ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

PREPARATION AND CHARACTERIZATION OF CHITOSAN/ POLYPYRROLE/ CLAY NANOCOMPOSITES

M.Sc. THESIS

Sevinç Sezin TARIMSAL GÜLMEN

Department of Polymer Science and Technology

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

ÇİTOSAN/ POLİPİROL/ KİL NANOKOMPOZİTLERİNİN SENTEZİ VE KARAKTERİZASYONU

YÜKSEK LİSANS TEZİ

Sevinç Sezin TARIMSAL GÜLMEN
(515131022)

Polimer Bilimi ve Teknolojisi Anabilim Dalı

Polimer Bilimi ve Teknolojisi Programı

Tez Danışmanı: Prof. Dr. Nilgün KIZILCAN

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Sevinç Sezin TARIMSAL GÜLMEN, a **M.Sc.** student of ITU **Institute of Science and Technology** student ID **515131022,** successfully defended the **thesis** entitled "**PREPARATION AND CHARACTERIZATION OF CHITOSAN/ POLYPYRROLE/ CLAY NANOCOMPOSITES**", which she prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

Thesis Advisor :	**Prof. Dr. Nilgün KIZILCAN** İstanbul Technical University	.....
Jury Members :	**Prof. Dr. Oya ATICI** İstanbul Technical University	.....
	Prof. Dr. Ayfer SARAÇ Yıldız Technical University	.....

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To Sevim & Volkan Tarımsal,

FOREWORD

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May 2015

S. Sezin TARIMSAL GÜLMEN
(Bioengineer)

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ABBREVIATIONS

AgnP **:** Silver Nanoparticles
CAN **:** Cerium Ammonium Nitrate
CPN **:** Clay Polymer Nanocomposites
CPs **:** Conductive Polymers
CS **:** Chitosan
FTIR **:** Fourier Transform Infrared Spectroscopy
NC **:** Nanocomposite
Py **:** Pyrrole
PPy **:** Polypyrrole
SEM **:** Scanning Electron Microscopy
Sep **:** Sepiolite

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PREPARATION AND CHARACTERIZATION OF CHITOSAN/ POLYPYRROLE/ SEPIOLITE NANOCOMPOSITES

SUMMARY

Many researchers studying on discovering new materials to enhance the quality of human life in all aspects. The challenging part of this quest is to find all desired properties in a single material. A composite material is composed of two or more constituents to unite all desired properties in one material. The goal of this study is to discover and produce a high conductivity nanocomposite which is biodegradable, biocompatible, and biofunctional so that it can be used in biomedical applications. Chitosan (CS) is chosen as one of the most attractive polymer due to its' specific properties; such as biocompatibility, biodegradability, and biofunctionality, etc. One of the most investigated conducting polymers is polypyrrole (PPy) because of its characteristics such as; easy synthesis and high conductivity. Recently, there have been many attempts to synthesize composites of CS and PPy to investigate what combined functionality can be obtained. Combination of pyrrole with cerium (IV) ammonium salts (Ce^{+4}) exhibits better solubility than PPy. In aqueous media, redox systems of Ce^{+4} and reducing agents such as acids are well known initiators for vinyl polymerization. Polymerization reaction in aqueous media has many technical advantages than other methods. Additionally, the preparation of polymers with clay minerals has been extensively studied topic due to understand the synergistic effect of them. In this work, Chitosan/Polypyrrole composites and Chitosan/ Polypyrrole/ Sepiolite (Cs/PPy/Sep) Nanocomposites (NC) were synthesized via redox polymerization in aqueous media with magnetic stirrer system in presence of ammonium cerium (IV) nitrate (Ce^{+4}) at room temperature. The roles of the oxidant/monomer mole ratio, on the yield, conductivity and morphology of the resulting products were investigated. Chitosan /Polypyrrole composites and Chitosan/ Polypyrrole/ Sepiolite Nanocomposites (Cs/PPy/Sep NC) were prepared with the oxidant to pyrrole mole ratios as 0.67:1, 0.8:1, and 1:1 for comparison. In addition, to understand the effect of inorganic agents to Cs/PPy/Sep nanocomposites, Silver (Ag) ions were added to blend. Ag particles has some unique characteristics increased optical, electromagnetic, and catalytic properties. The yield and electrical conductivity of the products (polymer) were investigated as physical characteristics. The electrical conductivities of Cs/PPy/Sep NC were determined by four point probe technique. In addition, the resulting NC were characterized with spectroscopic method that was Fourier Transform Infrared Spectroscopy (FTIR), and also morphological method, which was Scanning Electron Microscopy (SEM). According to conductivity results, Polypyrrole/Chitosan (PPy/CS) composite polymers showed conductivity between $1.8x10^{-6}$ and $1.4x10^{-2}$ S/cm. Polypyrrole-Chitosan/Sepiolite (Ppy-CS/Sep) nanocomposite polymers showed conductivity between $3.0x10^{-4}$ and $6.41x10^{-4}$ S/cm. Polypyrrole/$AgNO_3$ nanocomposite polymers had a conductivity between 0.755 and 7.2 S/cm. According to SEM results, PPy/CS-1 sample has average size of 28.90 nm and PPy-CS/Sep-1 sample has average size of 28.63 nm. In future, many applications will benefit from conductive materials like PPy/CS, PPy-

CS/Sep and PPy/Ag in biosensors, bioactuators and many other biomedical applications which will be very important in next century.

