospinning process—a review. *Journal of Materials Processing Technology*, **167(2)**, 283–293.
- [95] **Bae, J. W. Kim, H. K. Jo, H. W.** (2005), *Macromolecules*, **38**, 1044–1047.
- [96] **Deitzel, J.M. Kosik, W. McKnight, S. H. Tan, N. C. B. Desimone, J. M Crette, S.** (2002). Electrospinning of polymer nanofibers with specific surface chemistry, *Polymer*, **43**, 1025–1029.
- [97] **Bognitzki, M. Hou, H. Ishaque, M. Frese, T. Hellwig, M. Schwarte, C. Shaper, A. Wendorff, J. H. Greiner, A.** (2000). *Adv. Mater.* , **12**, 637–640.
- [98] **Dzenis, Y.** (2004), *Science*, **304 (5679)**, 1917–1919.
- [99] **Reneker, D. H. Chun, I.** (1996). Nanometre diameter fibres of polymer, produced by electrospinning. *Nanotechnology*, **7**, 216–223.
- [100] **X. Fang, D.H. Reneker,** (1997). DNA fibers by electrospinning. *J. Macromol.Sci.-Phys. B*, **36**, 169–173.
- [101] **Bognitzki, M. Frese, T. Steinhart, M. Greiner, A. Wendorff, J. H.** (2001). Preparation of fibres with nanoscaled morphologies: electrospinning of polymer blends. *Polym. Eng. Sci.* , **41**, 982–989.
- [102] **Frenot, A. & Chronakis, I. S.** (2003). *Current opinion in colloid & interface science*, **8(1)**, 64–75.
- [103] **Li, D. & Xia, Y.** (2004). Electrospinning of nanofibers: reinventing the wheel? *Advanced materials*, **16(14)**, 1151–1170.
- [104] **Jayaraman, K. Kotaki, M. Zhang, Y. Mo, X. & Ramakrishna, S.** (2004). Recent advances in polymer nanofibers. *Journal of Nanoscience and Nanotechnology*, **4(1-2)**, 1–2.
- [105] **Subbiah, T. Bhat, G. S. Tock, R. W. Parameswaran, S. & Ramkumar, S.** (2005). Electrospinning of nanofibers, *Journal of Applied Polymer Science*, **96(2)**, 557–569.
- [106] **Dersch, R. Steinhart, M. Boudriot, U. Greiner, A. & Wendorff, J. H.** (2005). Nanoprocessing of polymers: applications in medicine, sensors, catalysis, photonics *Polymers for Advanced Technologies*, **16(2-3)**, 276–282.
- [107] **Hille, B.** (2001). *Elementary properties of ions in solution, Ion channels of excitable membranes*. 3rd ed: Sinauer Associates, Inc. , 309–45.
- [108] **Taylor, I. G.** (1969). *A Math Phys Sci*, (1934–1990), **313**, 453–75.
- [109] **Huanga, Z.M. Zhang, Y. Z. Kotaki, M. Ramakrishna, S.** (2003). A review on polymer nanofibers by electrospinning and their applications in nanocomposites. *Composites Science and Technology*, **63**, 2223–2253.
- [110] **Yarin, L. A. Koombhongse, S. Reneker, H. D.** (2001). *J Appl Phys*, **89**, 3018–3026.
- [111] **Adomaviciute, E. Rimvydas, M.** (2007), *Fibers Text East Eur*, **15**, 64–65.
- [112] **Bhardwaj, N. & Kundu, S. C.** (2010). Electrospinning: a fascinating fiber fabrication technique *Biotechnology advances*, **28(3)**, 325–347.
- [113] **Chong, E. J. Phan, T. T. Lim, I. J. Zhang, Y. Z. Bay, B. H. Ramakrishna, S. & Lim, C. T.** (2007). Evaluation of electrospun PCL/gelatin nanofibrous scaffold for wound healing and layered dermal reconstitution. *Acta Biomaterialia*, **3(3)**, 321–330.

- [114] **Deitzel, M. Kleinmeyer, J. Harris, D. Beck, N.C.** (2001). The effect of processing variables on the morphology of electrospun nanofibers and textiles. *Polymer*, **42**, 261–272.
- [115] **Doshi, J. Reneker, H. D.** (1995). *J Electrostat*, **35**, 151–6.
- [116] **Hohman, M. M. Shin, M. Rutledge, G. Brenner, P. M.** (2001). Electrospinning and electrically forced jets. *Phys Fluids*, **13**, 2221–36.
