ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

COPOLYMERS OF POLYPYRROLE AND THIENYL END CAPPED POLYSULFONE

M. Sc. THESIS

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Department of Polymer Science and Technology

Polymer Science and Technology Programme

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

POLİPİROL VE TİYENİL UÇ GRUPLU POLİSÜLFON KOPOLİMERLERİ

YÜKSEK LİSANS TEZİ

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Tez Danışmanı: Doç. Dr. Nesrin KÖKEN

Nilay TANRIVER, a **M.Sc.** student of ITU **Institute of Science and Technology** student ID **515131020**, successfully defended the **thesis** entitled "**COPOLYMERS OF POLYPYRROLE AND THIENYL END CAPPED POLYSULFONE**", which she prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

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Date of Submision : **22 June 2015**
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To my family and friends,

FOREWORD

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May 2015

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ABBREVIATIONS

PSU **:** Polysulfone
PPy **:** Polypyrrole
Py **:** Pyrrole
ThCCl **:** Thiophene-2-carboxylic acid chloride
ThC **:** Thienyl
FTIR **:** Forrier Transform Infra Red
NMR **:** Nuclear Magnetic Resonance
SEM **:** Scanning Electron Microscope
XRD **:** X-Ray Diffraction

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POLİPİROL VE TİYENİL UÇ GRUPLU POLİSÜLFON KOPOLİMERLERİ

ÖZET

Polisülfon (PSU) çeşitli endüstriyel uygulamaları olan amorf yapılı özel bir mühendislik polimeridir. PSU zincir yapısında sülfon (SO2) grupları ile eter, izo-propilidin gibi çeşitli aromatik oluşumlar içerir. PSU sahip olduğu iyi ısıl stabilitesi, dayanımı, yüksek çekme gerilimi, basınç dayanımı gibi mekanik özellikleri ile kimyasal stabilitesi sayesinde mühendislik plastiği olarak kullanılmaktadır. Medikal, elektrik-elektronik, ve membran gibi pek çok kullanım alanına sahiptir. Ancak çoğunlukla su ve atık su arıtımı membranları için tercih edilmektedir.

PSU hidrofobik bir malzemedir ve bu sebeple membran kullanımlarında hızla tortu oluşmasına mahal vermekte ve kirlenmektedir. Bu durum membran kullanım ömrünü azalttığı için bir dezavantajdır. Her ne kadar membran kirlenmesi fiziksel veya kimyasal temizlik ile geri dönüştürülebilir olsa da bu işlem maliyetli olduğu için membran ömrünün uzun olması istenmektedir. Bu gibi durumlarda membran malzemesi iyileştirilerek daha uzun ömürlü ve daha kullanışlı membranlar elde edilebilmektedir. PSU'nun kopolimerlerinin sentezlenmesi veya nanokompozitlerinin hazırlanması da malzeme ömrünü uzatmakta, hatta ona yeni ve eşsiz yeni özellikler kazandırabilmektedir.

Polipirol (PPy) elektriksel iletkinlik özelliği olan bir polimerdir. Elektriksel iletkenliğinin yanı sıra mükemmel bir kimyasal dayanıma, yüksek yüzey enerjisine sahip olan ve pek çok organik çözücüye karşı dayanımı olan çözünmez bir polimerdir. Polipirol taşınabilir pillerin, elektro-kromik cihazların, sensörlerin, ışık yayıcı diyotların, kapasitörlerin ve enzim elektrotlarının üretimlerinde kullanılmaktadır. Bunun yanı sıra membran teknolojisinde polipirol gazların ayırma işlemlerinde ve pervaporasyonda kullanılmaktadır.

Polipirol gibi iletken polimererden yapılan iletken membranlar biyomedikal uygulamalarda, elektro-kimyasal cihazlarda, yakıt hücrelerinde ve çeşitli ayırma işlemlerinde kullanılabilmektedir. Fakat bunların üretim süreçleri zordur. Yapılan çeşitli bilimsel çalışmalarda polipirol ile polisülfonun kompozitleri hazırlanarak iki polimerin de dez avantajlarının giderilmesi ve daha sağlam ve yeni özelliklere sahip bir membran malzemesi üretilmesi hedeflenmiş ve başarılı olunmuştur.

Kompozit yapılarda hedeflenen malzeme iyileştirmeleri sağlanabilmesine rağmen kimyasal sentezle iki farklı polimerin kopolimerlerinin elde edilmesi bütün bu özellikleri ve daha fazlasını verebilmektedir. Ancak polisülfon ve polipirol gibi farklı sentez mekanizmalarına sahip olan polimerler için kopolimer sentezi daha zorlu ve neredeyse imkansiz olabilmektedir. Polisülfon polikondelizasyon yöntemi ile elde edilirken, polipirol redoks polimerizasyonu ile ve birbirlerinden farklı koşullarda elde edilmektedir.

Bu tez çalışmasında yeni bir yöntem ile birbirinden farklı üretim yöntemi olan bu iki polimerin blok kopolimerlerinin elde edilmesi sağlanmaştır. Bu yönteme göre

öncelikle yalıtkan polimer bloğu kendi yöntemiyle sentezlenir, sonra elde edilen homopolimerin uç gruplarının, iletken polimer ile tepkime verme ve bağlanabilme özelliği olan, bağlantı grubu ile fonsiyonelleştirilir. Bu sayede bir sonraki aşamada iletken polimer ile kopolimer verebilecek makromoleküller elde edilir. İletken polimerin monomerleri ile bu fonksiyonel uç gruplu makromoleküller bir arada polimerizasyon tepkimesine sokularak makromolekülün uç gruplarına bağlı iletken polimer bloklarının oluşması, yani blok kopolimer sentezi sağlanır.

Kopolimer eldesinin yanı sıra polisülfonun uygun nano-parçacıklar ile nanokompozitlerinin hazırlanması da membran ömrünü uzatan ve membrana yeni özellikler kazandıran yöntemlerden biridir. Bir maddenin nano partikülü o maddenin aynı miktardaki daha iri partiküllerine göre daha fazla yüzey alanına sahiptir. Maddelerin fiziksel ve kimyasal etkileşimleri temas yüzeyleri sayesinde sağlandığı için yüksek yüzey alanı oranı bu etkileşimin çok daha fazla olmasına olanak vermektedir. Bu sebeple nanokompozitler normal kompozitlere göre çok daha iyi mekanik ve kimyasal özellikler verebilmektedir. Hatta nano parçacıklardan düşük yüzdelerde eklenmesi bile eklendiği maddenin özelliklerini oldukça iyileştirebilmektedir.

Sepiloyit de doğal bir kil olup nanopartikül olarak kullanılabilmektedir. Sepiyolit magnezyum silikat ailesinden gelmektedir ve fiber yapılıdır. Sepiyolit tanecikleri fiber yapısına ek olarak içlerinde çokça ve eşsiz tüneller ile porlar içerir. Bu yapısı ona yüksek absorpsiyon yeteneği kazandırır. Bu durum özellikle polisülfon gibi hidrofobik bir malzeme için güzel bir avantaj sağlamaktadır. İyi mekanik özelliklere sahip olan bu malzeme aynı zamanda nem dayanımına, etkili yüzel mekanizmasına ve düşük maliyete sahiptir. Sepiyolitin Türkiye'de bolca bulunması ve doğada çözünür bir malzeme oluşu onu endüstriyel anlamda tercih edilir kılmaktadır.

Nanokopozitler genelde üç farklı yöntem ile elde edilebilmektedir bunlar çözelti karışımı, eriyik karışım ve yerinde sentez metotlarıdır. İlk iki yöntem fiziksel karışım yöntemidir, sonuncusu ise kimyasal bir yöntemdir. Yerinde sentez yönteminde polimerlerin monomerleri ile nano parçacıklar bir arada polimerizasyona sokulmakta, büyüyen polimer zincirleri bu taneciklerin etrafında onları çevreyip matriks yapısına fiziksel ve kısmi kimyasal bağlarla dahil etmektedir. Yerinde sentez metodunda nano parçacıklar polimer zincirlerine kimyasal olarak da bağlandığı için diğer iki yöntemle elde edilen nanokompozitlere göre daha etkili özellikler verebilmektedir. Bu sebeple tez çalışmasında da polisülfonun sepiyolit minerali ile nanokompoziti yerinde sentez yöntemi ile hazırlanmıştır.

Tez çalışması kapsamında bisfenol ile bis para-klorofenil sülfon kullanılarak potasyum karbonat eşliğinde kondenzasyon polimerizasyonu ile polisülfon ve aynı materyallerle yerinde sentezleme yöntemiyle de PSU ile ağırlıkça yüzde bir oranında sepiyolit minerali kulanılarak Polisülfon/Sepiyolit nanokompoziti sentezlenmiştir. Sonraki aşamada ise polimerin ve polimer nanokompozitinin uç grupları 2-tiyofenkarbonil ile ayrı olarak fonksiyonlandırılmış ve tiyenil uç grubu taşıyan polimer ve nanokompozit makromerleri elde edilmiştir. Bu makromerler pirol monomeri ile redoks polimerizasyonu verebilme yeteneğine sahiplerdir.

Son adımda ise biri tiyenil uç gruplu PSU, diğeri ise tiyenil uç gruplu PSU/Sepiyolit nanokompozitiyle olmak üzere, pirol monomeri ile demir (III) klorür eşliğinde yapılan oksidatif (yükseltgeyici) kimyasal reaksiyonla polipirollü iki blok kopolimer elde edilmiştir. Sentezlenen blok kopolimerler spektroskopik analizler ile karakterize edilmiş, dört nokta prob tekniği ile elektrik iletkenliği ile x-ışını kırınımlarına (XRD) bakışmış ve taramalı elektron mikroskopu (SEM) ile yapısal özellikleri incelenmiştir.

Yapılan analizler ışığında polisülfon ile PSU/Sepiyolit nanokompozitinin başarı ile sentezlenmiş olduğu, uç grup fonksiyonlandırılmasının başarıldığı ve iki malzemeden de bu yöntem ile yöntemle polipirollü blok kopolimerler elde edilebildiği bulunmuştur. Sonuç olarak polisülfon ile polipirolün mekanik ve kimyasal dayanımlarına ve özelliklerine, ayrıca sepiyolitin kazandırdığı yüksek absorpsiyon gibi diğer niteliklere sahip olan yeni bir membran malzemesi, yeni bir yöntem ile sentezlenmiştir.

COPOLYMERS OF POLYPYRROLE AND THIENYL END CAPPED POLUSULFONE

SUMMARY

Polysulfone (PSU) is a specialty engineering polymer having various industrial applications. PSU is especially used in waste water treatment membranes due to its good mechanical properties, structural and chemical stability. But it is a hydrophobic material and therefore its surface aim to pollute easily, which can be solved by preparetion PSU copolymer or nanocomposite. Polypyrrole (PPy) is a conductive polymer, which has extremely chemical resistance, high surface energy and it is insoluble in many organic solvent. In the membrane field, PPy based membranes used in gas separation and pervaporation. And sepiolite is one of the natural clays, which is a hydrate magnesium silicate fiber, also one of the well known layered clays of the montmorillonites where has several unique channels and pores within. It has also moisture durability, strength and low price. Sepiolite channels give great capacity of absorption and good surface properties, that is bebeficial for hydrophoby of PSU.

In this thesis study PSU was synthesized from bisphenol and bis (p-chlorophenyl) sulfone in presence of potassium carbonate by polycondensation and the nanocomposite of PSU with sepiolite were synthesized by in situ method. Their end goups were functionalized with 2-thiophenecarbonyl chloride in order to obtain macromonomers containing thienyl end-group (PSU-ThC and PSU/Sepiolite-ThC), which are capable of giving redox polymerization with pyrrole monomer. Finally copolymers of PPy with these two product were obtained via chemical oxidative polymerization by iron (III) chloride. The synthesized block copolymers were characterized by spectroscopic analysis and the electrical conductivities were investigated with four point probe technique. The obtained samples were also characterized by Scanning Electron Microscope (SEM) and X-Ray Diffraction (XRD).

1. INTRODUCTION

Polysulfone (PSU) is one of the amorphous engineering thermoplastic that can be used for special engineering purposes. PSU’s backbone contains the sulfone groups (SO2) in the main chain along with a variety of aromatic constituents like ether or iso-propylidene groups [1]. PSU is widely used as a specialty engineering plastic since its great thermal stability, durability, high tensile strength, good chemical stability and pressure resistance [2], [3]. It has many application areas such as medical, electric-electronic and membranes. But especially it is widely used in membrane production.

Polypyrrole (PPy) is a conductive polymer, which has good electrical conductivity, high air stability. Nowadays polypyrrole has become important material since its wide range of technological applications in several application fields like secondary batteries, electro-chromic display devices, sensors, light-emitting diodes, capacitors, and enzyme electrodes and also membranes [4-10].

There are many studies about conductive membranes, these having various usage areas such as seperation, biomedical field, electronic, electrochemical devices, and fuel cells [11-14]. But poor production and processibility there are also some new studies about PSU/PPy composite membranes where are used as a conductive membrane [15]- [16]. The combination of PSU and PPy brings better material properties to the final product. Not only both polymer’s properties are gained but also disadventages of their poor mechanical specialties are improved.

Although membranes serve many separation processes very well, they have some weaknesses as mainly as fouling, caused by hydrophobic absorption [17]. The fouling factor affects both membrane module cost and cost of energy used for flux. The membrane fouling can be overcome by modifying membrane. Adding additives, preparing polymer blends or producing copolymer, and making composites for membranes production are some of these methods [18].

Even though combination of two polymers enhances the material properties, addition of nanoparticles and nanocomposite production also affects the final product in a good way. Considering the PSU and PPy membranes, avoiding the fouling and extension of the membranes life span can be possible by using nanoparticle. Moreover nanoparticles also provide good structural properties like heat resistance, mechanical strength and impact resistance or to decrease other properties such as electrical conductivity or permeability for gases like oxygen or water vapor [19]. Clays like montmorillants are some of the nanoparticles used in membrane technology.

Sepiolite is a natural clay which is a member of montmorillant family. Sepiolite is considered also as nanoparticle, belongs to the phyllosilicate family [19]. It has hydrous magnesium silicate layered clays with $(Si_{12}Mg_8O_{30})(OH)_4(OH)_2 4.8H_2O$ theoretical unit cell formula. Moreover it has excellent fiber structure different than other montmorillonites of layered clays, which comes from its tetrahedral and octahedral oxide layers packaging [20]. This fiber structure is consist of various channels and tunnels that gives large surface are and porosity, resulting superior adsorption and surface features [21], [22]. Sepiolite has good mechanical qualities, resistance to humidity and low cost.

In this study, it is aimed to produce a new conductive membrane material from polysufone and polypyrrole copolymer with the addition of sepiolite as a nanoparticle to improve the material properties. The nanocomposite of polysulfone and sepiolite are synthesized by in-situ methode and 1% sepiolite is used. After that the end group of PSU/Sepiolit nanocomposite is functionalyzed by thiophene-2-carboxylic acid chloride for the purpose of copolymerization with pyrrole. Copolymers of pyrrole and nanocomposite are synthesized by using $Fe(III)Cl_3$. The FTIR, NMR, SEM and XRD analyses of PPy-PSU/Sepiolite copolymers are done.

2. THEORETICAL PART

2.1 Nanocomposites

Nanocomposites are one of the research fields of nanotechnology and greatly adopted by polymer science and technology. Nanocomposites are generally consist combination of two phases; one is the nano-scaled particles added to other phase is the hosting matrix like polymers. Nanocomposites of polymers are prepared in order to give enhanced abilities to the original polymer material, by bringing the specialties of nanoparticles [23].

The first commercial nanocomposite produced by Toyota by processing caprolactum and montmorillonite to obtain nylon-6 nancomposite, in early 1990's. As a result they obtained thermally and mechanically enhanced product, though only small amount of nanofiller was used [24]. Another commercial nanocomposite were polyolefin based clay nanocomposites produced by General Motor [25] and afterwards nylon-6, clay, ethylene vinyl alcohol and polypropylene nanocomposites processed by Mitsubishi Chemical Gas Motor company [26]. They also showed improvement on final products material properties. Today nanocomposites gives new opportunity for various application fields, these are specialty engineering products like of aerocrafts, automotive, packaging, medical, energy and separation industries [2, 27, 28].

In definition particles having smaller than 1μm (100nm) are called nanoparticles. Nanocomparticles have good structural properties like heat resistance, mechanical strength and impact resistance or to decrease other properties such as electrical conductivity or permeability for gases like oxygen or water vapor [29]. They are both applicable with thermosets and thermoplastics [30]. As a result nanocomposites show moderate and considerable strength, enhancement of fracture toughness and improvement on many other mechanical properties [31-33].

2.1.1 Morphology of Nanocomposites

Morphology of nanocomposites plays a vital role on the definition of material's final properties. Properties of a nanocomposite not only depends on the kind of the hosting matrix and nanoparticle; but also affected from the material morphology and their interfacial characteristic [34]. Specialities of nanoparticles directly related with their particle sizes [35]. Nanoparticles have larger surface area comparing with equal amount of same material's particle. Larger surface area/volume ratio is beneficial for better molecular attraction, due to chemical and physical interactions adopted by surface and surface properties [36]. Thus particle-polymer interface and surface attractions will be increased [37]. So that even small amount of nanoparticles can make desirable changes for polymer nanocomposite. Consequently the use of nanoparticles gives improved material properties and brings new and unique abilities to the final product.

Nanoparticles can be generally divided in three groups according to their shapes, which are fibrous, particle and layered materials; shown in Figure 2.1 [31, 38]. Particle shaped nanoparticles are silica, metal and other organic or inorganic particles. These are commonly used for reinforcement, by improving the elastic modulus and yield strength of the hosting polymer. Fibrous nanoparticles consist of nanofibers and nanotubes, which have various application fields [31]. And layered nanoparticles include clays and synthetic clays, that those are used as nanofiller. Especially montmorillonites are one of the most studied clays in polymer nanocomposite production [2].