ÇİTOSAN/ POLİPİROL/ KİL NANOKOMPOZİTLERİNİN SENTEZİ VE KARAKTERİZASYONU

ÖZET

Biyopolimerler, canlı kaynakların metabolizmalarının ürünlerinden doğal ya da sentetik polimerizasyon sonucu ortaya çıkan ürünlerdir. Geri dönüştürülebilir, biyo-bozunur, biyo-uyumlu malzemelerdir. Biyo-uyumlu polimerler canlı yapı ile kimyasal ve biyolojik açıdan uyumlu olan ve canlı yapının bağışıklık sistemi tarafından kabul edilebilir düzeyde tepki alan malzemelerdir. Biyo-bozunur polimerler ise mikrobiyal faaliyetler sonucunda mineralize olabilen malzemelerdir. Kitin, çitosan, guargam ve zantan gam ve ipek endüstride kullanılan en önemli biyopolimerler arasında bulunmaktadır. Biyopolimerler, hayatımızda giderek önemini artıran kompozit ve nanokompozit malzemelerde kullanılarak, malzemenin özelliklerini biyopolimerlerin avantajlarıyla birleştirmektedirler.

İki veya daha fazla sayıdaki, aynı ya da farklı gruptaki malzemelerin en iyi özelliklerini bir araya getirerek ortaya yeni bir özellik çıkarmak amacıyla bu malzemelerin birleştirilmesiyle oluşan malzemeye kompozit malzeme denir. Doğada oluşan veya uzun yıllardır insanlık tarafından üretilen kompozit malzemeler arasında ahşap, beton, asfalt vb. maddeler bulunmaktadır. İmalat sanayi ve geliştirilen malzeme sistemleri sayesinde yapay kompozitler; istenilen yapıya, özelliklere ve parça geometrisine ulaşmak için birleştirilebilmektedir. Kompozit malzemelerin tahmin edilen en eski kullanım alanı inşaat sektörüdür. Çamurun içine karıştırılmış saman ile yapılan duvarlar bilinen en eski yapay kompozit malzemelerin başında gelmektedir. İnşaat sektörünün gelişmesi ile kireç, taş, kum, demir ve çimento ile yapılan kompozit malzemeler üretilmiştir. Teknolojinin gelişmesi ile kompozit malzemeler enerji naklinde, otoyol yapımında, kağıt yapımında kullanılmaya başlanmıştır. Kompozit malzemeler mekanik (eğme, akma, sürünme, yorulma, sertlik, tokluk, vb.), fiziksel (iletkenlik, magnetik özellikler, yoğunluk vb.) ve kimyasal özellikleri (korozyon direnci, kararlılık, vb.) geliştirilmiş, işlenebilirlik ve şekillenebilirlik özellikleri, maliyet ve tonaj gibi etmenler dikkate alınarak geliştirilmiş malzemelerdir.

Nanokompozitler ise 1 nm ile 100 nm arasında maddeleri yapısında içeren kompozit malzemelerdir. 1980'li yıllarda yapılan çalışmalar sonucu ortaya çıkan ilk polimer-kil nanokompozitlerden sonra mühendislik bilimi ve teknolojinin gelişmesi ile nanokompozitlerin endüstride kullanımı her geçen gün artmaktadır. Nanokompozitler üstün fiziksel ve mekanik özelliklerinden dolayı yüksek performans uygulamalarında kullanılır. Nanoparçacıklarla güçlendirilen polimerlerin mukavemeti, iletkenliği, gaz geçirgenliği gibi özellikleri iyileştirilerek modifiye edilmemiş polimerlere göre daha çeşitli alanlarda polimer malzemelerin kullanılmasını sağlamaktadır. Özellikle nanokompozitlerde kullanılan malzemelerin fiyatlarının daha uygun olması ve kompozitlerin hazırlanmasındaki teknik zorlukların giderilmesinden kaynaklı polimer nanokompozitlerin kullanımı son yıllarda artmaya başlamıştır. Nanokompozitlerin kullanıldığı başlıca endüstriler

arasında havacılık, ambalaj ve otomotiv sanayi bulunmaktadır. Havacılık endüstrisi, nanokompozitleri kullanarak varolan ürünlerin hafiflemesini sağlamış ve mukavemetlerini artırmayı başarmıştır. Ambalaj sanayi ise nanokompozitleri kullanarak ürünlerin yırtılmaya ve delinmeye karşı dirençlerini artırarak, raf ömürlerinin uzamasına yardımcı olmuştur. Polimer nanokompozitlerin en çok gelişme gösterdiği ve gelecekte daha büyük beklentiler içeren sektörlerin başında biyomedikal endüstrisi gelmektedir. Biyomedikal endüstrisi, tıp alanlarında teşhis ve tedavi için kullanılabilecek tüm malzeme ve cihazların üretimi ile ilgilenen bilim dalıdır. Nanokompozitlerin kullanıldığı çalışmalar arasında biyomedikal endüstrisinde kullanılan protein terapisi, kontrollü ilaç salınımı çalışmaları, tıbbi teçhizat dizaynları ve protez uzuvlarının geliştirilmesi gibi alanlar bulunmaktadır.

Günümüzde petrol bazlı plastiklerin doğaya karşı olan zararlarını azaltmak için doğada kolayca çözünen biyolojik bazlı polimerler üzerine birçok araştırma yapılmaktadır. Çitosan polimeri, biyopolimer grubundan olup, eklem bacaklıların ana maddesi olan kitinin deasetile edilmesi yöntemiyle elde edilmektedir. Kitin selülozdan sonra doğada en fazla bulunan ikinci yenilenebilir polimerdir. Çitosanın en önemli avantajı yenilenebilir bir kaynak ve çevre dostu doğal bir biyopolimer olmasıdır. Dolayısıyla, çitosan özellikle son 50 yıldır araştırmacılar için önem arz etmekte ve birçok endüstriyel alanda gıdadan kozmetiğe, biyomedikalden tekstile olmak üzere çeşitli dallarda kullanılmaktadır.