- [117] **Fong, H. Chun, I. Reneker, D.H.** (1999). Beaded nanofibers formed during electrospinning *Polymer*, **40**, 4585–92.
- [118] **Zhang, C. Yuan, X. Wu, L. Han, Y. Sheng,** (2005). *Eur Polym J*, **41**, 423–32.
- [119] **Pham, Q. P. Sharma, U. & Mikos, A. G.** (2006). Electrospun poly (ϵ -caprolactone) microfiber and multilayer nanofiber/microfiber scaffolds: characterization of scaffolds and measurement of cellular infiltration. *Biomacromolecules*, **7(10)**, 2796–2805.
- [120] **Sukigara, S. Gandhi, M. Ayutsede, J. Micklus, M. & Ko, F.** (2003). Regeneration of *Bombyx mori* silk by electrospinning—part 1: processing parameters and geometric properties. *Polymer*, **44(19)**, 5721–5727.
- [121] **Ki, S. C. . Baek, H. D. Gang, K. D. Lee, H. K. Um, C. I. Park, H. Y.** (2005). *Polymer*, **46**, 5094–102.
- [122] **Jun, Z. Hou, H. Schaper, A. Wendorff, H. J. Greiner, A.** (2005). *e- Polym* **9**, 1–9
- [123] **Haghi, A. K. & Akbari, M.** (2007). Trends in electrospinning of natural nanofibers. *Physica status solidi (a)*, **204(6)**, 1830–1834.
- [124] **McKee, M.G. Layman, J.M. Cashion, M.P.** (2006). Phospholipid nonwoven electrospun membranes. *Science*, **311**, 353–355.
- [125] **Burger, C. Hsiao, B.S. and Chu, B.** (2006). Nanofibrous materials and their applications. *Annu. Rev*, **36**, 333–68.
- [126] **Hayati, I. Bailey, A. I. Tadros, F. T.** (1987). Investigations into the mechanisms of electrohydrodynamic spraying of liquids: I. Effect of electric field and the environment on pendant drops and factors affecting the formation of stable jets and atomization. *J. Colloid Interface Sci*, **117**, 205–21.
- [127] **Baumgarten, K. P.** (1971). Electrostatic spinning of acrylic microfibers. *J Colloid Interface Sci*, **36**, 71–9.
- [128] **Fong, H. Reneker, D. H.** (1999). Elastomeric nanofibers of styrene-butadiene-styrene triblock copolymer. *J. Polym. Sci: Polym. Phys.*, **37**, 3488.
- [129] **Huang, L. Nagapudi, K. P. Apkarian, R. & Chaikof, E. L.** (2001) Engineered collagen–PEO nanofibers and fabrics. . *Journal of biomaterials science, Polymer edition*, **12(9)**, 979–993.
- [130] **Zong, X. Kim, K. Fang, D. Ran, S. Hsiao, S. B. Chu, B.** (2002). *Polymer*, **439**, 4403–12.
- [131] **Jiang, L. H. Fang, F. D. Hsiao, S. B. Chu, B. Chen, L. W.** (2004), *Biomacromolecules*, **5**, 326–33.
- [132] **Mit-uppatham, C. Nithitanakul, M. & Supaphol, P.** (2004). Ultrafine Electrospun Polyamide - 6 Fibers: Effect of Solution Conditions on Morphology and Average Fiber Diameter. *Macromolecular Chemistry and Physics*, **205(17)**, 2327–2338.

- [133] **Zuo, W.M. M. W. Zhu, M. W. Yang, F. W. Yu, H. Chen, M. Y. Zhang, Y.** (2005), *Polym Eng Sci*, **45**, 704–9.
- [134] **Kim, B. Park, H. Lee, H.S. Sigmund, M. W.** (2005). *Mater Lett*, **59**, 829–32.
- [135] **Haghi, A. K. & Akbari, M.** (2007). Trends in electrospinning of natural nanofibers. *Physica status solidi (a)*, **204(6)**, 1830-1834.
- [136] **Ramakrishna, S. Fujihara, K. Teo, W. E. Ma, Z. W. and Lim T.C.** (2005). *World Scientific Publishing Co. Pte. Ltd. ISBN 981-256-415-2*.
- [137] **Taylor G.** (1964). *Disintegration of Water Drops in an Electric Field*, *Proc. R. Soc. Lond.* , **280**, 383-397.