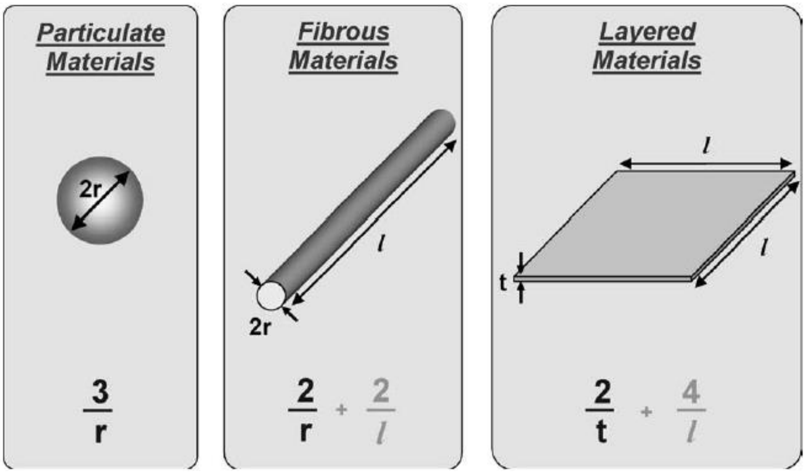


Figure 2.1 : Surface area/volume relations for varying reinforcement geometries

In a polymer nanocomposite, polymer creates the molecular matrix that nanoparticles can penetrate into. Polymers are suitable for nanocomposite matrix because of their chemical and mechanical properties, ease of processability and cost effectiveness [39-40]. Dispersion and diffusion of nanoparticles through to polymer matrix is crucial due to their morphological effects on final material properties. Dispersion and mixing degree show differences according to the choice of combination components and preparation method [41]. Literature generally asserts there are three types of morphology of nanocomposites; immiscible (phase-separated), intercalated and exfoliated [30, 42, 43]. Figure 2.2 illustrates these three types of morphological states of the nanocomposites with examples of transmission electron microscopic (TEM) images and wide angle X-Ray scans [43]. Phase separated is named for the composites where filler material tends to be immiscible in the polymer. Polymer chains cannot penetrate in the filler particles although particles simply dispersed, which brings poor mechanical properties. Intercalated systems are achieved when the polymer chains twine around the nano-layers, while the ordered structure of filler maintains. Since the surface attraction is increased, intercalated systems provide better reinforcement than phase-separated systems, but generally they may have low reinforcement comparing with exfoliated systems. When the individual nanoparticles are well dispersed and randomly distributed in the hosting polymer, exfoliated morphology is obtained. If the percolation threshold is attained, the distance between the nanoparticles can be independent from filler concentration, or the nanoparticles can become intercalated [30]. Nevertheless exfoliated structures procure maximum reinforcement and better material properties, due to the maximum nanoparticle-polymer surface interaction is gotten. This is the important difference between the nanocomposites and conventional composites.

Beside the improvements of mechanical properties, there are other facilities like flame retardancy, chemical resistance, electrical conductivity, optical clarity and lower gas emission are gained by exfoliated morphology [30, 37].

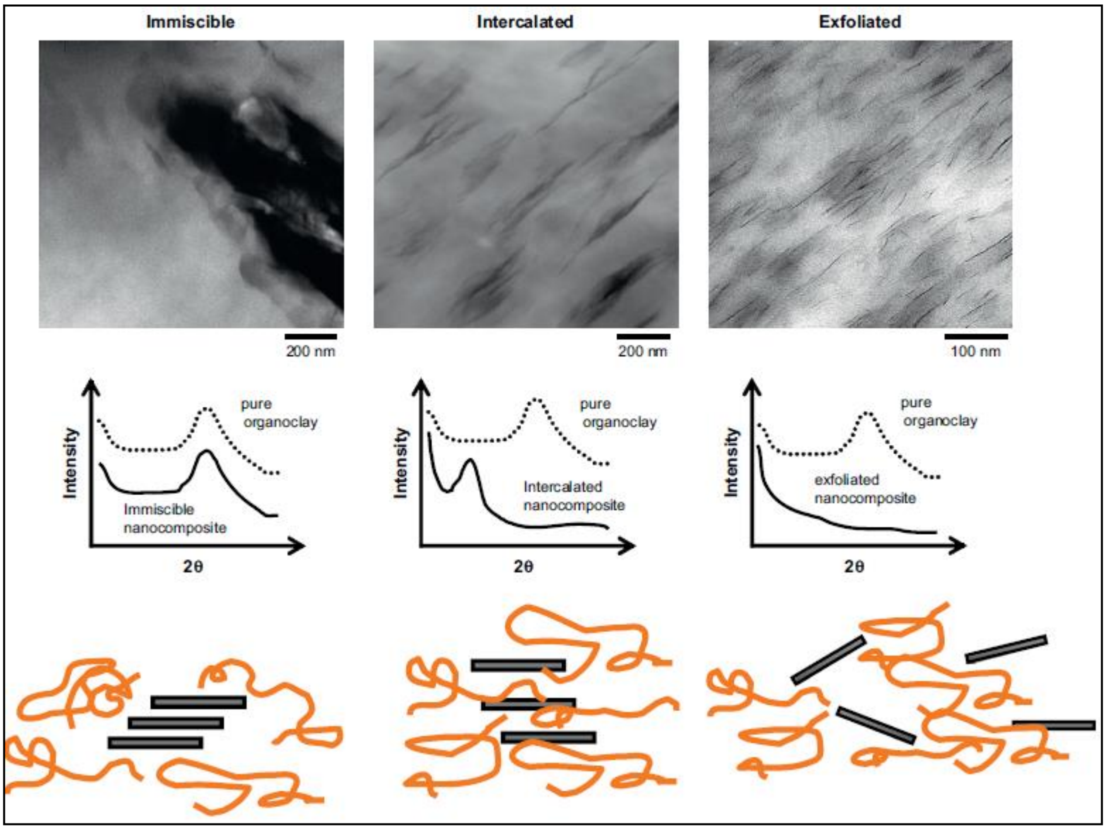


Figure 2.2 : Illustration of different states of dispersion of organoclays in polymers with corresponding WAXS and TEM results

2.1.2 Preparation of Nanocomposites

For a nanocomposite, exfoliated systems are mostly preferred but hard to achieve. Especially the filler-polymer choice and the preparation methods for nanocomposites play key role on the morphology [42, 43]. Nanocomposite specialities show poor or degraded facilities, unless proper dispersion is done [44]. Because material properties influenced by the degree of mixing between the two phases due to the surface chemistry as mentioned before.

There are mainly three methods used for the production of nanocomposites; these are melt compounding, solution mixing and in-situ methods [23, 30, 40, 45].

2.1.2.1 Melt Compounding Method

Melt compounding process is a physical method that combines the polymer with nanoparticles via extrusion mixing. Extruder provides the melting and mixing. Polymer granules are fed to the extruder with nanoparticles. As the polymer melts, nanoparticles disperse in the molten state by high degree of mixing. In the end of the process solidified polymer nanocomposite is gotten [40, 45, 46].

2.1.2.2 Solution Mixing Method

Similarly like melt compounding, solution mixing method also physically combines the polymer and nanoparticles. But this time they are combined in a solvent medium. Thusly solvent characteristics have vital effects on the process. In the other words viscosity of the solution and other rheological parameters, arising from the solvent characteristics, affect the intercalation and consequently nanocomposite structure [47]. Therefore the solvent chose should be properly made according to solubility of the polymer or prepolymer and swellability of the nano-materials. Intercalation of the nanoparticles in the polymer or pre-polymer solution is enabled as well as by high degree of mixing. Afterwards solvent is removed and intercalated nanocomposite structure remains [23].

2.1.2.3 In Situ Method

In-situ method is the chemical technique to produce nanocomposite, that the monomers or the pre-polymers are polymerized in the presence of the nanoparticles, together. Nanofillers swell in the liquid monomer or monomer solution. Polymerization reaction initiates by heat or radiation with the diffusion of suitable initiator [48-52]. In-situ process gives many advantages for nanocomposite morphology, since the dispersion of the nanoparticles through the polymer matrix is efficiently obtained because the propagating polymer chains cover the nanoparticles and make- partially- chemical connection with them during the polymerization as shown in the Figure 2.3.

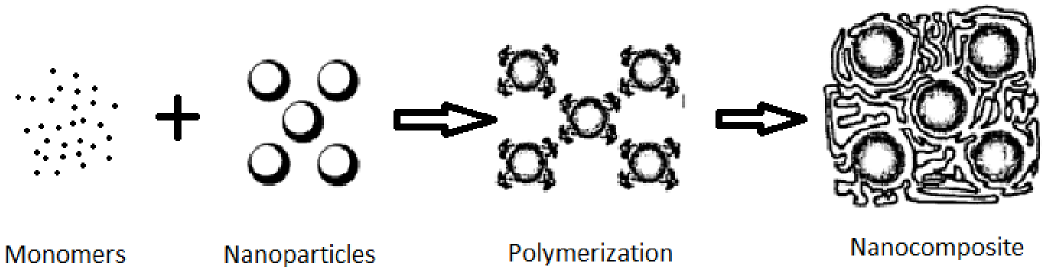


Figure 2.3 : Nanocomposite Synthesis by In Situ Method

Ultimately, exfoliation of the nanoparticles is aimed by the initiating molecular based chemical interactions between them and propagating polymer chains. Consequently in-situ method introduces newer and better properties of nanocomposites.

2.2 Polysulfone

Polysulphones are the members of amorphous engineering thermoplastics, which are containing the sulfone groups (SO_2) in the repeating units along with a variety of aromatic constituents like ether or iso-propylidene groups [1, 53]. Polysulfones are high temperature polymers with excellent thermal and chemical stabilities [53, 54].

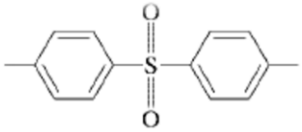
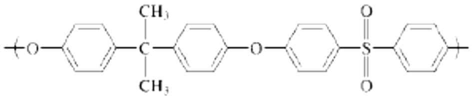
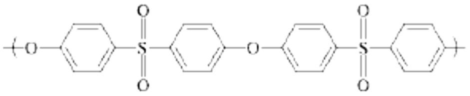
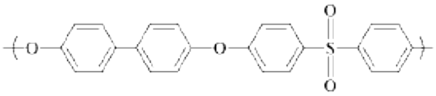


Figure 2.4 : Para-linked diphenylenesulfone

Basically as mentioned before a polysulfone includes sulfone, aryl and ether groups in their backbones; since in literature they are also called as poly(arylethersulfone)s. But they are characterized according to the presence way of para-linked diphenylenesulfone group, represented in Figure 2.4., in their repeating units. Accordingly there are three major members of the polysulfone family these are polysulfone, polyethersulfone (PES) and polyphenylsulfone (PPS), demonstrated in Table 2.1. with their glass transition temperatures. In addition to the phenyl, ether and sulfone groups, main chain may contain other connecting units, that isopropylidene linkage is one of the notable ones. This linkage is mostly found in the bisphenol-A based polysulfones [53].

Like the other members of this family, PSU is a high performance engineering plastic due to its longterm service temperature, remarkably high creep strength over a vide temperature range. Thus it is used in specialty engineering applications. Addition to its thermal stability, PSU also has good mechanical properties like stiffness, durability, high tensile strength, pressure resistance and good chemical stability [1-3, 53]. The aterial properties of PSU are represented in Table 2.1.

Table 2.1 : Chemical structures and glass transition temperatures (*T*g) of polysulfone, polyethersulfone and polyphenylsulfone

Polymer	CAS nos.	Repeat unit structure	T_g, °C
Polysulfone (PSF)	[25135-51-7]		185
Polyethersulfone[a] (PES)	[25667-42-9]		220
Polyphenylsulfone (PPSF)	[25608-64-4]		220

PSU is stable in the aqueous acids and bases and also in many non-polar solvents. Moreover it is highly resistant to oxidizing agents, surfactants and hydrocarbon oils and mineral acids, alkalis, and electrolytes, in the pH range of 2 to 13 [54, 55]. Hence PSU has high level of dimentional stability and good hydrolysis resistance for complete products.

Table 2.2 : Material properties of polysulfone

Values	PSU
Tg	188°C
Density	1.24g/cm^3
Modulus of elasticity	2700MPa
Tensile Strentgh	85N/mm^2
Service temperature, long term	160°C
Service temperature, short term	180°C
Lower service temperature	-50°C

2.2.1 Synthesis of Polysulfone

There are many methods for producing polysulfone but Aromatic Nucleophilic Substitution mechanism has been proven to be practical and efficient. In this polycondensation, equimolar quantities of 4,4-dihalodiphenylsulfone (DCDPS) and a bisphenol are reacted in the medium of base in order to form the aromatic ether bonds and eliminate an alkali salt as a by-product. Nowadays this route is preferred especially for the manufacturing of polysulfone in commercial scale [53].

Differentiation of polysulfones is derived from the choice of bisphenol. For the polycondensation of PSU, bisphenol-A is required. A typical polycondensation of polysulfone is demonstrated in Figure 2.5. Alkali base can be provided not only by KOH or K_2CO_3 but also NaOH or Na_2CO_3. Dipolar aprotic solvents like dimethylacedamide (DMAC), dimethyl sulfoxide (DMSO), n-methyl-2-pyrrolidinone (NMP) or combination of DMAC and toluene can be used as solvent [53, 54].

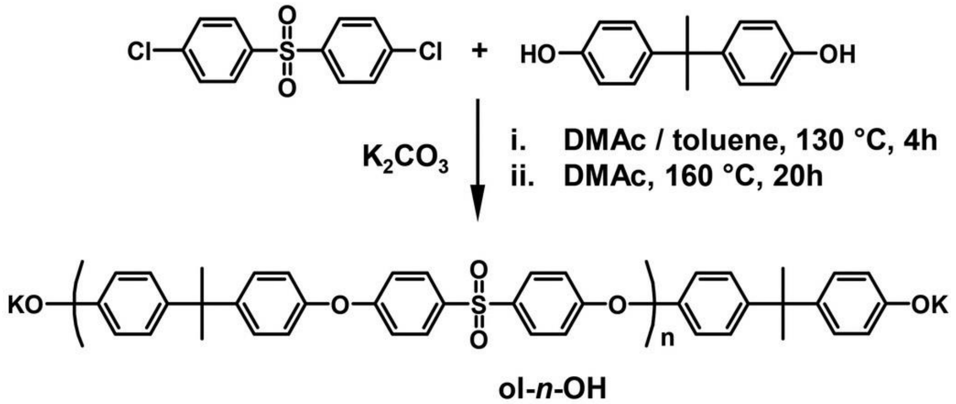


Figure 2.5 : Polycondensation of PSU

There is a two-step process carried out in the case of polysulfone (PSU) synthesis. Firstly bisphenol-A is converted in situ to the dialkali metal salt by the reaction with base (for instance two equimolar of K_2CO_3). This is followed by the nucleophilic substitution reaction of with 4,4-dichlorodiphenylsulfone. In this type of polycondensation, the rate of reaction depends on both the basicity of the bisphenol salt and the electron-withdrawing capacity of the activating group (SO_2) in the dihalide monomer. Hence the electronegativity of the halogen in the dihalide monomer also has a significant effect. Furthermore the purity of the 4,4-isomer in the dichlorodiphenyl sulfone monomer affects the reaction rate too, because of the chlorines in the meta position on the phenyl ring are neither activated nor do not undergo nucleophilic displacement. Polymerization is carried out in an inert nitrogen atmosphere in order to prevent oxidation of bisphenate salt, in the temperature range between 130^oC-160^oC. Water is one of the by-products of this reaction, is removed from the medium by azeotropic distillation, for prohibiting the possible reaction with dichloro monomer that leads to lower molecular weight. Dipolar aprotic solvents increases reaction rate of nucleophilic substitution, thus the molecular weight of the polymer can be very high, if it is not controlled. Addition of monofunctional halides or phenols help to control the reaction rate [53,54].

2.3 Redox Polymerization

Redox systems consist of the oxidation and reduction reactions that the oxidation states of the atoms are changed, where there is an electron transfer occurs between the species. In the oxidation reaction the molecule, atom or ion loses its electron and with the result of an increase at oxidation state. Inversely of that, in the reduction reaction molecule, atom or ion gains an electron and results its decrease at oxidation state. Hence the species increase the oxidation state of another species referred as oxidants, while species decrease the oxidation state of another, referred as reductants. There are many application areas of redox reactions, that the free radical polymerization reactions are one of them [55].

As with other chain reactions, free radical polymerization is a rapid reaction which consists of the characteristic steps of initiation, propagation, and termination. Table 2.3 shows the reaction steps of a general free radical polymerization with their rate constants and rate equations [56]. Almost all free radical polymerization have two initiation steps, first is the radical formation (a) that the species I dissociate to pair of radicals R^* homolytically. In the second step, radical is added to the monomer and creates the chain initiating monomer M_1(b). Later on the propagation step, monomers are added to the monomer radical and after each addition a new radical is generated that keeps on going the chain growing, by having same radical status with previous one. At some point, the propagating polymer chain stops growing and terminates. Termination may occur in two ways, one is the annihilation of the radical centers (c) happens by bimolecular reaction between two radical ends, resulting chain combination (coupling). Latter way is more rarely termination by disproportionation (d), where a hydrogen radical, that is beta to one radical center, is transferred to another radical center. This gives formation of two polymer molecules one is saturated and one is unsaturated.