Polimerlerin biyomedikal sektöründe kullanılabilmesi için önem arz eden bir diğer özellik iletkenliktir. Metaller ile karşılaştırıldığında, polimerler hafif ve kolay şekil alabilmektedir. Metaller ise zor işlenebilen, ağır ve pahalı olmalarına rağmen yüksek iletkenlikleri ile dikkat çekmektedirler. Polimerler ve metallerin üstün özelliklerinin bir araya getirilmesi sonucu ortaya çıkan malzemelere iletken polimerler denir. Bu konuda ki araştırmalar 1950'li yıllarda başlamış, 1970'li yılların sonunda pirolün elektrokimyasal yöntemle yükseltgenmesi ve polipirolün üretilmesi ile önemli bir buluşa imza atılmıştır. Polipirol kolay sentezlenebilir ve yüksek iletkenlik özelliğine sahiptir. Özellikle bu sebeplerden dolayı en çok araştırılan iletken polimerdir. Ancak polipirolün sentetik olarak kolay sentezlenebilme özelliğine rağmen, çözücüler içinde çözünmeme ve kolay işlenememe gibi sorunlardan kaynaklı kullanım alanları azdır. Polipirolün seryum amonyum tuzları ile sentezlenmesi, çözünürlük problemini ortadan kaldırmaktadır. Ayrıca solüsyon halinde hazırlanması, kimyasal olarak kompozitinin oluşturulması ve kopolimerlerinin sentezlenmesi polipirolün işlenebilirlik özelliğini kazanmasını sağlamaktadır.

Seryum (Ce^{+4}) tuzlarının redox reaksiyon sisteminde, sulu ortamda vinil polimerizasyonunu başlattığı daha önceki çalışmalarımızdan bilinmektedir. Sulu ortamda polimerizasyon reaksiyonunun teknik açıdan birçok avantajı bulunmaktadır. Sulu ortam reaksiyon sisteminde seryumla reaksiyona giren indirgen maddeler, glikoz, maltoz, karboksilli asit, hidroksi asit, aminoasit, amin tetra asetik asit, aminotri metilen fosfonik asit kullanılmıştır.

Bu çalışmada pirol monomeri, Ce^{+4} ve çitosan varlığında sulu ortamda polimerleştirilmiştir. Monomer / oxidant (Pirol / Ce^{+4}) mol oranlarının, elde edilen polimer verimi ve iletkenlik gibi fiziksel özellikleri ve morfolojisi üzerindeki etkisi araştırılmıştır. Ayrıca polimerizasyon ortamına sepiloyit eklenerek nanokompozitleri de sentezlenmiştir. Karşılaştırma olması açısından gümüş iyonları eklenerek de denenmiştir. Elde edilen polimerlerin spektroskopik olarak karakterizasyonu ve elektron mikroskop ölçümleri ile de morfolojisi tespit edilmiştir. Çalışmanın esas

amacı, biyomedikal endüstrisinde kullanılabilecek yüksek iletkenliğe sahip nanokompozitlerin üretilmesidir.

Araştırma planına göre, sırasıyla polimerlerin sentezi, pirolün, seryumun amonyum nitrat varlığında sulu ortamda, oda sıcaklığında, manyetik karıştırıcılı sistemde redox polimerizasyonu ile yapılmıştır. Ayrıca sisteme aynı zamanda çitosan eklenerek kopolimer sentezleri de farkı mol oranlarında da yapılmıştır. Çitosan' ın Ce^{+4} ile oksidayon reaksiyonu vermesi ile pirol ve çitosan kimyasal olarak bağlanmıştır. Ayrıca polimerizasyon ortamına lif yapılı sepiloyit eklenerek nanokompozit özellikli kopolimerlerde sentezlenmiştir. Gümüş iyonları eklenen nanokompozitleri de karşılaştırma olması için sentezlenmiştir. Kopolimerin ve kompozitlerinin fiziksel özellikleri tespit edilip, 4 nokta prob yöntemi ile iletkenlikleri ölçümleri yapıldıktan sonra hesaplanmıştır. Bu sistemle tek aşamada su bazlı sistemlerde biyo uyumlu olabilecek polimerler ve kompozitlerin sentezi gerçekleştirilmiştir.

Polimerin iletkenliği, serik amonyum nitrat (CAN) konsantrasyonu ile doğru orantılı olarak artmıştır. CAN konsantrasyonunun 0.09M üzerine çıktığı durumlarda ise polimer iletkenliğinde düşüş gözlenmiştir. Bunun sebebi olarak, yükselen seryum iyon konsantrasyonunun oksidatif zincir tepkimelerine neden olduğu düşünülmektedir. Polipirol/Çitosan (PPy/CS) kompozit polimerinin iletkenliği $1.8x10^{-6}$ ile $1.4x10^{-2}$ S/cm değerleri arasında bulunmuştur. Polipirol-Çitosan/Sepiolit (PPy-CS/Sep) nanokompozitinin iletkenliği $3.0x10^{-4}$ ile $6.41x10^{-4}$ S/cm arasında tespit edilmiştir. Polipirol/Gümüş nitrat (PPy/Ag) nanokompozitinin ise iletkenliği 0.755 ile 7.2 S/cm arasında bulunmuştur. Bu sonuçlara istinaden, PPy/CS kompozitleri, geniş iletkenlik aralığına sahip olduğundan, çok çeşitli alanlarda kullanılabilirler. Diğer yandan, PPy-CS/Sep nanokompozitleri kısıtlı bir iletkenlik aralığına sahip olduklarından, belirli alanlarda kullanılabilirler. Buna rağmen, Sepiolit malzemesinin getirdiği karakteristik özellikler sayesinde bu nanokompozit kullanımda tercih edilmektedir. Beklendiği gibi, gümüş iyonlarının eklenmesi, iletkenlik değerlerini fazlasıyla artırmıştır. Ayrıca gümüş iyonları hücre duvarını aşabildiğinden, bu nanokompozitler anti-mikrobik özellik aranan alanlarda kullanılabilirler.