- [138] **Zhong, X. H. Kim, K. S. Fang, D. F. Ran, S. F. Hsiao B. S. and Chu, B.** (2002). Structure and process relationship of electrospun bioabsorbable nanofiber membranes. *Polymer*, **43**, 4403-4412.
- [139] **Deitzel, J.M. Kosik, W. McKnight, S.H. Tan, N.C.B. DeSimone, J.M. and, Crette, S.** (2002). Electrospinning of polymer nanofibers with specific surface chemistry. *Polymer*, **43**, 1025-1029.
- [140] **Jarusuwannapoom, T. Hongrojjanawiwat, W. Jitjaicham, S. Wannatong, L. Nithitanakul, M. Pattamaprom, C. Koombhongse, P. Rangkupan, R. Amd Supaphol, P.** (2005). Effect of solvents on electro-spinnability of polystyrene solutions and morphological appearance of resulting electrospun polystyrene fibers. *Euro. Polym. J.* , **41**, 409-421.
- [141] **Wang, C. Hsu, C. H. & Lin, J. H.** (2006). Scaling laws in electrospinning of polystyrene solutions. *Macromolecules*, **39(22)**, 7662-7672.
- [142] **Baker, S. C. Atkin, N. Gunning, P. A. Granville, N. Wilson, K. Wilson, D. Southgate, J.** (2006). *Biomaterials*, **27**, 3136-6146
- [143] **Yuan, X. Y. Zhang, Y. Y. Dong, H. C. Sheng, J.** (2004). Morphology of ultrafine polysulfone fibers prepared by electrospinning. *Polym Int*, **53**, 1704–10.
- [144] **Megelski, S. Stephens, J. S. Chase, D. B. Rabolt, F. J.** (2002). *Macromolecules*, **35**, 8456–66.
- [145] **Zong, X. Kim, K. Fang, D. Ran, S. Hsiao, S. B. Chu, B.** (2002). *Polymer*, **439**, 4403–12.
- [146] **Yuan, X. Zhang, Y. Dong, C. & Sheng, J.** (2004). Morphology of ultrafine polysulfone fibers prepared by electrospinning. *Polymer International*, **53(11)**, 1704-1710.
- [147] **Baker, N. C. S. Atkin, P. A. Granville, N. Wilson, K. Wilson, D. and Southgate, J.** (2008). *Biomaterials*, **27(16)**, 3136–3146.
- [148] **Megelski, S. Stephens, J. S. Chase, D.B. and Rabolt, J.F.** (2002). Micro- and nanostructured surface morphology on electrospun polymer fibers. *Macromolecules*, **35**, 8456-8466.
- [149] **Jarusuwannapoom, T. Hongrojjanawiwat, W. Jitjaicham, S. annatong, L. Nithitanakul, M. Pattamaprom, C. Koombhongse, P. Rangkupan, R. Amd Supaphol, P.** (2005). *Euro. Polym. J.* , **40**, 409-421.
- [150] **Wang, C. Hsu, C. H. and H. Lin, J.** (2006). Scaling laws in electrospinning of polystyrene solutions. *Macromolecules*, **39**, 7662-7672.
- [151] **Wang, X. Um, C. I. Fang, D. Okamoto, A. Hsiao, S. B. Chu, B.** (2005). *Polymer*, **46**, 4853–67.

- [152] Sundaray, B. Subramanian, V. Natarajan, T. S. Xiang, Z. R. Chang, C. C. Fann, W. S. (2004). *Appl Phys Lett*, **84**, 1222–4.
- [153] Li, D. & Xia, Y. (2004). Electrospinning of nanofibers: reinventing the wheel? *Advanced materials*, **16(14)**, 1151-1170.
- [154] Xu, Y. C. Inai, R. Kotaki, M. Ramakrishna S. (2004). Potential of nanofiber matrix as tissue-engineering scaffolds. *Biomaterials*, **25**, 877– 86.
- [155] Ki, S. C. Kim, W. J. Hyun, H. J. Lee, H. K Hattori, M. Rah., K. D. (2007). Electrospun three-dimensional silk fibroin nanofibrous scaffold. *J.Appl Polym Sci*, **106**, 3922–8.
- [156] Kumbar, G. S. Nukavarapu, P. S. James, R. Hogan, V. M. Laurencin, T.C. (2008). *Biomed Eng*, **1**, 68–78.