Table 2.3 : Reaction steps of free radical polymerization

Initiation	Propagation	Termination
$I \xrightarrow{k_d} 2R\bullet$	$M_1\bullet + M \xrightarrow{k_p} M_2\bullet$	$M_n\bullet + M_m\bullet \xrightarrow{k_{tc}} M_{n+m}$
(a)	$M_2\bullet + M \xrightarrow{k_p} M_3\bullet$	(c)
$R\bullet + M \xrightarrow{k_i} M_1\bullet$	$M_3\bullet + M \xrightarrow{k_p} M_4\bullet$	$M_n\bullet + M_m\bullet \xrightarrow{k_{td}} M_n + M_m$
	$\downarrow$	
(b)	$M_n\bullet + M \xrightarrow{k_p} M_{n+1}\bullet$	(d)

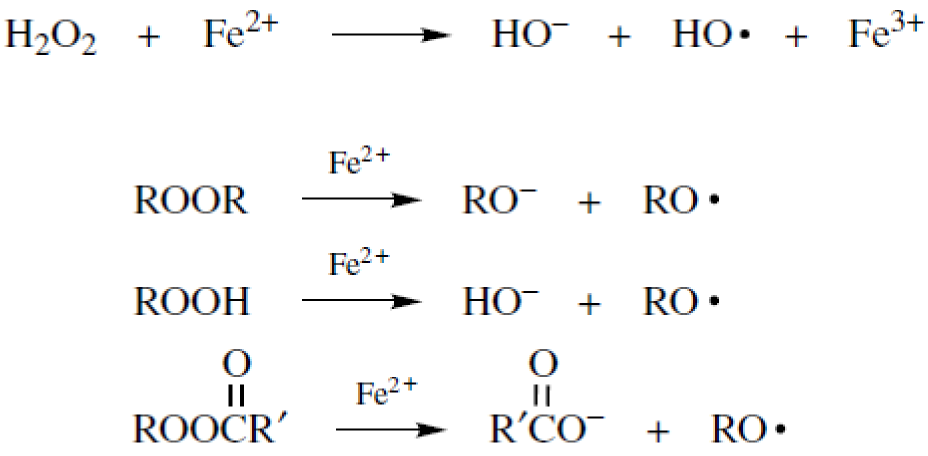
Radical initiation reactions can be divided into two general types according to the manner of first radical species formation, one is the homolytic decomposition as mentioned before and latter one is the electron transfer from ions or atoms containing unpaired electrons followed by bond dissociation in the acceptor molecule. These oxidation-reduction reactions generate radicals, which can be used for initiating polymerization reactions [57]. This kind of initiation is called as redox initiation, redox catalysis or redox activation. And the polymerizations initiated by a reaction between an oxidizing and a reducing agent are called redox polymerizations. In this process an oxidant such as Ce(IV) or Mn(III) forms initially a complex by reacting simply with organic molecules which then decomposes unimolecularly to produce free radicals that initiate polymerization [58].

The great advantage of redox polymerization is that the radical production and polymerization can be achieved at a mild temperature range between 0-50^{o}C with reasonable reaction rates. This is beneficial not only for freedom of choice of the polymerization temperature, but also for prohibiting some of the side reaction that may occur during polymerization at high temperatures [56-59]. Moreover redox initiation requires short induction period since these systems have much larger decomposition rate and polymerization happens in a short time with high yield [60, 61]. Apart from the fact that low temperatures can be employed with redox systems, the reaction rate is easy to control by varying the concentration of metal ion or peroxide [62].

Redox polymerizations are usually carried out in aqueous solution, suspension, or emulsion- more rarely in organic solvents. Most of the redox reactions involve both of organic and inorganic species in a whole or partially ways. Although some of the redox systems contain direct electron transfer between reductant and oxidant, others contain intermediate formation of reductant-oxidant complexes, these are also change transfer complexes for some situations.

2.3.1 Types of redox initiators

Peroxides in combination with a reducing agent are a common source of radicals; for example, the reaction of hydrogen peroxide with ferrous ion. Ferrous ion also promotes the decomposition of a variety of other compounds including various types of organic peroxides [63]. Other reductants such as Cr^{2+}, V^{2+}, Ti^{3+}, Co^{2+} and Cu^{+} can be employed in place of ferrous ion in many instances.



$$H_2O_2 + Fe^{2+} \longrightarrow HO^- + HO\bullet + Fe^{3+}$$

$$ROOR \xrightarrow{Fe^{2+}} RO^- + RO\bullet$$

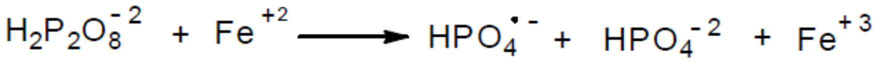
$$ROOH \xrightarrow{Fe^{2+}} HO^- + RO\bullet$$

$$RO\overset{O}{\overset{\|}{O}C}R' \xrightarrow{Fe^{2+}} R'\overset{O}{\overset{\|}{C}}O^- + RO\bullet$$

Figure 2.6 : Redox initiation by peroxides

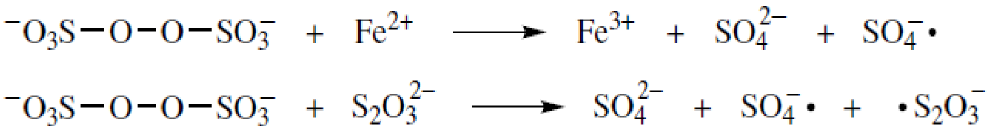
The combination of a variety of inorganic reductants and inorganic oxidants initiates radical polymerization, for example like in Figure 2.6. Other redox systems include reductants such as HSO^{3-} , SO_2^{-3}, $S_2O_3^{2-}$, $S_2O_5^{2-}$ in combination with oxidants such as Ag^{+}, Cu^{2+}, Fe^{3+}, ClO^{3-} and H_2O_2**.**

A new water soluble initiator for vinyl polymerization, peroxydiphosphates was introduced by Hariharan and Meenakshi in Figure 2.7 and 2.8. In conjunction with Ag^{+}, V^{5+}, Co^{2+} peroxydiphosphate forms an efficient redox system for the polymerization of acrylonitrile [64].



$$H_2P_2O_8^{-2} + Fe^{+2} \longrightarrow HPO_4^{\bullet -} + HPO_4^{-2} + Fe^{+3}$$

Figure 2.7 : Redox initiation by peroxydiphosphates

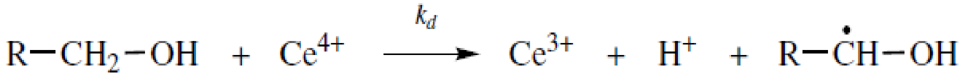


$$^{-}O_3S-O-O-SO_3^{-} + Fe^{2+} \longrightarrow Fe^{3+} + SO_4^{2-} + SO_4^{-}\bullet$$

$$^{-}O_3S-O-O-SO_3^{-} + S_2O_3^{2-} \longrightarrow SO_4^{2-} + SO_4^{-}\bullet + \bullet S_2O_3^{-}$$

Figure 2.8 : Redox initiation by inorganic reductants and oxidants

Organic–inorganic redox pairs initiate polymerization, usually but not always by oxidation of the organic component, for example, the oxidation of an alcohol by Ce^{4+}, or by V^{5+}, Cr^{6+}, Mn^{3+} shown in Figure 2.9 [65-67].



$$R-CH_2-OH + Ce^{4+} \xrightarrow{k_d} Ce^{3+} + H^{+} + R-\dot{C}H-OH$$

Figure 2.9 : Initiation by organic-inorganic redox pairs

There are some initiator systems in which the monomer itself acts as one component of the redox pair. Examples are thiosulfate plus acrylamide or methacrylic acid and N,N-dimethylaniline plus methyl methacrylate [68,69].

2.3.2 Rate of Redox Polymerization

Many of the radical polymerizations proceed in the same way, as the propagation and termination steps; but the only difference of redox system is the source of radicals for the initiation step. The initiation step represented in Figure 2.10. The rate of monomer disappearance, which is synonymous with the rate of polymerization, is given by equations starting from (2.1) [56]. In the first equation R_i and R_p are the rates of initiation and propagation, respectively.

$$M + I \longrightarrow M\cdot + R\cdot$$

Figure 2.10 : Initiation step of free radical polymerization

$$\frac{-d[M]}{dt} = R_i + R_p \qquad \textbf{(2.1)}$$

The number of monomer molecules reacting in the initiation step is lesser than the number in the propagation step. Hence for making a good approximation R_i can be neglected and the polymerization rate becomes as given in equation (2.2) simply by the rate of propagation.

$$\frac{-d[M]}{dt} = R_p \qquad \textbf{(2.2)}$$

The rate of propagation also known as the rate of polymerization is the sum of many individual propagation steps. Because the rate constants for all the propagation steps are the same, the polymerization rate can be written as in equation (2.3), where [M] is the monomer concentration and $[M^*]$ is the total concentration of all chain radicals.

$$R_p = k_p[M][M^*] \qquad \textbf{(2.3)}$$

According to the steady-state assumption the concentration of radicals increases initially, but after a while reaches a constant steady-state value. Consequently the rate of change of the concentration of radicals becomes and remains zero fast, during the polymerization. Thus the rates of initiation R_i and termination R_t of radicals are may be stated equal.

$$R_i = R_p = 2k_t[M^*] \qquad \textbf{(2.4)}$$

The right side of equation (2.4) represents the rate of termination. Due to the both of terminations follow the same kinetic expression there is no specification whether is by coupling or disproportiation. The use of the factor of 2 in the equation comes from the generally accepted convention for reactions destroying radicals in pairs. This equation can be rearranged like below.

$$[M^*] = \left(\frac{R_i}{2k_t}\right)^{1/2} \qquad \textbf{(2.5)}$$

$$R_p = k_p[M]\left(\frac{R_i}{2k_t}\right)^{1/2} \qquad \textbf{(2.6)}$$

The kinetics of redox polymerizations generally are examined in two categories depending on the termination mode. For the redox polymerizations having bimolecular termination reaction of propagating radicals, the initiation and polymerization rates are like given in equation (2.7) and (2.8). Since the initiation step for redox polymerization involves oxidation and reduction reactions, [M*] is depended on both reductant and oxidant concentrations.

$$R_i = k_d[Reductant][Oxidant] \qquad \textbf{(2.7)}$$

$$R_p = k_p[M](\frac{k_d[Reductant][Oxidant]}{2k_t})^{\frac{1}{2}} \qquad \textbf{(2.8)}$$

There might be change in the termination step, for some redox polymerizations, from the usual bimolecular reaction to monomolecular termination includes the reaction of propagating radicals and a component of the redox system. As in the case of alcohol-Ce^{4+} system, the termination step occurs according to reaction shown in Figure 2.11. This leads to noticeably different kinetics from the previous redox termination mechanism.

$$M_n\cdot + Ce^{4+} \longrightarrow Ce^{3+} + H^+ + \text{dead polymer}$$

Figure 2.11 : Monomolecular termination reaction of alcohol-Ce^{4+} system

The propagating radical loses a hydrogen to form a dead polymer with a C-C end group. The rates of initiation and termination are given in equations (2.9) and (2.10).

$$R_i = k_d[Ce^{4+}][Alcohol] \qquad \textbf{(2.9)}$$

$$R_t = k_t[Ce^{4+}][M^*] \qquad \textbf{(2.10)}$$

By making the usual steady-state assumption, the redox polymerization rate is obtained as in equation (2.11). First order dependence of R_i on [M] results in 3/2 and 2 order dependencies of R_p on the [M], for bimolecular and for monomolecular terminations respectively.

$$R_p = \frac{k_d k_p[M][Alcohol]}{k_t} \qquad \textbf{(2.11)}$$

2.3.3 Synthesis of Block Copolymers via Redox Polymerization

Although there are several methods in the literature for preparing block copolymers, initiation by a redox process is only a method to obtain some types of polymers [70-72]. Basically a polymer having functional end groups is treated with the other monomer medium in a redox system, and then polymer chains become macro initiator- initiated by redox reactions- that the monomers attached them and propagates [72,73]. An example to these kinds of copolymerization studied by Catula and co-workers [74,75], that the hydroperoxide terminated poly (styrene) was prepared by a reaction sequence as shown in Figure 2.12. Reacting polymeric hydroperoxide with ferrous sulphate in the presence of a second monomer afforded block copolymers.

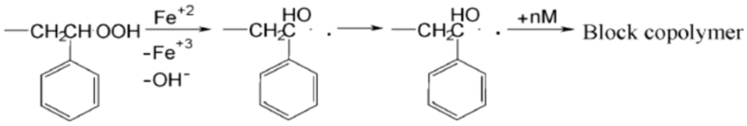


Figure 2.12 : Synthesis of block copolymers via Fe^{2+}/hydroperoxy containing polymers

The synthesis of block copolymers by redox systems asserts various technical and theoretical advantages over other methods, due to the applicability at low temperatures, minimized side reactions [59]. Hence this method has found broad application field in the initiation of a lot polymerization reactions [66, 77] and with an industrial importance arising from low-temperature emulsion polymerizations [57, 78]. There are diverse redox systems, such as ceric, manganese, cupper, iron, vanadium ion, and hydrogen peroxide, have been used as catalysts for synthesis of block copolymers via redox polymerization.

2.4 Conducting Polymers

Polymers had been thought as insulating materials and mostly used for this purpose until mid-seventies. However that fact has been changed by Plastics Research Laboratory of BASF in Germany thirty years ago, who discovered first conducting polymers [79]. Since then, an entire class of polymeric conductors was developed. The well known representers of this class of polymers are poly(p-phenylene), polythiophene and its 3-methoxy- derivative polyaniline and polypyrrole [80-84].

The conducting polymers attract attention of researchers and engineers due to having several application areas in science and technology, such as promising electrode materials for energy storage devices, biosensors, photoluminescent and electroluminescent materials, artificial muscles, membranes, anticorrosive coatings, electromagnetic shields etc. [85]. Beside these applications, the possibilities to produce conducting polymers electrochemically and to control their properties by electrochemical means are of interest on their own.

2.4.1 Doping

The common feature of the structure of conducting polymers is polyconjugation which is the placement π-bond sequentially on their backbone like in the Figure 1. Polyconjugation acquires the electronic properties of metals to the polymers, while maintaining the mechanical properties and processibility of them. The resulting materials have typical conductivities of metals or semiconductors, 1 to 10^5 S/cm [86]. Although polyconjugation has a key role on polymer conductivity, it is not enough to obtain a good conductive polymer. Shirikawa and co-workers made experiments on semi-conductive polymers, in order to increase the conductivity of them, by oxidizing the polymer film with halogen vapors such as chlorine, bromine or iodine, which resulted a hundred times better conductive polymer film [87]. The procedure called as "doping".

The doping is performed by means of chemical or electrochemical oxidation (p-doping) or reduction (n-doping) of a polymer. The doping is reversible; as a result of dedoping (removal of dopant), the initial polymer can be obtained with its polymeric structure intact. Regulation of the level of doping provides a possibility to prepare polymers with widely varied electric conductivity, from insulating or semiconducting forms of the polymer in the undoped state to highly conductive ones in the strongly doped state. As a result, the polymeric chains acquire positive or negative charges, respectively [88]. Electroneutrality of the material as a whole is protected by incorporation of dopants (counterions) from electrolyte solution into the polymeric matrix.

The oxidation of polymers with electron-accepting compounds referred as "p-doping" [89]. These oxidizing compounds of the p-doping are the p-dopants, consist Br_2, I_2, Cl_2, and AsF_5. The conductivity of these polymers is considered as a result of the creation of charge-transfer complexes between the polymer and halogen [90]. Charge-transfer generated from polymer to the p-dopant; where polymer chain acts as a cation and the p-dopant behaves as an anion.

Conductive polymers can also be prepared by utilization of n-doping, which charge transfer complexes are created like the p-doping, but differently from the other method the polymer backbone behaves anionic and the dopant acts as cationic. Naturally n-dopants are the electron donating compounds include lithium, sodium and potassium [91]. The increase in conductivity upon treatment with an n-type dopant is not as significant as those achieved upon treatment with a p-type dopant.

2.5 Polypyrrole

Among the conducting polymers known to date, polypyrrole based ones have a attracted special interest due to their high conductivity, their ease and high flexibility in preparation, their stability and good mechanical properties [86]. PPy has a wide technological application field consist electronic and electrochromic devices [92-93], counterelectrode in electrolytic capacitors [94] sensors [95-96], chromatographic stationary phases [97], light-weight batteries [98] and membrane separation [99]. The usefulness of this polymer has been realized as this material exhibits several interesting properties such as reversible redox activity [100], ability to form thin films, nanowires with room temperature conductivity ranging 10^{-4} to 10^{-2} S/cm charge/distance processes [101,102] and catalytic activity [103-105].

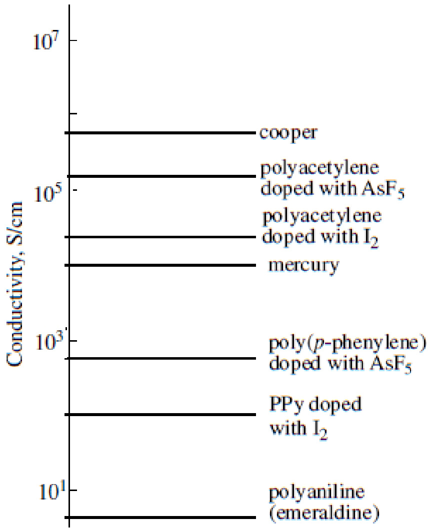
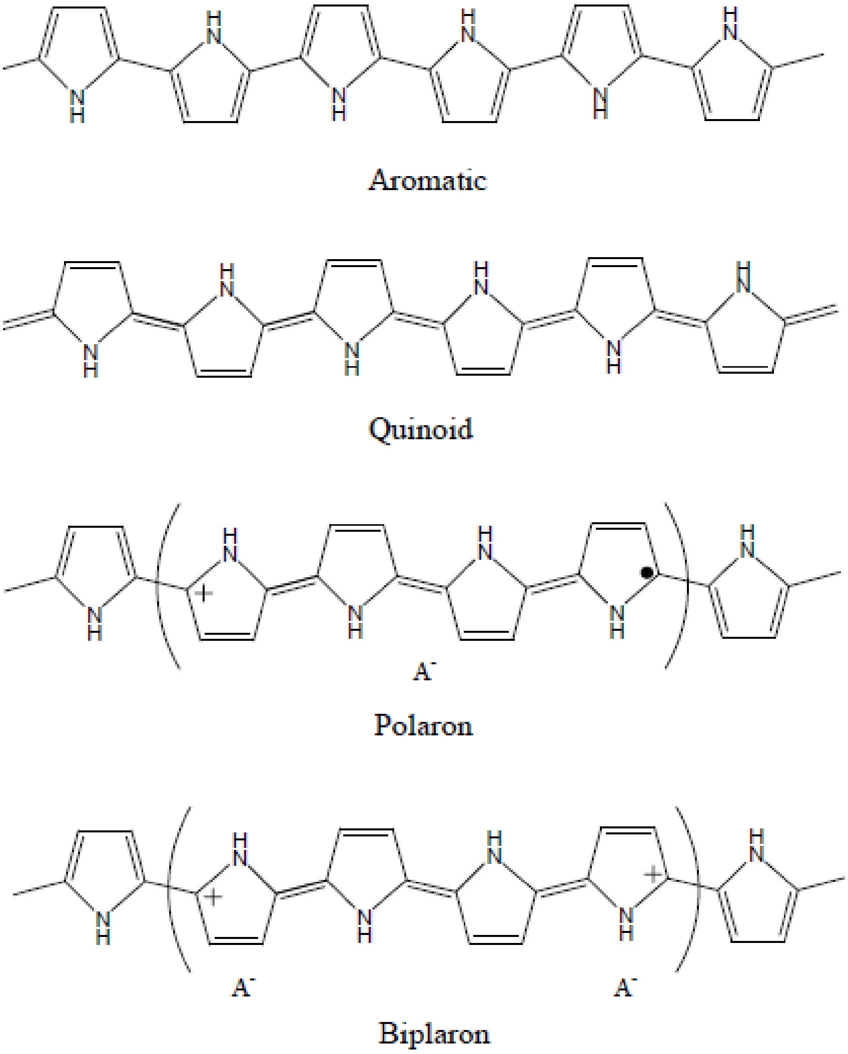


Figure 2.13 : Conductivity levels of polymers

Polypyrrole has a long conjugated backbone obtained from the polymerization of pyrrole monomer as seen in Figure 2.14. The polymer has resonance structures that resemble the aromatic or quinoid forms. In this neutral state the polymer is not conducting unless it is oxidized. Polypyrrole only becomes conducting when it is oxidized since the charge associated with the oxidized state is typically delocalised over several pyrrole units and can form a radical cation (polaron) or a dication (bipolaron). The physical form of polypyrrole is usually an intractable powder resulting from chemical polymerization and an insoluble film resulting from electropolymerization [106].