Yapılan seri deneyler sonucunda polimerizasyon veriminin, CAN konsantrasyonu ile doğru orantılı olduğu görülmüştür. Bazı durumlarda, bu hipotez doğrulanmamış ve artan CAN konsantrasyonu ile verimde düşük gözlenmiştir. Bunun sebebi olarak, numunelerin filtre kağıdından elde edilmesi sırasında yaşanan zorluklar gösterilebilir.

Elektron mikroskopu ile yapılan morfoloji çalışmaları sonucu, PPy/CS – 1 numunesinin ortalama çapının 28.90 nm, PPy-CS/Sep – 1 numunesinin ise ortalama çapının 28.63 nm olduğu belirlenmiştir. Çitosan ve sepiolit, resimlerde rahat bir şekilde ayırt edilebilmiştir.

Önümüzde ki yüzyıl içerisinde, Polipirol/Çitosan kompoziti, Polipirol-Çitosan/Sepiolit ve Polipirol/Gümüş nitrat nanokompozitleri gibi iletken polimerler, biyomedikal araştırmaları başta olmak üzere birçok alanda ufuk genişleten sonuçlar alınmasında rol oynacaktır.

1. INTRODUCTION

Recently, composite polymers especially bio-composites and intrinsic conducting polymers (CPs) with conjugated double bonds have been attracted much attention. Composite material is made from two or more component with different physical or chemical properties that when combined to produce a new material which has different properties from the original components. Bio-composites are composite materials and formed by a resin and reinforcement of natural fiber. Among those, bio-composites, which is made of chitosan (CS) (Fig. 1.1), is used for commercial applications because of having many good characteristics such as biocompatibility, biodegradability, and bio-functionality etc. [1, 2]. Chitosan has both reactive amino and hydroxyl groups that can be used to modify its properties under mild reaction conditions [3]. In addition, it is the second most abundant natural polymer on earth found mostly in the insect's cuticle, cell wall of fungi, and crustacean's shells [4]. Therefore, it has been used in many industrial application areas such as cosmetics, paper and textile industries, food packaging, wastewater treatment, photography, solid-state batteries, biomedical applications (wound healing and dressing, burn treatment, artificial skin, ophthalmology, biosensors), and separation membranes [1, 5].

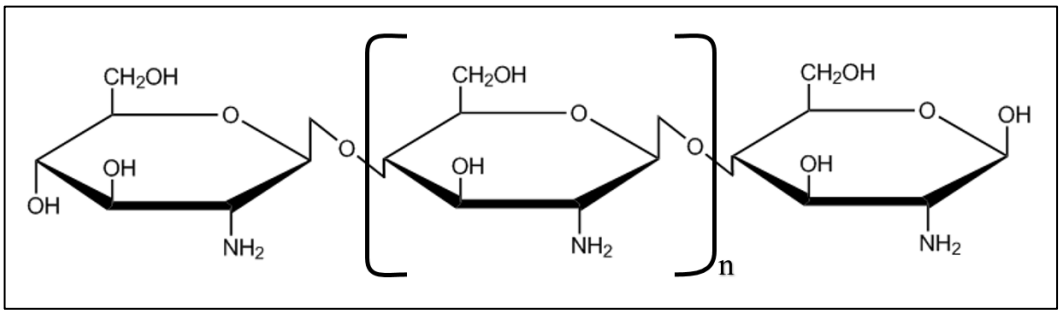

Figure 1.1: Planar structure of Chitosan.

Polypyrrole (PPy) is one of the most used conductive polymers (CPs) that have the capability to conduct electricity for commercial applications because of its special characteristics, such as; good environmental stability, facile synthesis, and also higher conductivity than other conducting polymers [6]**.** In addition, it is

biocompatible with mammalian cells [7, 8]. PPy can be used in production of biosensors, gas sensors, microactuators, wires, solid electrolytic capacitor, electrochromic windows and displays, anti-electrostatic coatings, polymeric batteries, functional membranes etc. [9- 13]. However, it has limited large-scale industrial applicability due to its brittle nature and poor post-synthesis processability, which are low solubility in solvents, inadequate heat annealing properties, and poor compatibility affect that to produce coherent, self-standing films, wires, or other moulded or cast forms [14]. Therefore, researchers are continuously investigating polypyrrole blends to get rid of these drawbacks.

Chitosan - Polypyrrole (CS-PPy) composites have formed to investigate its potential benefits for biomedical applications [15]. Redox polymerization system is choosen for these composite experiments because it has many technical and theoretical advantages over other methods for synthesis of copolymers such as applicability at low temperatures, and decreasing possibility of side reactions [16]. In acidic media, ceric ions are used as oxidizing agents for many organic substrates to initiate the vinyl polymerization [17]. To form ceric ions, ceric ammonium nitrate (CAN) can be used and it is one of the important reagents, which have unique role in chemical reactions such as an oxidant. It has been widely used in industry and academia due to commercial availability after 1980s.