- [157] Cetiner, S. Kalaoglu, F. Karakas, H. & Sarac, A. S. (2010). Electrospun nanofibers of polypyrrole-poly (acrylonitrile-co-vinyl acetate). *Textile Research Journal*, **80(17)**, 1784-1792.
- [158] Cetiner, S. Sen, S. Arman, B. & Sarac, A. S. (2013). Acrylonitrile/vinylacetate copolymer nanofibers with different vinylacetate content. *Journal of Applied Polymer Science*, **127(5)**, 3830-3838.
- [159] Cetiner, S. Kalaoglu, F. H. Karakas, H. Sarac, A. S. (2011). *Poly. composites*, 21075.
- [160] Cetiner, S. Kalaoglu, F. Karakas, H. Sarac, A. S. (2011). Characterization of conductive poly (acrylonitrile-co-vinyl acetate) composites: Matrix polymerization of pyrrole derivatives. *Fibers and Polymers*, **12, 2**, 151-158.
- [161] Cetiner, S. Kalaoglu, F. Karakas, H. Sarac, A. S. (2010). Electrospun nanofibers of polypyrrole-poly (acrylonitrile-co-vinyl acetate). *Textile Research Journal*, **80 (17)**, 1784–1792.
- [162] Vishhuvardhan, T. K. Kulkarni, V. R. Basavaraja, C. Raghavendra, S. C. (2006). Synthesis, characterization and ac conductivity of polypyrrole/Y2O3 composites. *Bull. Mater. Science*, **29, 1**, 77-83.
- [163] Lu, X. Niu, M. Qiao, R. & Gao, M. (2008). Superdispersible PVP-Coated Fe3O4 Nanocrystals Prepared by a “One-Pot” Reaction *The Journal of Physical Chemistry B*, **112(46)**, 14390-14394.
- [164] Zhang, Y. Liu, J. Y. Ma, S. Zhang, Y. J. Zhao, X. Zhang, X. D. & Zhang, Z. D. (2010). Synthesis of PVP-coated ultra-small Fe3O4 nanoparticles as a MRI contrast agent. *Journal of Materials Science: Materials in Medicine*, **21(4)**, 1205-1210.
- [165] Salehi, M. T. Esfahani, M. N. Ekramian, E. (2011). 2nd International Conference on Chemistry and Chemical Engineering, 14, IACSIT Press, Singapore
- [166] Zhao, B. Nan, Z. (2012). Enhancement of electric conductivity by incorporation of Ag into core/shell structure of Fe₃O₄/Ag/PPy NPs. *Materials Science and Engineering C*, **32**, 804–810.
- [167] Laot, C. M. (1997) Spectroscopic Characterization of molecular Interdiffusion at a poly(vinyl pyrrolidone) / vinyl ester interface, Blacksburg, Virginia.
- [168] Sivaiah, K. Rudramadevi, B. H. Buddhudu, S. Kumar, G. B. Varadarajulu, A. (2010). Structural, thermal and optical

- properties of Cu 2+ Co 2+: PVP polymer films. *Indian Journal of Pure & Applied Physics*, **48**, 658- 662.
- [169] **Wu, J.** (2011). Poly(3,4-ethylene dioxythiophene) (PEDOT) Thin Films, Crystals, Cubic Phases, Fibers and Tubes, In The university of Michigan.
- [170] **Vinod Selvaganesh, S. Mathiyarasu, J. N. Phani, K. L. Yegnaraman, V.** (2007). *Nanoscale Res Lett*, **2**, 546–549.
- [171] **Sarac, A.S. Sonmez, G. Cebeci, F.C.** (2003). Electrochemical synthesis and structural studies of polypyrroles, poly (3, 4-ethylene-dioxythiophene) s and copolymers of pyrrole and 3, 4-ethylenedioxythiophene on carbon fibre microelectrodes. *Journal of Applied Electrochemistry*, **33**, 295–301.
- [172] **Meng, X. Wang, Z. Wang, L. Pei, M. Guo, W. Tang, X.** (2013). *Electronical Materials Letters*, **9**, 5.
- [173] **Bhaumik, A. Samanta, S. Mal, N. K.** (2005). *Pramana J. Phys*, **65**, **5**, 855-862.
- [174] **Alqudami, A. Annapoorni, S.** Fluorescence from metallic silver and iron nanoparticles prepared by exploding wire technique, University of Delhi.
- [175] **Kim, K. D. Kim, S. S. Kim, H. T.** (2005). Formation and surface modification of Fe₃O₄ nanoparticles by co-precipitation and sol-gel method. *J. Ind. Eng. Che.*, **11**, **4**, 584- 589.