Aromatic

Quinoid

Polaron

Biplaron

Figure 2.14 : Polypyrrole and its oxidazing states

Polypyrrole is amorphous [84]. The experimental data indicate that the crystalline regions have a monoclinic lattice; the pyrrole rings are oriented so that nitrogens of neighboring rings are oriented in opposite directions [107]. The films prepared by electro-deposition in the presence of inorganic anions are relatively brittle; their mechanical properties are usually higher than those of the films doped with bulky organic anions [108-110]. The tensile strength for PPy films with different dopant anions varies from 8 to 100 MPa; the elongation at break, is within 2%-8%; the Young's modulus, 0.4-4GPa [108,110,111]. The elongation at break can be substantially enhanced (to 70%), when PPy is synthesized at low temperatures [107] According to Ref. [111], the elasticity of the freshly prepared films, which contain solvent, is higher, their elongation at break reaches 60%. The films reversibly absorb solvent (water, AN); they also absorb water vapor from air [112,113].

The stability in air of the doped PPy films is relatively high; their degradation occurs only above 150-300^{o}C (depending on the dopant anion) [84,114]. Thermal degradation of PPy starts with the loss or decomposition of dopant [115]. Further deprotonation or further dopant loss at higher temperatures is alwaysaccompanied by formation of imine-like structures in the polymer. The thermal stability of the films esteblished by their treatment with H2SO4, Na2SO4 or NaHSO4, before electro plymerization [116].

2.5.1 Synthesis of Polypyrrole

Polypyrrole (PPy) can be formed chemically or electrochemically through oxidative polymerization of pyrrole monomer. PPy is already synthesised from a range of aqueous and non-aqueous solvents [117]. In fact, PPy is one of the few electronically conducting polymers that can be prepared in aqueous solutions [118].

2.5.1.1 Electrochemical Polymerization of Pyrrole

Preparing conducting polymers electrochemically is a complex process, and the yield and quality of the resulting polymer films are affected by various factors [119]. Many experimental factors (chemical and physical) such as pH, electrodes, temperature, nature and concentration concentration of monomer/counterion, potential of growth, and even cell configuration affect the electrical, electrochemical, mechanical, and morphological properties of the resultant films.

Although there are number of mechanisms have been proposed, among these, Diaz’s mechanism is the most accepted one supported [120, 121]. In this mechanism, the pyrrole (Py) activation occurs through electron transfer. Electropolymerization starts from monomer forming a radical cation-rich solution near the electrode in several steps. Details of these reaction steps given in Figure 2.15.

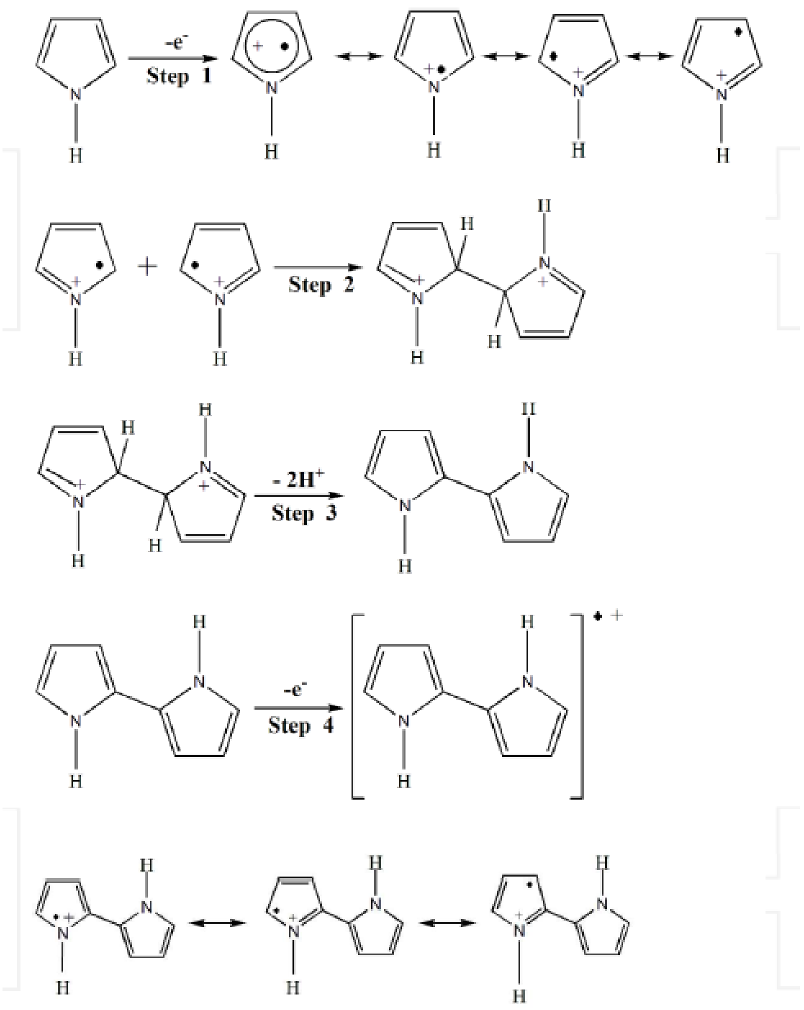


Figure 2.15 : Electrochemical polymerization mechanism of PPy

The propagation continues via the sequences of oxidation, coupling and deprotonation until the final polymer product is formed in Figure 2.16 (a). The electro polymerization gives oxidized conducting form (dopped) of the polymer. By the way the final polymer chain carries a positive charge every 3-4 pyrrole units, which is counter balanced by an anion. The structure of the doped polymer can be given as shown in Figure 2.16 (b). Electrochemical film formation is often followed by stoichiometric determination of the number of electrons donated by each molecule. This value is generally found to be in between 2 and 2.7, where 2 electrons serve in the film formation and the excess charge is consumed by the polymer oxidation [121].

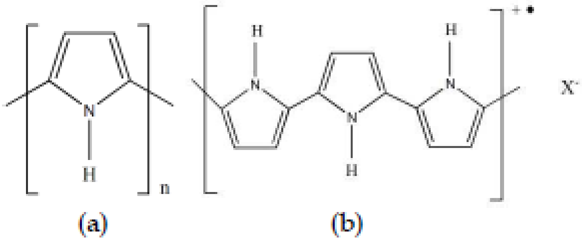


Figure 2.16 : General formula of PPy and doped PPy

Termination occurs when no further monomer is present for oxidative polymerization or side reactions terminate the PPy chain. An example of a termination reaction is the reaction with water to form the amide group. It is believed that the reaction with water could be responsible for the polymerization quench [106, 122].

2.5.1.2 Chemical Polymerization of Pyrrole

Chemical synthesis of PPy prepared by oxidation of the monomer with chemical oxidants has a form of black powder. Aqueous or anhydrous $FeCl_3$, other salts of iron(III) and copper(II) are widely used as chemical oxidants [123,124]. The mechanismis similar to that for electropolymerisation of pyrrole and conductivities are comparable [106]. As in the reaction mechanism in Figure 2.17, when PPy is produced by oxidation in the presence of $FeCl_3$, the polymer is doped with Cl- anions, where y is the degree of PPy oxidation (doping level) stochiometricly [123].

$$\begin{aligned} n\,C_4H_5N + (2+y)n\,FeCl_3 \rightarrow [(C_4H_3N)_n^{y+}\;ny\,Cl^-] &+ \\ + (2+y)n\,FeCl_2 + 2n\,HCl&, \end{aligned}$$

Figure 2.17 : Chemical oxidative polymerization of PPy with $FeCl_3$

The yield and conductivity of the PPy produced are affected by a variety of factors, among which are the choice of solvent, pH and oxidant, initial pyrrole/oxidant ratio, duration and temperature of the reaction [119]. For instance at the optimal ratio of Fe(III)/monomer which is 2.4, the yield of PPy approaches 100% [125]. Also shorter times of polymerization and lower temperatures (0 to 5oC) generates PPy with an enhanced conductivity [126].

2.6 Polysulfone-Polypyrrole Membranes and Their Synthesis Routhes

Membrane technology has a significant role on separation techniques, since membranes are applied on many areas such as water and wastewater treatment, chemical, petrochemical, metallurgical related industries, gas separation, food industries and bioseperations [127]. Polysulfone (PSU) is one of the most preferred polymers for membrane production due to its properties. PSU membranes used in the fields of microfiltration, ultrafiltration, reverse osmosis and gas separation and so on [2]. Addition to that polypyrrole also has membrane applications apart from its electronic usage areas. Polypyrrole membranes especially prefferd for gas separation Polypyrrole (PPy) is a chemically extremely resistant polymer, being insoluble inmany organic solvent. Compared with conventional polymers, PPy has a high surface energy, as well as good electro-conductive and acid–base properties [128]. In the membrane field, PPy based membranes have already been mentioned in gas separation and pervaporation [129, 130].

Although both polymer material provides good membrane properties, either of them have weaknesses, caused by fouling effect and mechanical disadvantages [8,131,132]. These problems can be overcome by making copolymer, graft and composite/nanocomposite production. Besides this, new additional properties com be discovered such as pH sensivity [133], UV resistance [134], antimicrobiality [135] and conductivity [16]. Hence these researches are important not only improving drawbacks, but also it is essential to modify the properties of a polymer according to tailor-made specifications designed for target applications.

There are studies about polysulfone-polypyrrole composite membranes, generally applies the phase invertion thecnique with chemical reaction in order to obtain composite combination of them [15, 16]. PSU membranes are gained conductivity via their combination with PPy, and by the way PPy membrane’s mechanical properties improved by PSU.

Phase inversion technique is generally consist of the exchange of the solvent from the polymeric solution with a non-solvent for the polymer, but which is miscible with the solvent [136]. The polymerization of pyrrole (non-solvent) in PSU (polymer) occurs after inversion and membrane casting, where PSU-pyrrole mixture immersed into a oxidant, such as Fe(III)Cl_3, containing medium in order to initiate redox polymerization of pyrrole monomers in the PSU matrix. Hence this reaction results a composite of two polymer.

There is also another option to combine the properties of these two polymer in one case, which is copolymerization. However in normal circumstances it is hard to copolymerize two different polymers having different polymerization routes. But some studies supports new copolymerization technique which makes possible the pyrrole monomer can make copolymers with polymers like PSU by end-capping of other polymer [137,138]. In this method non-conductive polymer's end groups functionalized by a linkage group, such as thienyl end group for PPy [138], afterwards pyrrole monomers attach the end groups of that macromer and polymerize from here. The general reaction mechanism is shown in Figure 2.18 [137]. Consequently blocks of two chemically different polymers are covalently bonded.

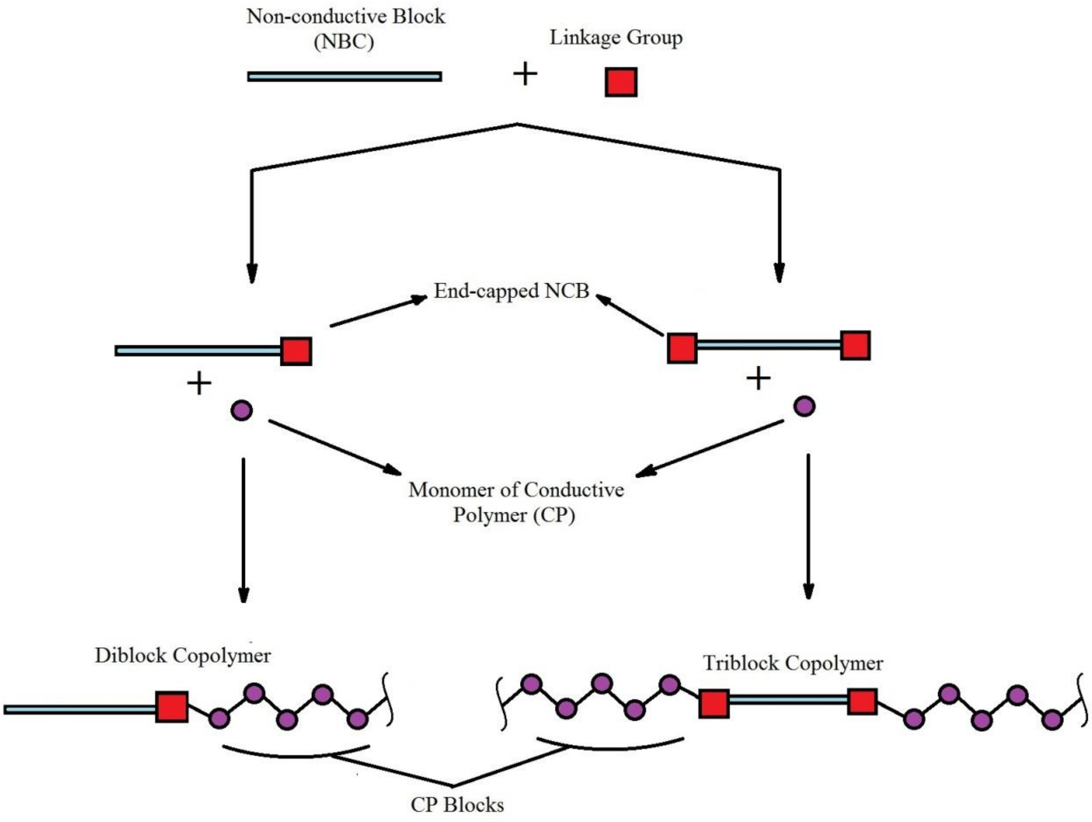


Figure 2.18 : General reaction mechanism of block copolymer synthesis for chemically different polymers

2.7 Sepiolite

Sepiolite is a montmorillonite, belongs to the phyllosilicate family [19]. It has hydrous magnesium silicate layered clays with $(Si_{12}Mg_8O_{30})(OH)_4(OH)_2 4.8H_2O$ theoretical unit cell formula and its molecular structure shown in Figure 2.19. Moreove it has excellent fiber structure different than other montmorillonites of layered clays, which comes from its tetrahedral and octahedral oxide layers packaging [20]. This fiber structure is consist of various channels and tunnels that gives large surface are and porosity. Therefore sepiolite channels give great capacity of absorption and good surface properties, which is also uselful for membrane production [3,21,22]. Sepiolite has good mechanical qualities, resistance to humidity and low cost. Additionally sepiolite has good mechanical qualities, resistance to humidity and low cost. It is also used for biomedical application since it is a natural and biodegradable product [22]. Therefore sepiolite is used in many industrial products.

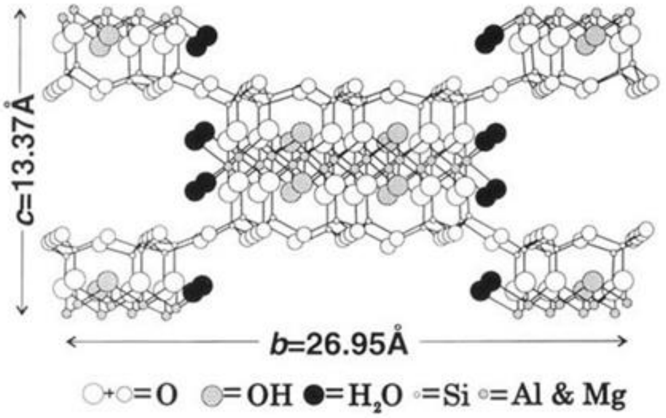


Figure 2.19 : Structure of sepiolite

3. EXPERIMENTAL PART

3.1 Material

Sepiolite was commercially purchased from Tolsa Group in Turkey. Bisphenol-A (BPA), 2-thiophenecarbonyl chloride (ThCCl), p-chlorophenylsulfone, pyrrole (Py), iron (III) Chloride ($FeCl_3$) and hydrochloric acid (HCl) are supplied from Sigma Aldrich. Sodium bicarbonate ($NaHCO_3$) is from Tekkim; pyridine is from Analar, dichloromethane (DCM) and N,N-dimethylacetamide (DMAC) are from Merck; and toluene is from Alfa Aesar. All ingredients are reagent-grade chemicals of the highest purity, so they were used without further purification.

3.2 Analyses

For solution mixing, Heidolph magnetic stirrer (MR Hei-Standart) was used. Fourier transform infrared spectra were recorded on a Perkin-Elmer FT-IR Spectrum One B spectrometer. SEM images taken by The Philips XL30 ESEM-FEG/EDAX system: Microscopy & Microanalysis Lab. Electrical conductivities of the solid products were measured by using four point probe technique and WTW micro processor type conductometer. NMR analysis was made Agilent VNMRS 500 MHz Nuclear Magnetic Resonance Spectrometer.