Clay polymer nanocomposites (CPN) can show good modifications such as improved mechanical and barrier properties, thermal stability, high transparency etc., depending on the clay mineral and its interaction with the polymer [18]. Sepiolite is chosen as a clay mineral for this composite experiments because of having high specific surface area, high porosity, and high surface activity etc. so that it can be used in some processes such as oil refining, wastewater treatment, odor removal, drug & pesticide carriers, paper and detergent manufacturing etc. [19]. Currently, polymer science researchers want to develop especially biomimetic or bioinspired materials based on the combination of natural polymers with inorganic solids like chitosan - sepiolite combination as a nanostructured biohybrid material. This combination can be used in electrochemical sensors [20].

Lately, using combination of biological materials like those that chitosan with inorganic agents such as Ag, Zn, CuO etc. has became popular to improve the antimicrobial activity [21]. Silver (Ag) ions have attracted special attention because

of their positive impact on the food and health care industries [22, 23]. A particle of Ag element, which is nano-silver, is named as a new class of material because of its unique and improved properties than bulk materials such as increased optical, electromagnetic, and catalytic properties [24]. Due to be chitosan's poor mechanical properties barrier for using it in a wider application areas, so that researchers have focused on improving that with using combination of clay polymer like sepiolite, montmorillonite, etc. [25]. Therefore, silver loaded chitosan-sepiolite blend can achieve significant improvement in mechanical and functional properties for using in different biological research and biomedical applications. In this study, we formed different biocomposites to demonstrate their specific charecteristics and provide an idea about which composite would be used in future discoveries.

2. THEORETICAL PART

2.1 Chitosan

Chitosan (CS) the second most abundant natural polymer on earth, is a crystalline polysaccharide derived from chitin, is provided with positively charged amino groups, which is found mostly in the insect's cuticle, cell wall of fungi, and crustacean's shells [4].

It was discovered in 1859 by French Professor C. Rouget [26]. He isolated chitosan from chitin found that insoluble chitin became soluble in acids when it was boiled in concentrated potassium hydroxide solution. In the year 1894, Hoppe- Seyler studied modified chitin and named it chitosan [27].

It has a unique combination of properties which have been found to be useful for a wide range of applications, because it is produced by the partial de-acetylation of chitin which means it is formally a co-polymer of glucosamine and *N*-acetylglucosamine residues [28]. So that it's structure is composed of *N*-glucosamine (deacetylated unit) and *N*-acetyl-D-glucosamine (acetylated unit) units in which the number of *N*- glucosamine units exceeds 50% [29]. In other words, when the degree of deacetylation of chitin exceeds 50% depending on the origin of the polymer, it becomes soluble in aqueous acidic media and called as chitosan. Protonation of the -NH_2 function at the C-2 position of the D-glucosamine repeated unit causes solubility function so that the polysaccharide is converted to a polyelectrolyte in acidic media [30]. Chemical name of chitosan is 2–amino-2-deoxy-β-D-glucopyranose and molecular formula is shown as $(C_6H_{11}O_4N)_n$. Chitosan structure shown in Figure 2.1.

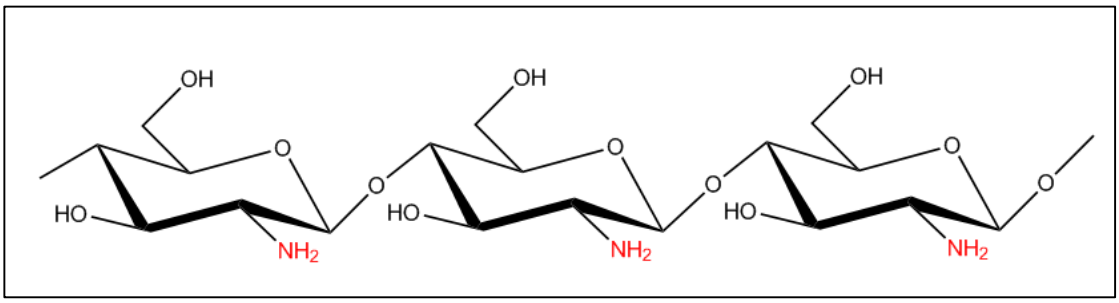

Figure 2.1: Chair conformation of Chitosan [29].

Chitosan has both reactive amino and hydroxyl groups which can be used to modify its properties under mild reaction conditions [3]. It has primary and secondary hydroxyl groups at the C-3 and C-6 positions [31]. Especially, the prominent structural feature of chitosan is its primary amine at the C-2 position of the glucosamine residues. Chitosan's amine rich chemical functionality is important because neither nature-derived polymers having rich amine functionality nor synthetic amine containing polymers are available in the industry. In addition to that, these amine groups are responsible many of the chitosan's useful functional properties. For example, Table 2.1 shows that chitosan's properties and details about especially for building and communication across the bio-device interface [28].

Table 2.1: Important properties of chitosan for building the bio-device interface and establishing communication across this bio-device interface [28].