- [176] **Kwon, K. W. Shim, M.** (2005). γ -Fe₂O₃/II-VI sulfide nanocrystal heterojunctions. *JACS*, **127**, 10269-10275.
- [177] **Sahoo, S. K. Agarwal, K. Singh, A. K. Polke, B. G. Raha, K. C.** (2010). Characterization of γ - and α -Fe₂O₃ nano powders synthesized by emulsion precipitation-calcination route and rheological behaviour of α -Fe₂O₃. *International Journal of Engineering, Science and Technology*, **2**, **8**, 118-126.
- [178] **Hyeon, T. Lee, S. S. Park, J. Chung, Y. Na, H. B.** (2001). Synthesis of highly crystalline and monodisperse maghemite nanocrystallites without a size-selection process. *JACS*, **123**, 12798-12801.
- [179] **Layek¹, S. Pandey, A. Pandey, A. Verma, H. C.** (2010). Synthesis of γ -Fe₂O₃ nanoparticles with crystallographic and magnetic texture *Journal of Engineering, Science and Technology*, **2**, **8**, 33-39.
- [180] **Aronniemi, M. Lahtinen, J. Hautoja, P.** (2004). Characterization of iron oxide thin films. *Surf. Interface Anal.*, **36**, 1004–1006.
- [181] **Dawy, M. El-Mahy, S. K. Abd El Aziz, E.** (2012). Synthesis, Characterization and Electrical Properties of α -Fe₂O₃ Nanoparticle. *Australian Journal of Basic and Applied Sciences*, **6**(4), 55-62.
- [182] **Wei, Z. W ng, C. Zou, S. Liu, H. Tong, Z.** (2011). Fe₂O₃ nanoparticles as particulate emulsifier: Preparation of magnetic and biocompatible PLGA microcapsules. *Colloids and Surfaces A: Physicochem. Eng. Aspects*, **392**, 116– 123.
- [183] **Ciprari, D. L.** (2004). Mechanical Characterization of Polymer Nanocomposites and the Role of Interphase, Georgia Institute of Technology.

- [184] **Chronakis, I. S. Grapenson, S. Jakob, A.** (2006). Conductive polypyrrole nanofibers via electrospinning: electrical and morphological properties. *Polymer*, **47**, 1597–1603.
- [185] **Nikolic, M. V. Slankamena, M. P. Nikolic, N. Sekulic, D. L Aleksic, O. Mitric, S. M. Ivetic, T. Pavlovic, V. B. Nikolic, P. M.** (2012), *Science of Sintering*, **44**, 307-321.
- [186] **Hirschorna, B. Orazema, M. E. Tribollet, B. Vivier, V. Frateurc, I. Musianid, M.** (2010). *Electrochimica Acta*, **55**, 6218–6227.
- [187] **Giray, D. Balkan, T. Dietzel, B. Sarac, A. S.** (2013). Electrochemical impedance study on nanofibers of poly (m-anthranilic acid)/polyacrylonitrile blends. *European Polymer Journal*, **49**, 2645–2653.
- [188] **Dolas, H. Sarac, A. S.** (2012). Electrosynthesis of Poly (3-dodecylthiophene) in Acetonitrile with Boron Trifluoride Diethyl Etherate: The Effect of the Electrolyte on Electrochemical Impedance and Morphology *Journal of the Electrochemical Society*, **159** (1).

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List of Publications and Patents:

- **M. T. Satici**, A. S. Sarac, “Synthesis and Characterization of P(AN-co-VAc)/Fe₂O₃ Core Shell Structured Nanocomposite”, EPF (European Polymer Federation) ,16-21 June 2013, Pisa, Italy.
- E. Polat, **M. T. Satici**, T. Balkan, A. S. Sarac, “Polycaprolactone/Poly(anthranilic acid) Scaffolds for Improved Cell Adhesion in Tissue Engineering Applications”, The European Chapter Meeting of the Tissue Engineering and Regenerative Medicine International Society TERMIS-EU 2013, İstanbul, Turkey.
- **M. T. Satici**, A. S. Sarac, “Synthesis, Characterization and Magnetic Properties of P (AN-co-VAc)/Fe₃O₄ Core Shell Structured Nanocomposite”, International conference on NanoScale Magnetism, 2-6 September 2013, Istanbul, Turkey.