3.3 Conductivity Measurement

To measure electrical conductivity of precipitates, compact thin pellets were prepared under 8-10tons/cm2 pressure. A typical sample has diameter 13mm at a thickness of 0.6mm. Conductivity measurements of polymers were performed by the four probe technique and calculated from the following equation (2.1).

$$\sigma = V^{-1} * I * (ln2\ /\pi d_n) \qquad \textbf{(3.1)}$$

Parameters are explained individually, where σ is resistance (kΩ), V is the potential (V), I is the current (A), and dn is the thickness of the samples (cm).

3.5 Preparation of Blank Polypyrrole

Polypyrrole was synthesized by chemical oxidative polymerization using iron (III) chloride as an oxidant. Reaction medium was selected as pure water. First, 0,3 ml pyrrole monomer (0,0043 mol) was dissolved in 20 ml water and put on the magnetic stirrer. Then 1,673 g FeCl3 which dissolved in 35 ml water was added to the reaction medium dropwise by a dropping funnel. The color of the reaction mixture was turned from yellowish to black while oxidant addition.The reaction took place at 25 ^{o}C and lasted about 24 hours.

At the end of the reaction, black powders were observed. The product was filtered with filter paper, washed with water, methanol and acetone several times, in order to eliminate any unreacted parts including remaining iron (III) chloride and oligomers. The resultant polymer was dried at 45 ^{o}C in vacuum oven.

3.6 Synthesis of Polysulfone

In this study it is considered to synthesize polysulfone with lower molecular weight comparing with commercial PSU, to achieve its end-group functionalization and via its copolymerization in the later steps. In order to obtain PSU-4000, bisphenol A and p-chlorophenylsulfone were taken 6:5 molar ratio respectively. After that dried potassium carbonate was taken 1:1 ratio with p-chlorophenylsulfone. All those materials were weighted and added into a 2 necked round bottom flask. N,N-dimethyl acetamide and toluene mixture was added to the reaction flask as solvent medium. DMAC and Toluene mixture were combined with 8:1 ratio respectively. One of the necks of the flask was fitted with nitrogen inlet, and the other neck was fitted with a Dean and Stark trap for the removal of the water by-product from the reaction medium. The reaction proceeded by mixing, under reflux at 150°C, for 12h, in the N_2 atmosphere. Polycondensation occurs as shown in Figure 3.1.

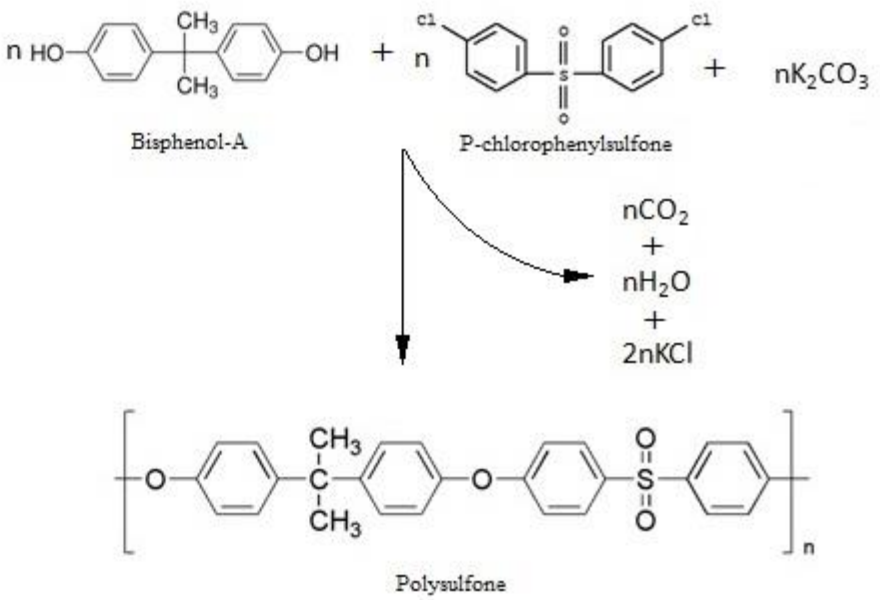


Figure 3.1 : Polycondensation of PSU

After the reaction, the reaction flask was leaved to cool for 2 hours at room temperature. The reaction mixture was filtered to remove the salts occurred as by-product. Filtered polymer solution was poured into methanol and water mixture, which was prepared with 4:1 volume ratio respectively. The precipitated polymer was filtered, and washed several times with methanol. Finally, the polymer was dried in a vacuum oven at 65°C for 12h.

3.7 Synthesis of Polysulfone-Sepiolite Nanocomposite

Polysulfone-Sepiolite nanocomposite was prepared by in situ method. It has basically the same reaction route with normal polysulfone synthesis except addition of nanoparticles. Bisphenol-A and bis p-chlorophenylsulfone were taken 6:5 ratio respectively and dried potassium carbonate was taken 1:1 ratio with p-chlorophenylsulfone. Sepiolite was taken 1% of the total solid mass. All ingredients were weighted and added into a 2 necked round bottom flask. N,N-dimethyl acetamide and toluene mixture was added to the reaction flask as solvent medium, that DMAC and Toluene mixture were combined with 8:1 ratio respectively. One of the necks of the flask was fitted with nitrogen inlet, and the other neck was fitted with a Dean and Stark trap for the removal of the water by-product from the reaction medium. The reaction proceeded by mixing, under reflux at 150°C, for 12h, in the N_2 atmosphere.

In the end of the reaction product was filtered by filtrate paper for the removal of salt by products. Later methanol water solution with 4:1 volume ratio respectively was prepared and poured into the reaction mixture, which resulted polysulfone-sepiolite polymer nanocomposites precipitation. Polymer nanocomposite was filtered again and residue was washed with methanol for several times. Afterwards polymer nanocomposite was dried in vacuum at 65^{o}C for 12h.

3.8 End Group Functionalization of Polysulfone

The end groups of the polysulfone was reacted with 2-thiophenecarbonyl chloride in order to synthesize a macromonomer containing thienyl (ThC) end-group. The reaction proceeded in the N_2 atmosphere at 0^{o}C for 24 hours. For this reaction a 3 necked 200ml round bottom flask, a mechanical mixer, a dropping funnel, condenser, N_2 adapter and ice bath were used. 3g of PSU was weighed and added in to the reaction balloon, then chloroform was taken as the solvent medium with the ratio of 35ml for 10g PSU. Afterwards prydine was poured into the balloon, in order to eliminate chloride part, which comes from 2-thiophenecarbonyl chloride, with the estimated amount by the following equation (3.1).

$$n_{Prydine} = 1.2 * n_{Tyofen} \qquad \textbf{(3.2)}$$

Thiophene-2-carboxylic acid chloride amount was calculated according to the equation (3.2) and added into the dropping funnel with 5ml chloroform.

$$n_{Tiyofen} = 2.2 * n_{PSU} \qquad \textbf{(3.3)}$$

Reaction balloon was placed on the ice bath, to prevent a violent reaction may be happened between thiophene-2-carboxylic acid chloride and PSU. Then mechanic stirrer was assembled at the middle neck of the reaction flask. One of the empty necks was attached with the condenser and the other neck was connected with N_2 adaptor and stirrer was switched on. For an hour N_2 gas passed through the reaction medium. Latter N_2 adaptor is ejected and dropping funnel was attached with the neck. Dropping rate was adjusted to finish its content in 30min. After all the material in the funnel was dropped in the reaction medium, N_2 adaptor was placed on the neck again and reaction proceeded for 24 hours with the mechanism given in Figure 3.2.

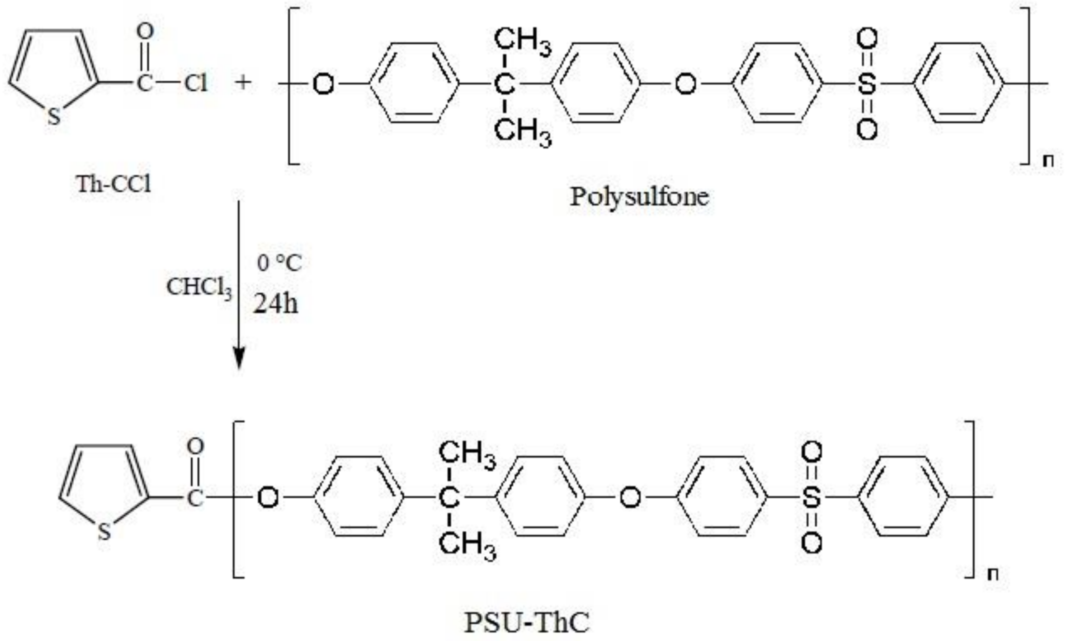


Figure 3.2 : Thienyl end capping reaction mechanism of PSU

After reaction, hot dichloromethane was added in order to eliminate pyridium chloride for purification. Then, reaction mixture was extracted by 5% HCl solution and 10% $NaHCO_3$ solution, respectively. In order to crystallize the PSU-ThC, the extracted solution was washed with hot methanol and filtrated to obtain crystals. Finally, the product was dried at 65^{o}C in vacuum oven for 6 hours.

3.9 End Group Functionalization of Polysulfone/Sepiolite Nanocomposite

The end groups of the PSU/Sepiolite nanocomposite has the same reaction steps with end capping reaction of PSU mentioned before. Similarly PSU/Sepiolite was reacted with 2-thiophenecarbonyl chloride for obtaining a macromonomer containing thienyl (ThC) end-group. The reaction proceeded under N_2 atmosphere at 0^{o}C for 24 hours.

A 3 necked 200ml round bottom flask with a mechanical mixer, a dropping funnel, condenser, N_2 adapter and ice bath were used for this reaction in the same way. 3g of PSU/Sepiolite was added into the reaction balloon then dissolved by chloroform, which was added with the ratio of 35ml for 10g PSU/Sepiolite. Afterwards prydine was added, with the estimated amount by equation (3.1). Thiophene-2-carboxylic acid chloride amount was calculated according to the Equation (3.3) and added into the dropping funnel with 5ml chloroform.

$$n_{Tiyofen} = 2.2 * n_{PSU\,/Sepiolite} \qquad \textbf{(3.4)}$$

Reaction balloon was placed on the ice bath, then mechanic stirrer was assembled to the flask from the middle neck. One of other necks was attached with the condenser and the other neck was connected with N_2 inlet and stirrer was switched on. Similarly N_2 gas was passed through for 1h, latter on N_2 adaptor was replaced with dropping funnel. Dropping rate was adjusted to finish its content in 30min. After all the material in the funnel is emptied, N_2 adaptor was placed on the neck again and reaction proceeded for 24 hours.

Hot dichloromethane was added in reaction product for elimination of pyridium chloride from the medium. Then, reaction mixture was extracted by 5% solution and 10% $NaHCO_3$ solution, respectively. For crystallization of PSU/Sepiolite-ThC, the extracted solution was washed with hot methanol and filtrated. At last, the product was dried at 65^{o}C in vacuum oven for 6 hours.

3.10 Preparation of Thyenil End-Capped Polysulfone-Polypyrrole Copolymers

Copolymers of PSU-ThC and pyrrole were synthesized by chemical oxidative polymerization using iron (III) chloride as an oxidant. PSU-ThC served both as a macromonomer and acquires some of the polysulfone's good chemical and mechanical properties to the polypyrrole. Pyrrole and PSU-ThC amounts were taken according to the following equation (3.4).

$$n_{Pyrrole} = 50 * n_{PSU-ThC} \qquad \textbf{(3.5)}$$

PSU-ThC was taken 1g and dissolved with pyrrole in 40ml DMAC solvent and added into a beaker glass. The molar ratio of iron (III) chloride to pyrrole was determined by equation (3.5). Then $FeCl_3$ mixture was prepared with 25ml DMAC.

$$n_{FeCl_3} = 2.4 * n_{Pyrrole} \qquad \textbf{(3.6)}$$

$FeCl_3$-DMAC mixture was given to the reaction mixture via a dropping funnel, about 10 minutes. The reaction took place at 25^{o}C and lasted about 24 hours. End of the reaction it was observed that the color of reaction mixture is black and copolymer is soluble in its solvent. Copolymerization mechanism is shown in Figure 3.3.

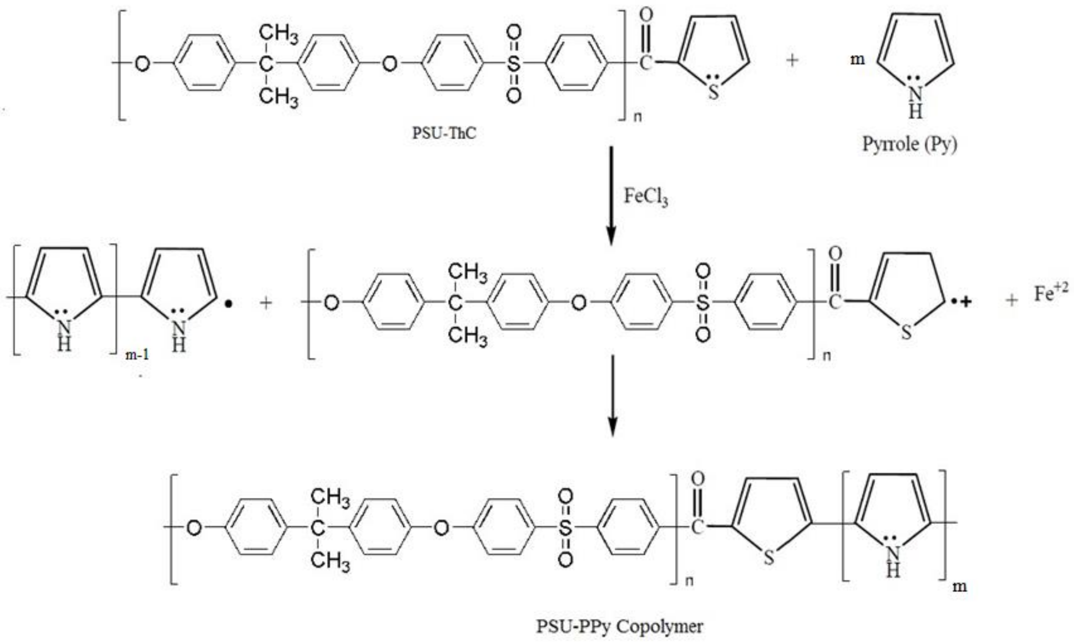


Figure 3.3 : Copolymerization of PPy and PSU-ThC

After the reaction, methanol was poured in the reaction mixture, then PSU-PPy copolymers starts to precipitate. Copolymer product was filtered by thin filter paper, later on the product washed with methanol first, then with acetone for several times for getting rid of the $FeCl_3$ remaining. The resultant polymer was dried in the vacuum at 45°C.

3.11 Preparation of Thyenil End-Capped Polysulfone/Sepiolite-Polypyrrole Copolymers

Copolymers of PSU/Sep-ThC and pyrrole were synthesized by chemical oxidative polymerization with using iron (III) chloride as the oxidant. The reaction route is same with the reaction route of the PSU-ThC-PPy synthesis. PSU/Sep-ThC served both as a macromonomer. As a result polysulfone’s and sepiolite’s chemical and mechanical properties were acquired to polypyrrole. Pyrrole and PSU/Sep-ThC amounts are taken according to equation (3.6).

$$n_{Pyrrole} = 50 * n_{PSU/Sep-ThC} \tag{3.7}$$

PSU/Sep-ThC was weighted 1g and dissolved with pyrrole in 40ml DMAC solvent and added into a beaker glass. The amount of iron (III) chloride was again determined by equation (3.5). Latter $FeCl_3$ mixture was prepared with 25ml DMAC. $FeCl_3$- DMAC mixture was given to the reaction mixture via a dropping funnel, about 10 minutes as usual. The reaction went on at 25^{o}C and for 24 hours. In the end of the reaction methanol was poured in the reaction mixture, then PSU-PPy copolymers starts to precipitate. Copolymer product was filtered by thin filter paper, later the product was washed with methanol first, then with acetone for several times for getting rid of the $FeCl_3$ remaining. The resultant polymer was dried in the vacuum at 45^{o}C.

4. RESULT AND DISCUSSION

The FTIR, SEM, NMR and XRD analysis of PSU and PSU/Sepiolite were made. Also with them, FTIR, XRD and SEM results of PSU-PPy and PSU/Sepiolite-PPY copolymers were exemined. Polymer, nanocomposite and copolymer existances were characterized by spectroscopic methods.

4.1 Polysulfone and PSU/Sepiolite Nanocomposite

In the end of the both materials synthesis, homogenious broken white colored dusts were obtained. FTIR of the PSU, Sepiolite and PSU/Sepiolite nanocomposite are given Figure 4.1, 4.2 and 4.3 below. FTIR data of PSU/Sepiolite shows the characteristic bands for the polysulfone backbone and sepiolite structure weak peaks around 3435 cm^{-1}, indicates the presence of phenolic end groups. The formation of the new ester carbonyl peak at around 1735 cm^{-1}, less broad peak at around 3400 cm^{-1} indicates that small amount of nonfunctionalized hydroxy groups comes from sepiolite.