Property	**Details**
Stimuli-responsive (pH-responsive)	Chitosan undergoes a soluble to insoluble transition with a change in pH
Self-assembly (self-association)	Chitosan's interchain associations can yield a 3 dimensional hydrogel network
Polycationic	Positive charges on chitosan's amines can undergo electrostatic interactions with (poly)anions
Nucleophilic	Unshared electrons on chitosan's amines enable chemical modification under facile conditions
Metal-binding	Chitosan chelates metals through interactions with its amino and hydroxyl groups
Oxidizable	Chitosan (like many polysaccharides) can be partially oxidized to generate reactive moieties (e.g., aldehydes)

Due to the amines, chitosan is a weak polyelectrolyte which has pH responsive features (Figure 2.2). At low pH, its primary amines are protonated for making it a cationic polyelectrolyte (polycation which promotes electrostatic interactions with (poly)anions) that is soluble in aqueous solution and also bioadhesive which binds to negatively charged surfaces such as mucosal membrane [29]. On the other hand at high pH, these amines are deprotonated (having an unshared pair of electrons that are nucleophilic and can be modified by electrophiles) for making it neutral and also insoluble. Significantly, it gets through its soluble to insoluble transition near when its pKa value is (≈6.2-6.6), which means it is convenient for biological applications due to be within a convenient range. Also, chitosan's pKa value is less than the value of 7.7 [28].

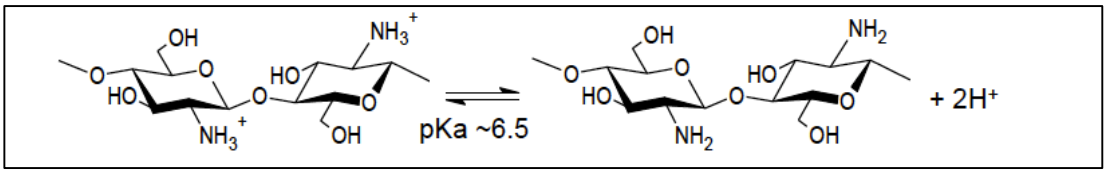

Figure 2.2: Chitosan's amines confer pH-responsiveness [28].

To form a three dimensional hydrogel network, chitosan chains can undergo self-associations. At low pH when chitosan is soluble in aqueous solution, these self-associations are suppressed by the electrostatic repulsions. However, when the pH is increased, chitosan loses its charge and the balance between the attractive and repulsive interactions is changed so that chitosan is insoluble in aqueous solution because the chains can undergo self- associations to form the hydrogel.

Furthermore, amines of chitosan can undergo chelation interactions with metals. In addition, it can be partially oxidized and it is used for producing reactive aldehydes moieties to get easily covalent grafting to the polysaccharide [28].

Chitosan has an antimicrobial effect on bacteria such as *Staphylococcus aureus, Listeria monocytogenes, Pseudomonas aeruginosa, Escherichia coli, Shigella dysenteriae, Vibro cholera*, and fungi such as *Sclerotinia sclerotium, Botrytis cinerea, Monilinia fructicola, Rhizopus stolonifer* , and also *Aspergillus niger*. There are mainly three mechanisms have been proposed based on results from previous investigations to explain the chitosan's antimicrobial activity. According to the first one, the positive charges, which at the polymeric chain of it due to its amino group, interact with the negative charges from the lipopolysaccharides and proteins in the microbial cell membranes, interfere with the nutrient exchange between the exterior and interior of the cell. The second one proposes that chitosan acts as a chelating agent and it creates compounds from traces of metals, which are essential to the cell. The last one establishes that low molecular weight chitosan is able to enter the cell's nucleus and it can interact with DNA, interfere with the messenger RNA synthesis, affect the synthesis of proteins, and also inhibit the action of many enzymes [2].

Other than the amine group importance, chitosan has a primary and secondary hydroxyl groups for good chemical modifications. Therefore, its properties can be changed to get improved physical, mechanical, biological, and solution features so that chitin and chitosan are different than cellulose due to have acetamido and amine groups and also this possession affects their properties. With regard to this, chitosan

is more preferred than chitin because of improved functionality, and modification [26].

Chitosan is chosen as one of the most attractive biopolymers due to its' specific properties; such as chemical inertness, high mechanical strength, antimicrobial activity, high quality film forming properties, and low cost, besides being biocompatible, biodegradable, and bio-functional [1, 2]. In addition to that, chitosan is hydrophilic, non-toxic, and non-antigenic as well as it has bioadherence, cell affinity and hemostatic potential properties [8, 32]. This properties depend on the degree of N-acetylation and distribution of N- acetyl groups [26].

It has been used in many industrial application areas such as cosmetics, paper, textile, food packaging, wastewater treatment, photography, solid-state batteries, biomedical applications (tissue engineering applications, drug delivery systems, wound healing and dressing, burn treatment, artificial skin, ophthalmology, biosensors), and separation membranes [5].

Some of the main commercial applications of chitosan are indicated in the Table 2.2 with commercial sectors and also Table 2.3 shows that potential biomedical applications of chitosan and its principal characteristics [29].

Table 2.2: Commercial applications of Chitosan [29].

Commercial Sector	**Applications**
Agriculture	Defensive mechanism in plants Stimulation of plant growths Seed coating, Frost protection Time release of fertilizers and nutrients into the soil
Water & Waste Treatment	Flocculants to clarify water (drinking water, pools) Removal of metal ions Ecological polymer (eliminate synthetic polymers) Reduce odors
Food & Beverages	Not digestible by human (dietary fiber) Bind lipids (reduce cholesterol) Preservative Thickener and stabilizer for sauces Protective, fungistatic, antibacterial coating for fruit

Table 2.2 (Continued): Commercial applications of Chitosan [29].

Commercial Sector	Applications
Cosmetics & Toiletries	Maintain skin moisture Treat acne Improve suppleness of hair Reduce static electricity in hair Tone skin Oral care (toothpaste, chewing gum)
Biopharmaceutics	Immunologic, anti-tumoral Hemostatic and anticoagulant Healing, bacteriostatic

Table 2.3: Potential biomedical-pharmaceutical applications of Chitosan [29].