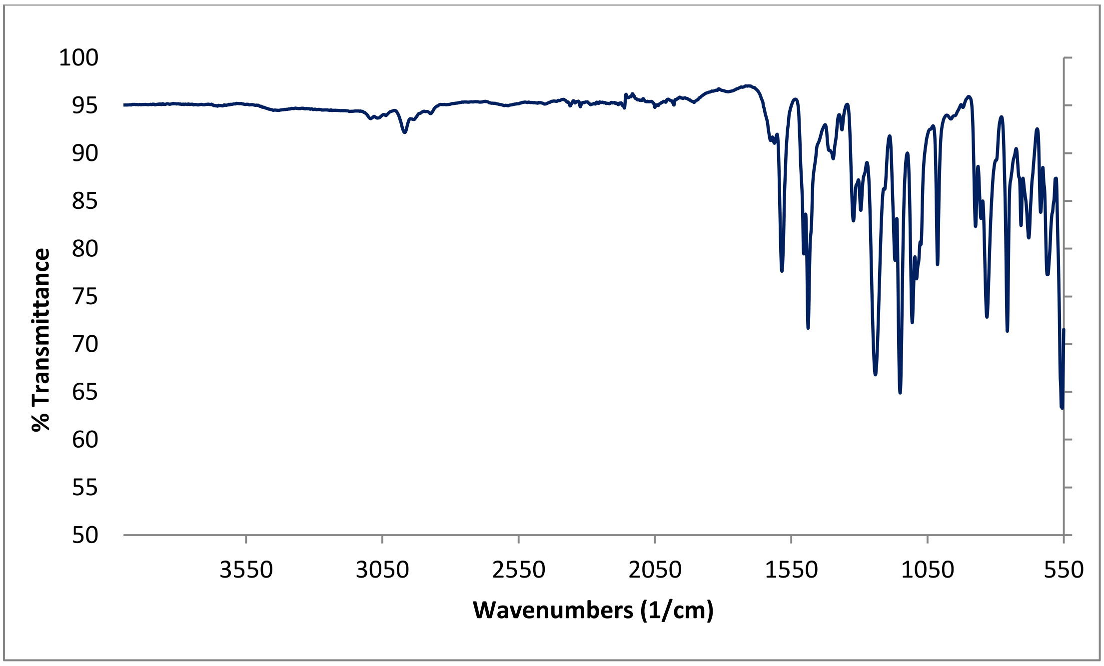


Figure 4.1 : FTIR of PSU

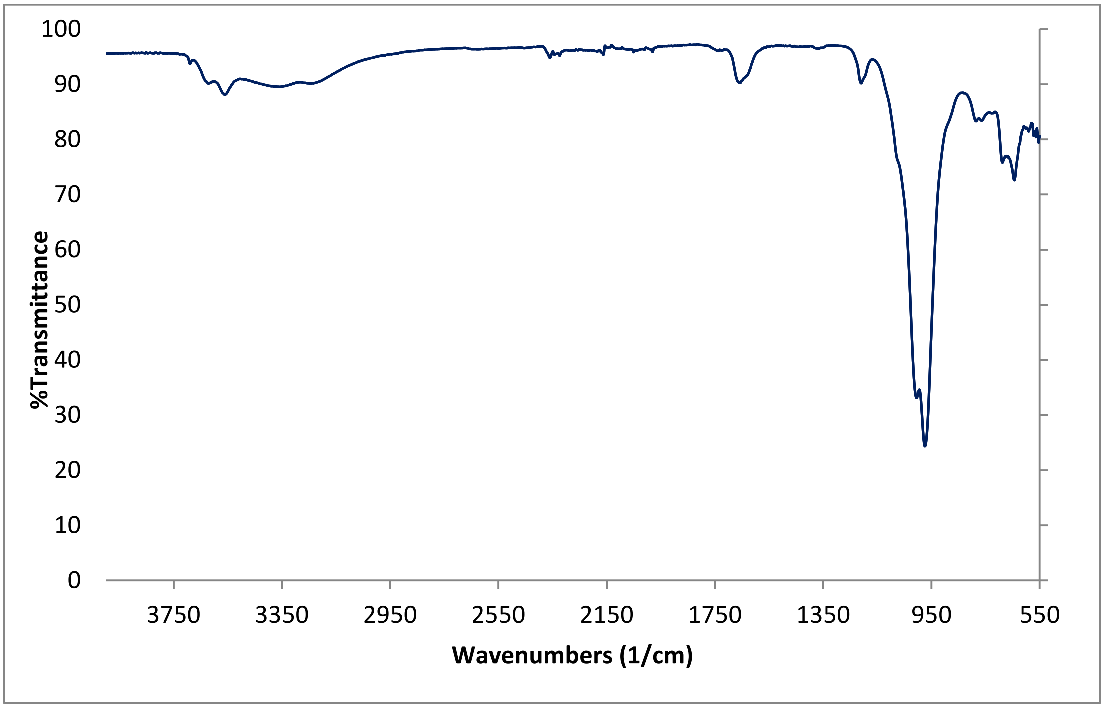


Figure 4.2 : FTIR of sepiolite

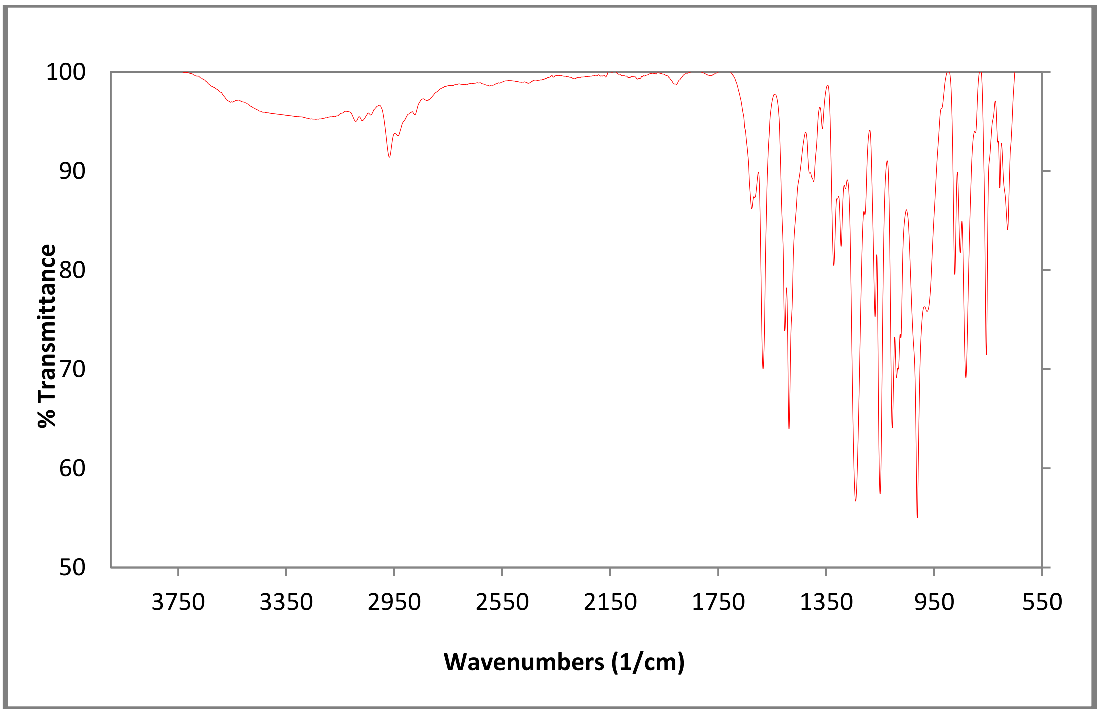


Figure 4.3 : FTIR of PSU/Sepiolite nanocomposite

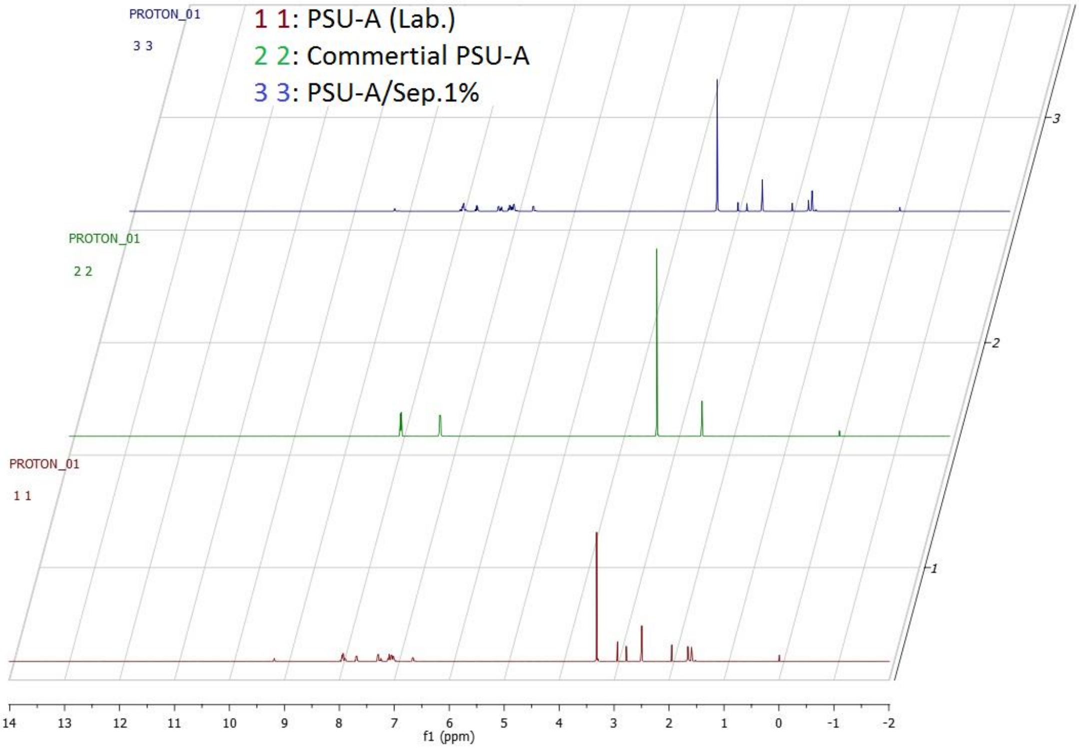


Figure 4.4 : Proton NMR of PSU, commercial PSU and PSU/Sepiolite nanocomposite

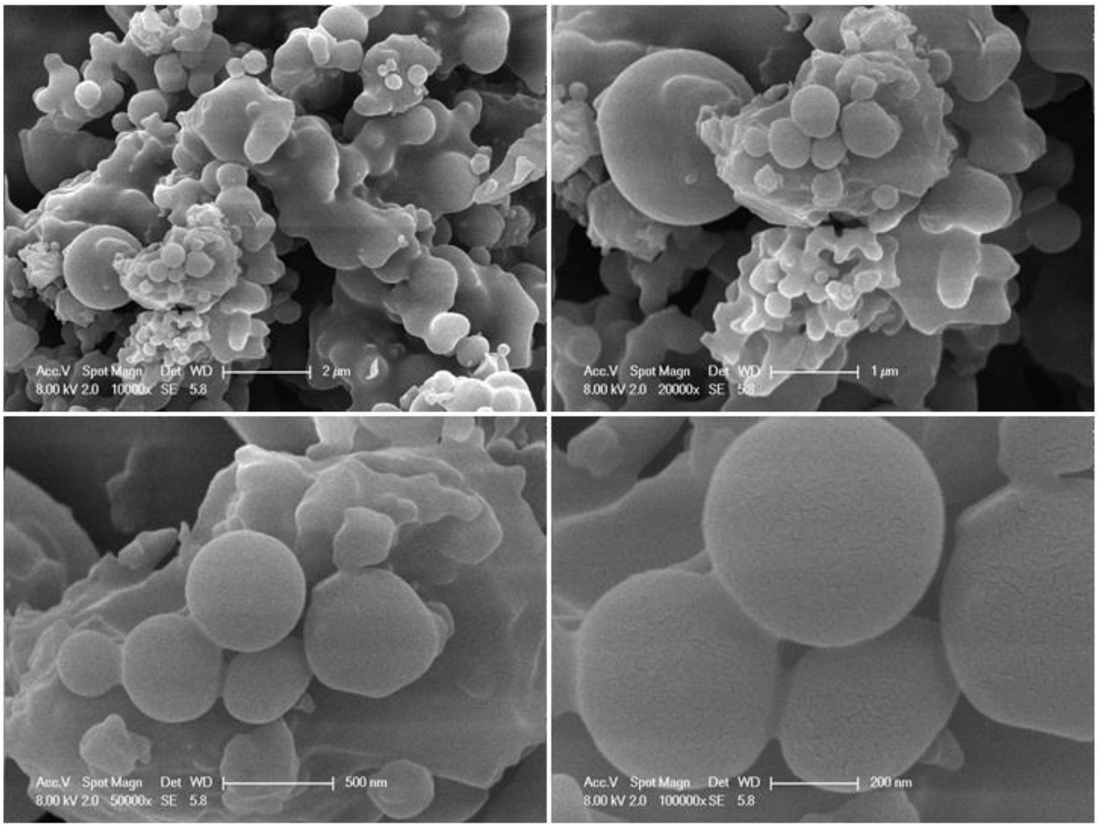


Figure 4.5 : SEM micrographs of PSU

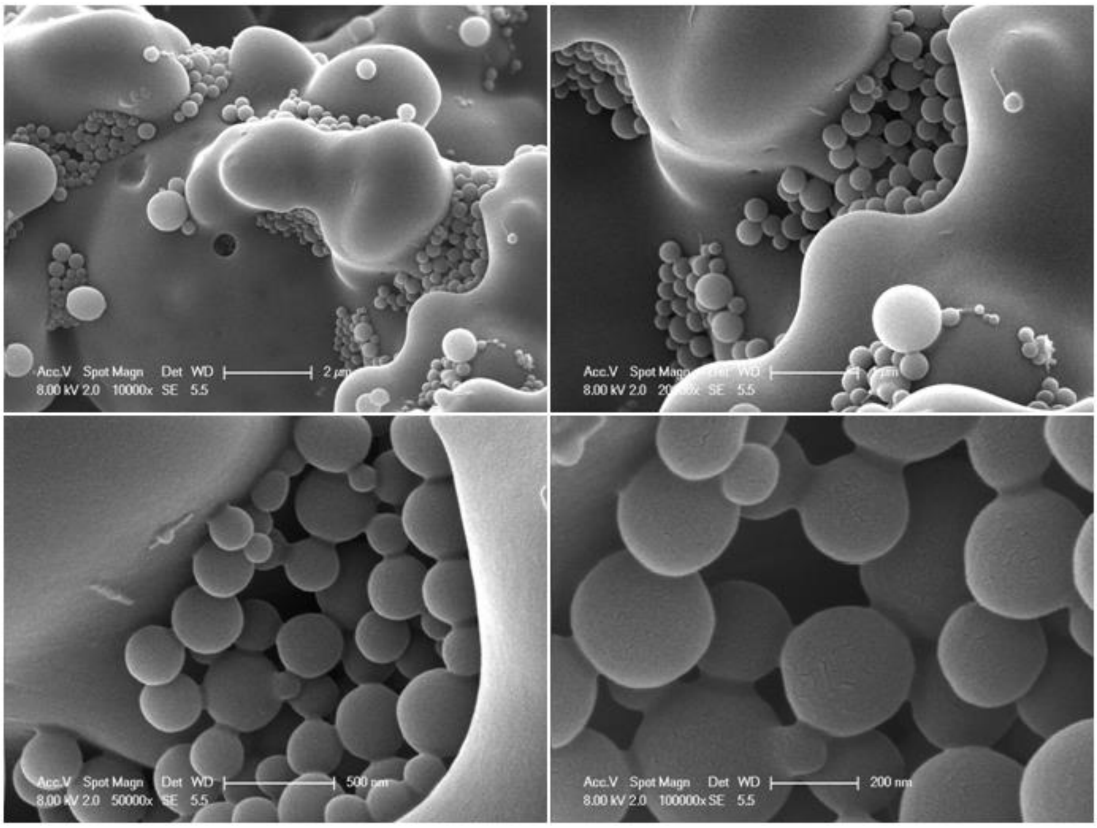


Figure 4.6 : SEM micrographs of PSU/Sepiolite nanocomposite

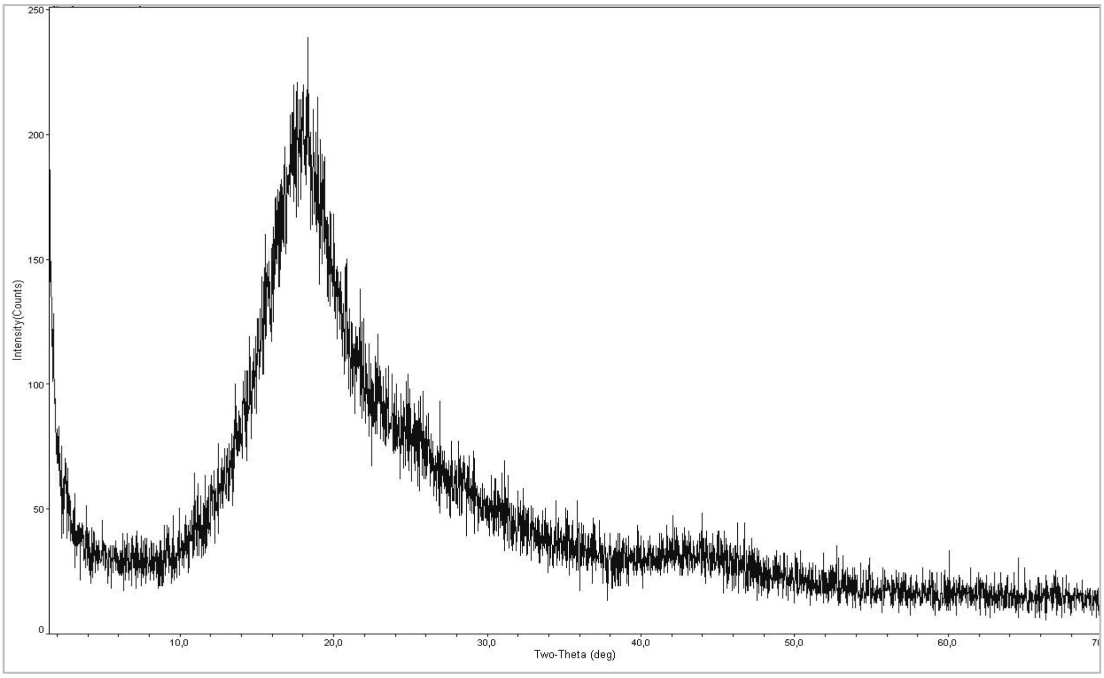


Figure 4.7 : XRD result of PSU

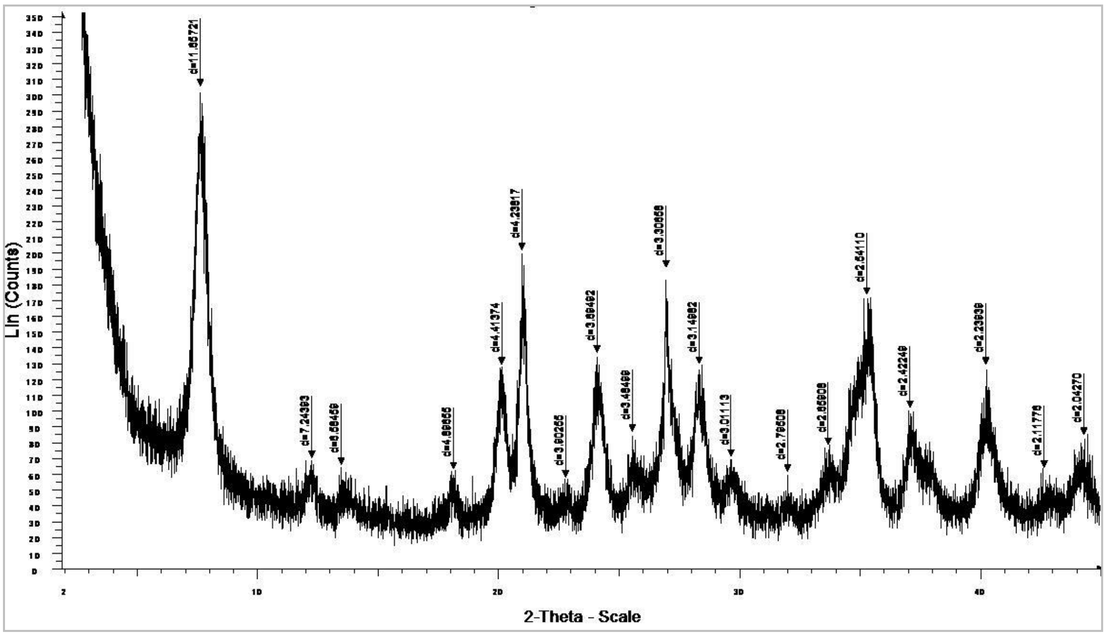


Figure 4.8 : XRD result of Sepiolite

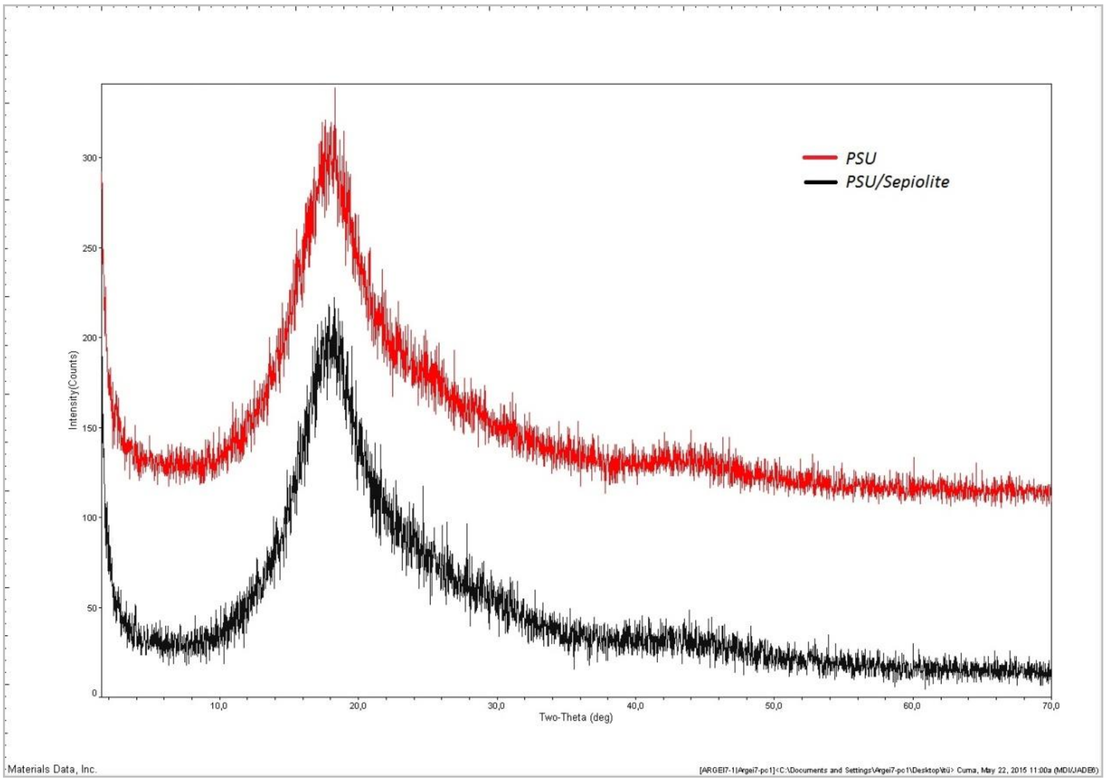


Figure 4.9 : XRD results of PSU and PSU/Sepiolite nanocomposite

SEM micrograph of PSU was taken from 2µm to 200nm. It was observed the material has smooth coral and spherical shape. In the ın the SEM images of PSU/ Sepiolite, nanoparticles were observed around PSU corals.

XRD analysis of PSU, sepiolite and PSU/Sepiolite nanocomposite gives coherent results. The distance "d" between layers may be estimated from the XRD graphs according to the Bragg's Law, represented in the equation below, where "λ" is the wavelength of the X-Ray light (equals 0.15406 nm), "n" is the diffraction degree (taken as 1), "2" is the constant and "θ" is the half of the theta angle read from XRD graph.

$$n * \lambda = 2 * d * sin\theta \qquad \textbf{(4.1)}$$

In Figure 4.7 PSU gives one strong theta angle peak at 18^o and one weak peak at 42^o, which have d=0.49252 and d=0.21493 respectively. By the way, XRD result of sepiolite in Figure 4.8 gives different and several theta angle peaks. Although most of the theta angle peaks of sepiolite cannot be seen in the PSU/Sepiolite nanocomposite XRD result in Figure 4.9, material includes sepiolite according to the other analysis. Therefore these results indicate that the nanocomposite structure is exfoliated.

4.2 End Group Functionalization

The reaction results of end group functionalization of PSU and PSU/Sepiolite analyzed by FTIR, shown in Figure 4.10 and 4.11 respectively. According to the FTIR spectras of thienyl end capped PSU and PSU/Sepiolite, the OH peaks of PSU and PSU/Sepiolite in Figure 4.1 and 4.3 around $3400cm^{-1}$, looks more smoothened in Figure 4.10 and 4.11, which means the end groups of PSU and PSU/Sepiolite were end capped by thienyl.

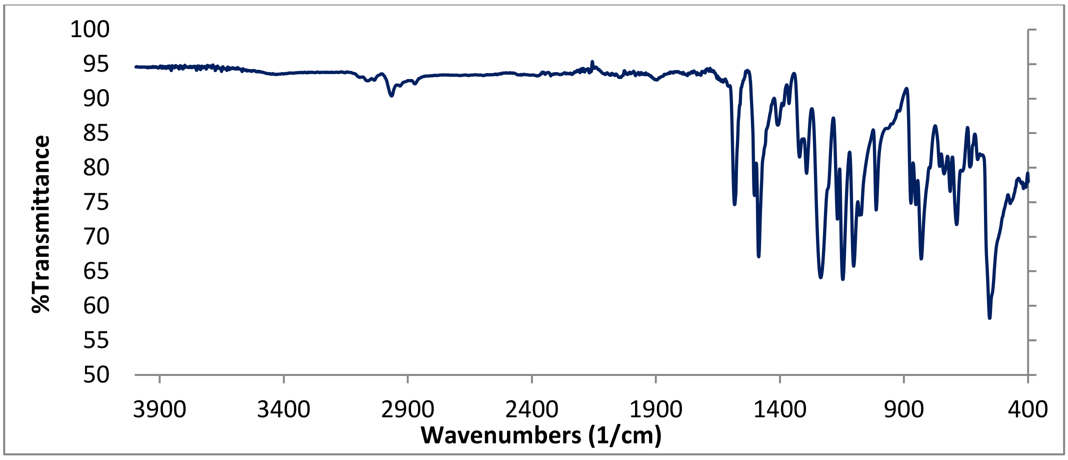


Figure 4.10 : FTIR of thienyl end capped PSU

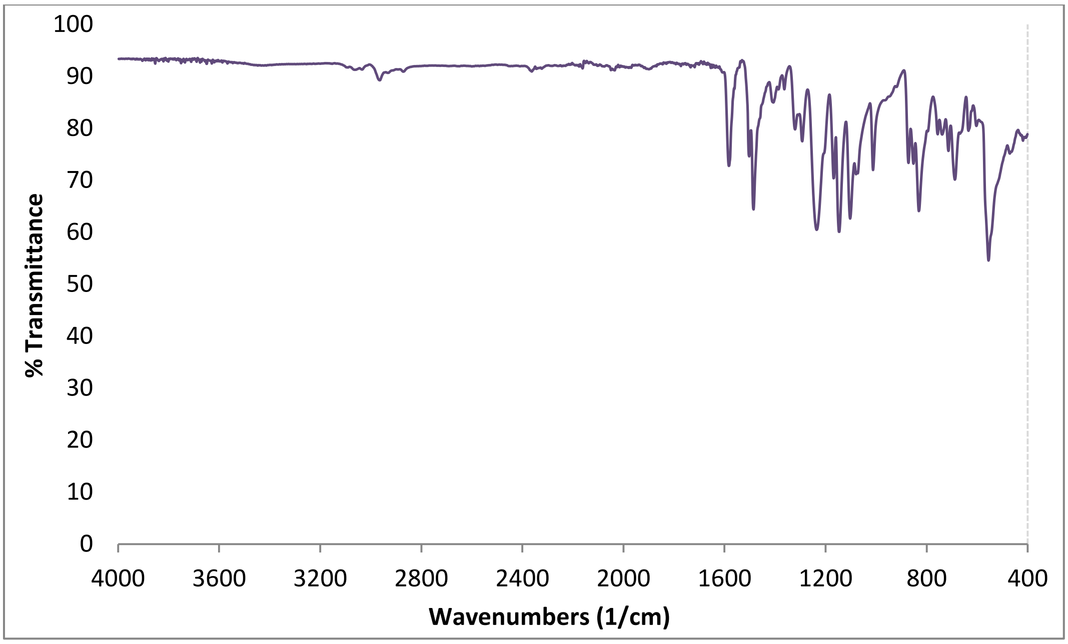


Figure 4.11 : FTIR of thienyl end capped PSU/Sepiolite nanocomposite

4.3 Copolymers of PSU and PSU/Sepiolite with Polypyrrole

Copolymers of PSU-PPy and PSU/Sepiolite-PPy were prepared in same routes. In the end of the both reactions black colored dust products obtained, that is also soluable in its reaction solvent- DMAC- solvent, inspite of homopolymer of PPy, which is not soluable in DMAC. FTIR results of PSU-PPy and PSU/Sepiolite-PPy copolymers are given with FTIR of PPy hopolymer in below.

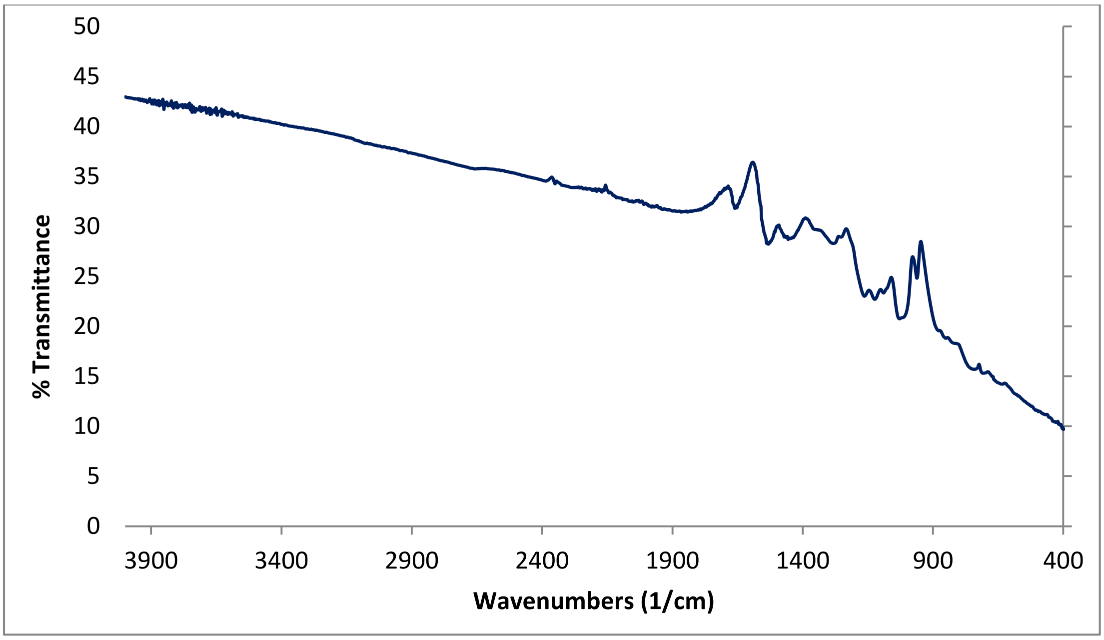


Figure 4.12 : FTIR of PPy homopolymer

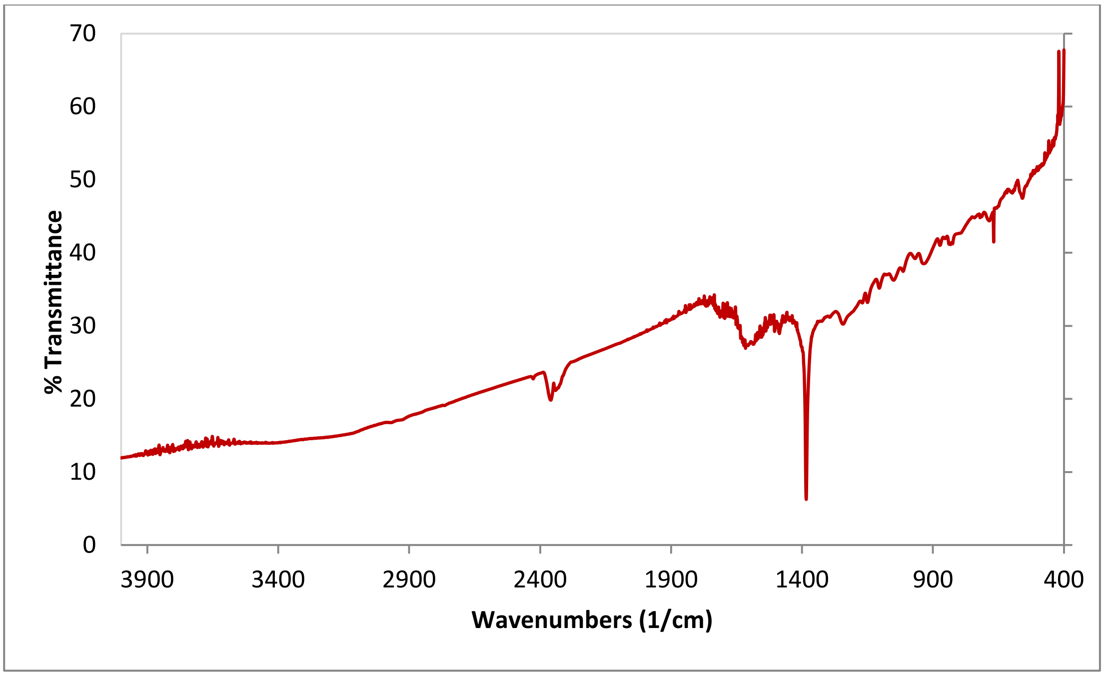


Figure 4.13 : FTIR of PSU-PPy copolymer

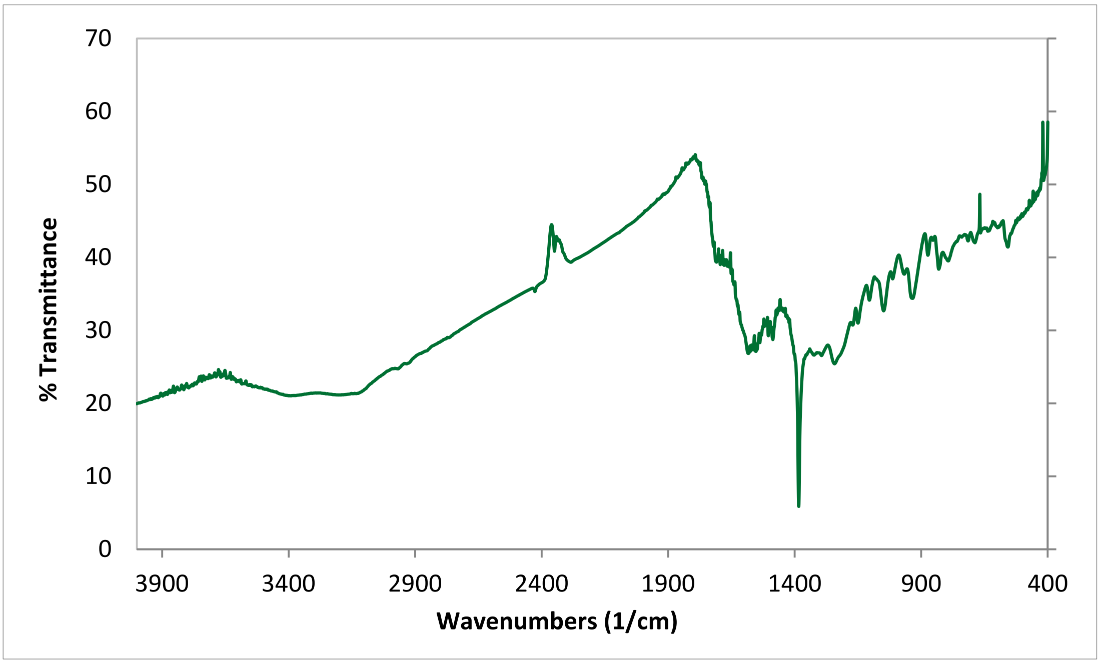


Figure 4.14 : FTIR of PSU/Sepiolite-PPy copolymer

The peak of the PPy around 1220cm^{-1} in Figure 4.12, atributes the C-N screcthing band, which can be observed both in the FTIR spectrums of PSU-PPy and PSU/Sepiolite-PPy. In the FTIR spectrum of PSU/Sepiolite-PPy the weak peaks around 2950cm^{-1} is due to the aliphatic C-H bonds of the materials. Also the peak in Figure 4.12 1170cm^{-1} indicates the C-O scretching band. The aromatic peaks of PSU in PSU/Sepiolite-PPy and PSU-PPy FTIR can be seen at $1400cm^{-1}$ that also strengthened by C-N bonds. The peaks about $1670cm^{-1}$ represent C=N bonds. The occurrence of small peaks at PSU-PPy around $3700cm^{-1}$ is assigned to presence of N–H stretching vibrations. FTIR data of the PSU/Sepiolite-PPy shows the ester carbonyl peak around $1750cm^{-1}$. In the same time the weak peaks of sepiolite around $3400cm^{-1}$ appears in PSU/Sepiolite-PPy copolymer FTIR.