Potential Biomedical Applications	Principal Characteristics
Surgical sutures Dental implants Artificial skin Rebuilding of bone Corneal contact lenses Time release drugs for animals and humans Encapsulating material	Biocompatible Biodegradable Renewable Film Forming Hydrating agent Nontoxic, biological tolerance Hydrolyzed by lysozyme Wound healing properties Efficient against bacteria, viruses, fungi

However, chitosan's flexibility in regulating mechanical properties is less and especially in wet state it has limitations in usage due to weak feature [8]. Also, under physiological conditions its' mechanical strength is low, for instance; pure chitosan conduits could be easily degradable and brittle which limits its usage as a nerve conduits for the clinical applications [33-35]. Besides that, the mechanical and water and oxygen permeability properties of chitosan films can be controlled by choosing suitable molecular weight and solvent system. Also, plasticizer, dispersants, and compatibilizers addition can affect the results. Unfortunately, adding these compounds can negatively affect the antimicrobial activity of chitosan films [2].

2.1.1 Chitin

Firstly, the French Proffesor Henri Braconnot discovered chitin at mushrooms in 1811. After a decade, it was isolated from insects. Chitin has 2-acetamido -2-deoxy-β-D-glucose through a β-(1→4) linkage [26]. At the chitin structure; two of the *N*-acetylglucosamine units repeats to form long chains in β-(1→4) linkage (Figure 2.3) [29].

Chitin is the most abundant natural fiber after the cellulose. Mostly chitin is found from the shell of crab and shrimp [26]. It acts as a structural component to form a complex network of proteins and calcium carbonate deposits, which forms the rigid shell in crustaceans, that supplies strength and protection in the shell and cuticle. Covalent bonding occurs between the chitin and protein interaction and it can be said that it is basically polysaccharide–protein complex [36].

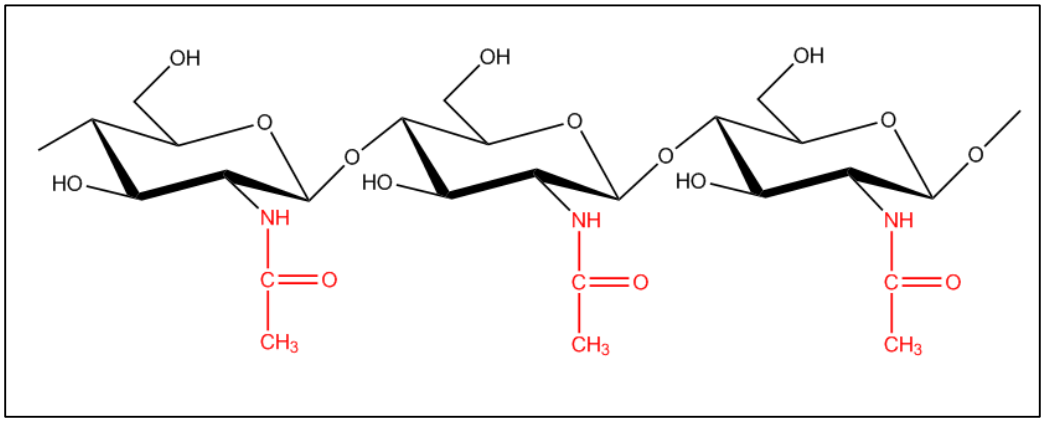

Figure 2.3: Structure of Chitin [29].

Deacetylated version of chitin known as a chitosan which means it can be water-soluble because chitin is insoluble in water, dilute acids, and alcohol [26]. Chitosan is also simplest and least expensive derivatives of chitin. In addition to that it is not native to animal sources [31]. Commercial chitin is usually produced from shrimp and crab shells. In nature, it occurs as in ordered crystalline state and presents in the cell wall of fungi and yeast or in the structural component of exoskeleton of arthropods [30]. Shellfish chitin is more chemically stable and crystalline also more acetylated than fungal chitin because it is softer , less crystalline, and less acetylated. These differences affect the extraction processes for producing chitin and Figure 2.4 shows the differences [36].