SEM images of the both copolymer also promotes the copolymerization. SEM of PSU in Figure 4.5 shows more spherical small corals, while SEM of PPy in Figure 4.15 shows couli shaped big particles. However SEM of the PSU-PPy copolymer consist combination of both shapes as it can be seen in Figure 4.16. Besides that SEM of PSU/Sepiolite-PPy copolymer in Figure 4.17 not only shows this two combination, but also shows nanoscale buds around lettuce-like particles.

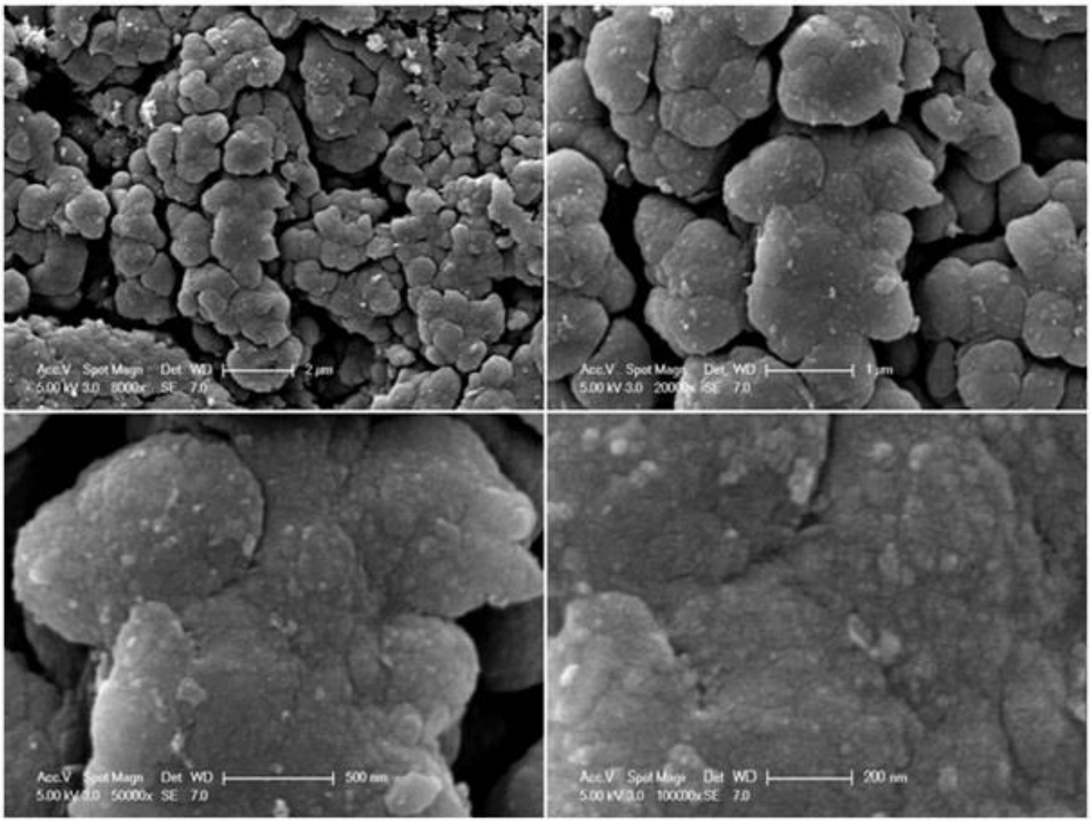


Figure 4.15 : SEM micrographs of PPy

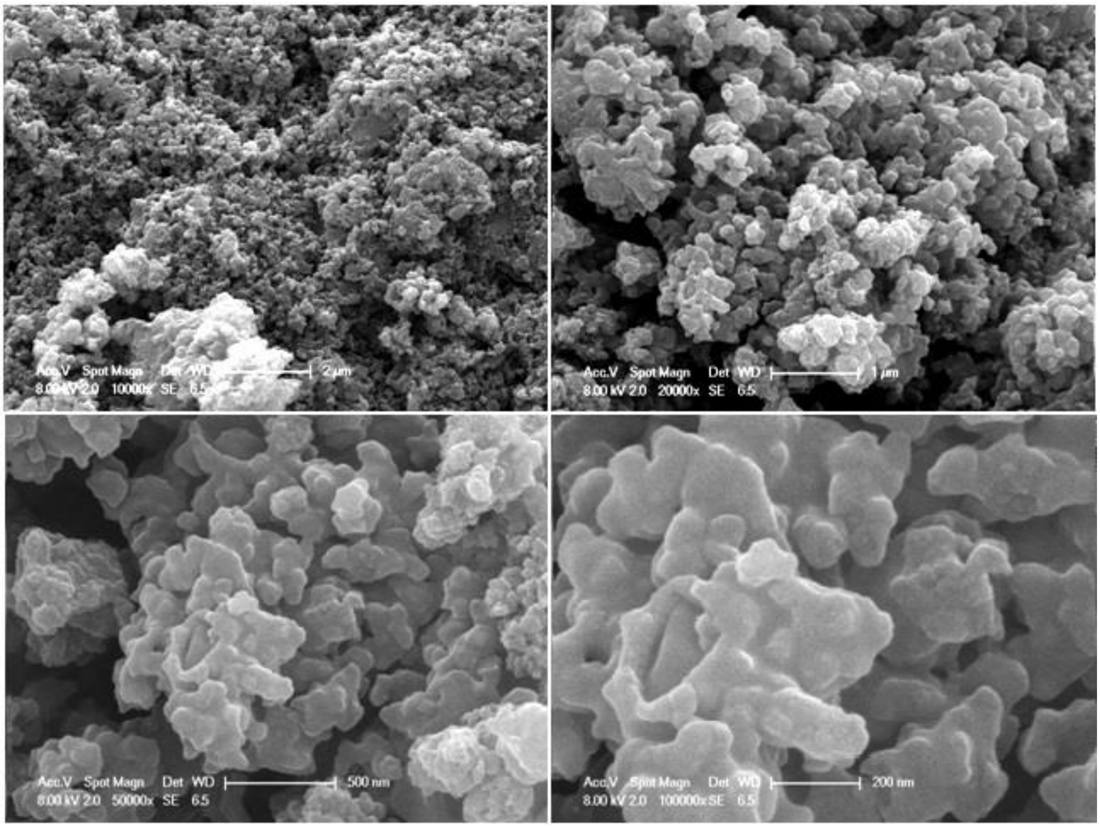


Figure 4.16 : SEM micrographs of PSU-PPy

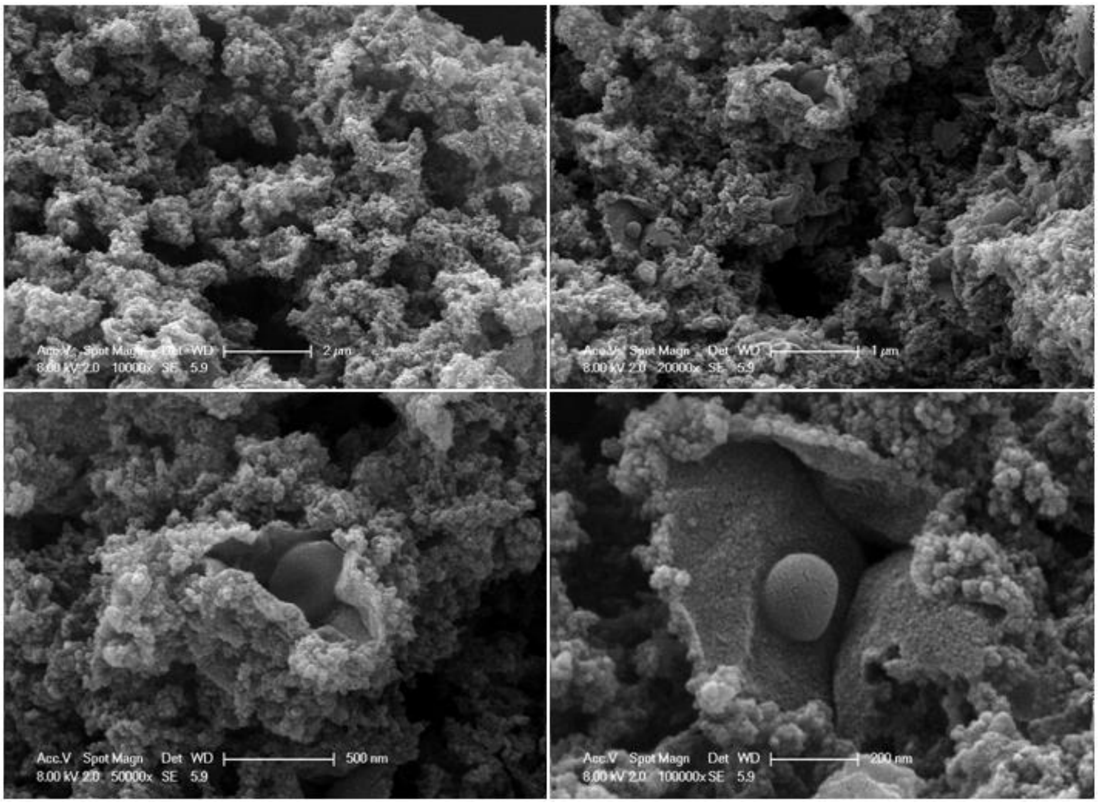


Figure 4.17 : SEM micrographs of PSU/Sepiolite-PPy

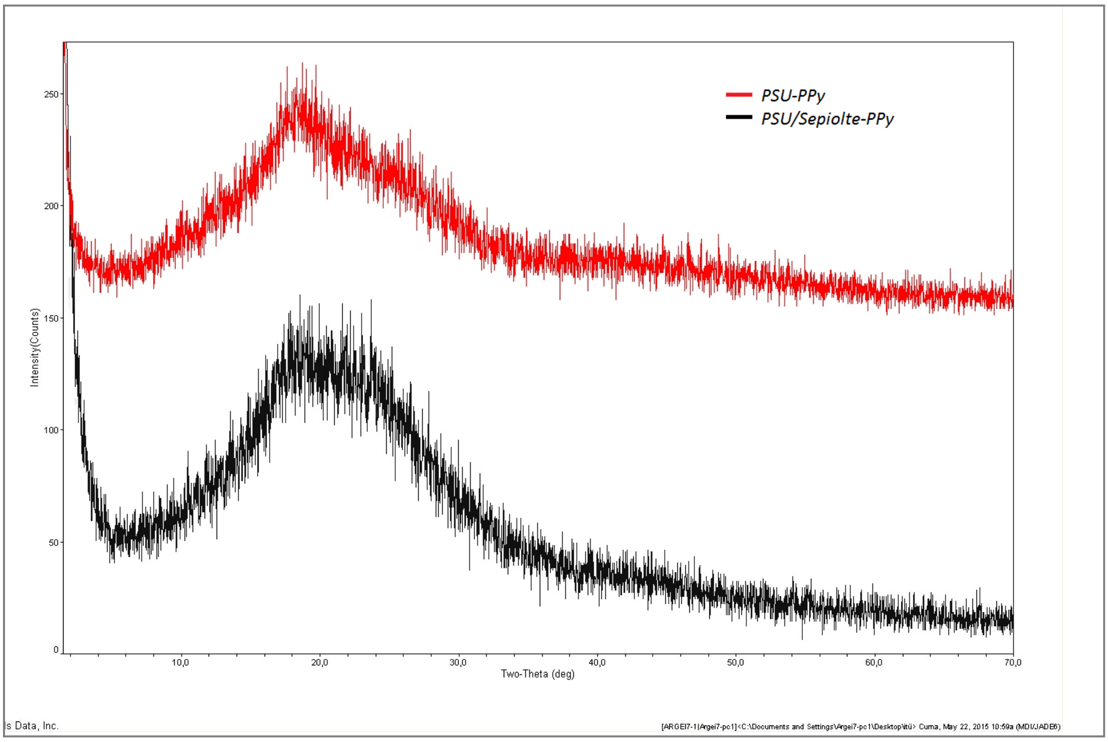


Figure 4.18 : XRD results of PSU-PPy and PSU/Sepiolite-PPy

According to the XRD results of PSU-PPy and PSU/Sepiolite-PPy in Figure 4.18, three theta angle peaks are seen where at 18^o, around 26^o and around 42^o. The peaks at 18^o and 42^o comes from the PSU, while theta angle peaks around 24^o and 26^o derived from PPy. Though FTIR and SEM analysis show that sepiolite remains in the PSU/Sepiolite-PPy copolymer, theta peaks of sepiolite disappears in both XRD graphs. Thusly one can say sepiolite distributed in the copolymer matrix as exfoliated. Addition to these, theta angle of PPy at 26^o in PSU-PPy copolymer; but in the PSU/Sepiolite-PPy graph PPy peak is seen at 24^o, so one can comment the PSU and PPy peaks are superpositioning by the addition of sepiolite. Table 4.1 and 4.2 shows the XRD parameters of PSU-PPy, PSU/Sepiolite-PPy and sepiolite.

Table 4.1 : XRD parameters of PSU-PPy and PSU/Sepiolite-PPy copolymers

Material	Theta Angle	sinθ	d
PSU	18^o	0.15643	4.92425
	42^o	0.35837	2.14945
PPy	26^o	0.22495	3.42432
	24^o	020791	3.70497

Table 2.2 : XRD parameters of sepiolite

Theta Angle	sinθ	d
7.2	0.06279	12.26788
12.1	0.1054	7.308349
13.6	0.1184	6.505912
18	0.15643	4.924247
20	0.17365	4.435934
21	0.18224	4.226844
22.8	0.19766	3.897096
24	0.20791	3.704968
25.6	0.22155	3.476868
27	0.23345	3.299636
28.4	0.24531	3.140108
29.6	0.25545	3.015463
32	0.27564	2.794587
33.8	0.2907	2.649811
35.3	0.3032	2.540567
37	0.3173	2.427671
40.3	0.34448	2.236124
43	0.3665	2.101774
44.2	0.37522	2.052929

4.3.1 Conducting Measurement of PSU/Sepiolite-PPy copolymer

To measure electrical conductivity of PSU/Sepiolite-PPy copolymer compact thin pellet were prepared under 8-10 tons/cm^2 pressure from its precipitates. The sample diameters were 13mm at a thickness of 0.6mm. Following results are found with the measurement by four probe technique and listed in Table 4.3.

Table 4.3 : Conductivity parameter of PSU/Sepiolite-PPy copolye

Parameters	Values
d_n	0.60mm
I	4.53mA
V	19.2V
σ	8.67x10^{-4}S/cm

According to these results one can say that copolymer has poor conductivity but can be enhanced.

5. CONCLUSION

In this study a three step process was attempted in order to prepare block copolymers of polysulfone and polypyrrole. In the first step it was aimed to synthesis PSU and PSU/Sepiolite nanocomposite. Polysulfone and its nanocomposite with sepiolite were synthesized and spectrophotomectric analyses are supporting this. Second step involves end functionalization of those two materials by 2-thiophenecarbonyl chloride for obtaining thienyl end capped macromonomer, which is capable of give oxidative reaction with pyrrole monomers. FTIR data of thienyl end capped PSU and PSU/Sepiolite confirm that thienylation was succesfully achieved. The last step is the oxidative copolymerization of pyrrole monomer with thienyl end capped PSU and PSU/Sepiolite by using Fe(III)Cl_3 as the oxidant. The formation of both PSU-PPy and PSU/Sepiolite-PPy copolymers were observed according to their FTIR spectrums. Moreover SEM images and product colors also promotes these results.

If one compares the SEM micrographs of PSU and PSU/Sepiolite, it can be seen that sepiolite containing PSU has nano scaled polymer particles. Even though sepiolite particles cannot be observed in SEM images, FTIR analyses assert sepiolite presence. Furthermore XRD analyses maintains nanocomposite has exfoliated structure which also explains why sepiolite may not be seen in SEM. Addition to that also sepiolite involving copolymer has nano-buds comparing with PSU-PPy copolymer. It was also experianced that thin pellet of PSU-PPy copolymer is much more fragile than PSU/Sepiolite-PPy copolymer. Thus in a way sepiolite also acts as a plasticizer. Besides these PSU/Sepiolite-PPy copolymer has poor conductivity parameters may arising from the exinstance of PSU in the morphology. Nevertheless resistance of PSU/Sepiolite-PPy gives white hope and can be enhanced by dopant usage. In the light of this research two thing were obtained; first a usefull membrane material containing sepiolite nanoparticles and combination of two polymers having good material properties was produced, and second they were synthesized with a new method.

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- Erkman, E., **Tanrıver, N.,** Köken, N., Kızılcan, N., 2014: Synthesis and Characterization of Polysulphone from Different Bisphenols. *27th International Symposium on Polymer Analysis and Characterization*, June 16-18, 2014, Les Diablerets, Switzerland.
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