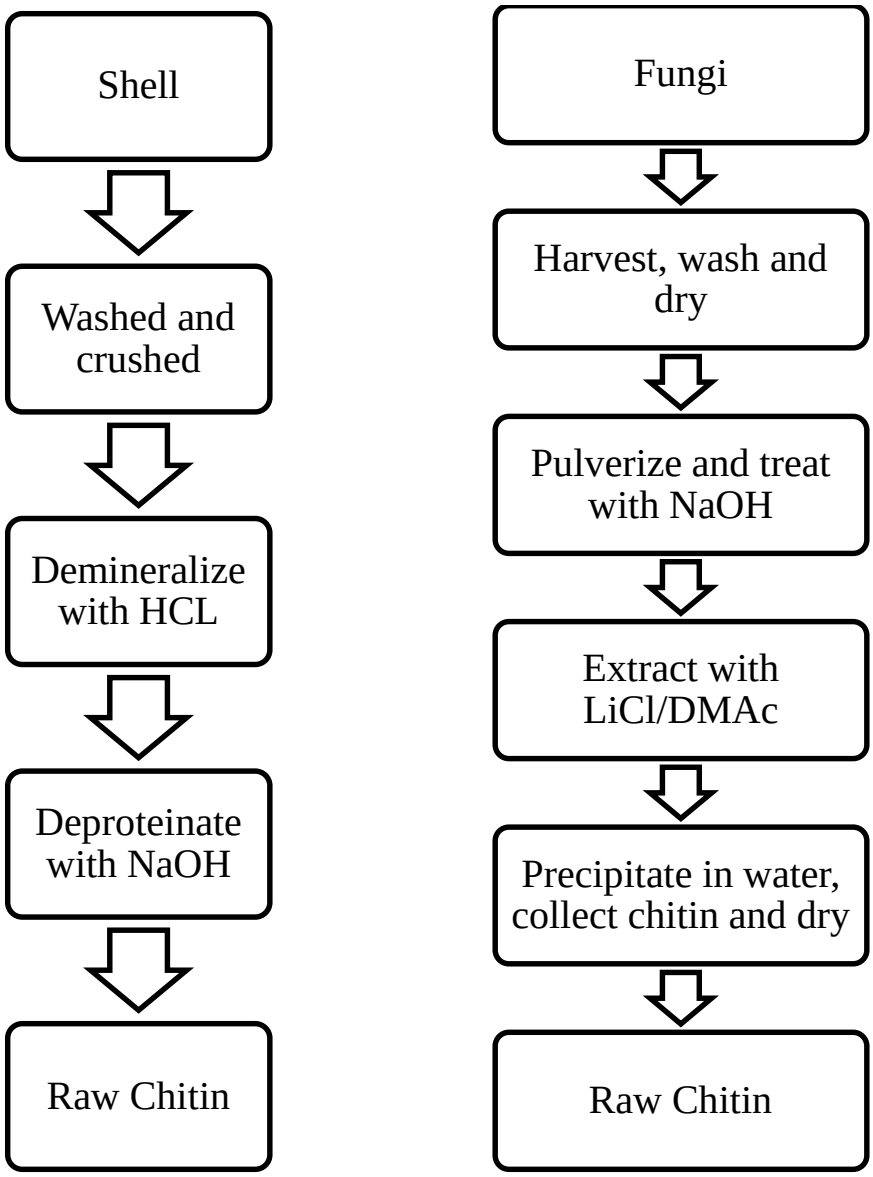

Figure 2.4: Chitin production from fungi and crustaceans [36].

Both chitosan and chitin have similarities with cellulose (Figure 2.5), in which C-2 hydroxyl groups are replaced by acetamido residue [26].

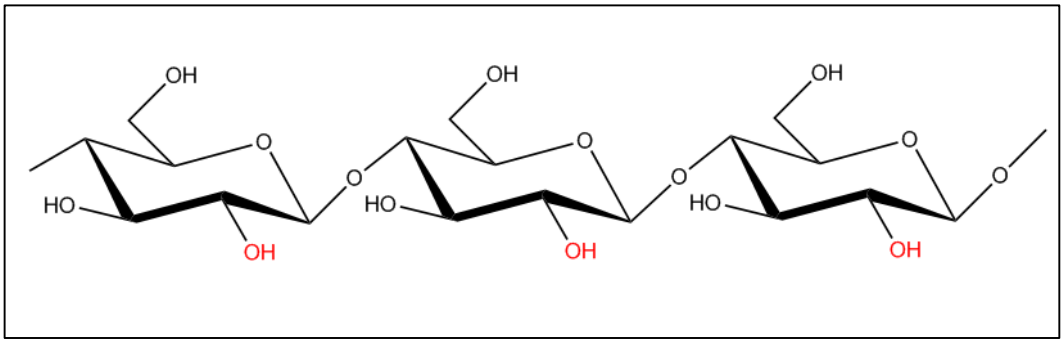

Figure 2.5: Structure of Cellulose [29].

2.2 Conductive Polymers (CPs)

Conductive polymers (CPs) are the polymers that have the capability to conduct electricity. These kinds of polymers have attracted more attention due to their unique properties and wide range of application potential in different electronics and device applications [6].

Firstly, conductive polymers (CPs) were produced in the mid-1970s as a novel generation of organic materials which means they have both electrical and optical properties similar with the those of metals and inorganic semiconductors, but also they have the attractive properties related with conventional polymers such as flexibility in processing and easy synthesis option [37].

The conjugated structure with alternating single and double bonds or conjugated segments that coupled with atoms providing *p*-orbitals for a continuous orbital overlap is the requirement of naturally conductive polymers. For instance; metals have high conductivity due to the free movement of electrons through their structure so that like them polymers which, to be electronically conductive, must have not only charge carriers but also an orbital system that allows the movement of charge carriers [38].

The discovery of conducting polymers was in 1960s but it was not understood so that it was lost. In 1977, Alan MacDiarmid, Hideki Shirakawa, and Alan Heeger reported that ten million–fold increase found in the conductivity of polyacetylene when doped with iodine so that the first time naturally conductive polymer was recognized [39, 40]. As a prototype, Polyacetylene has been widely studied due to its simple conjugated molecular structure and good electronic properties [38]. Many researches have been done to process and fabricate of CPs. Among the others, Polypyrrole (PPy), Polyaniline (PANI), and Polythiophene (PTh) and their derivatives are widely used because they can be synthesized easily and their some properties; such as enhanced thermal stability, high electrical conductivity, excellent chemical stability etc. [6].

After polyacetylene, the most commonly explored conducting polymers for biomedical applications are Polyyrrole, Polythiophene, Poly(3,4-ethylenedioxythiophene), and Polyaniline (Figure 2.6). With the development of aromatic CPs for different kind of application, they get much attention. Table 2.4

shows that mostly used broad range of different CPs and their conductivity values [37].

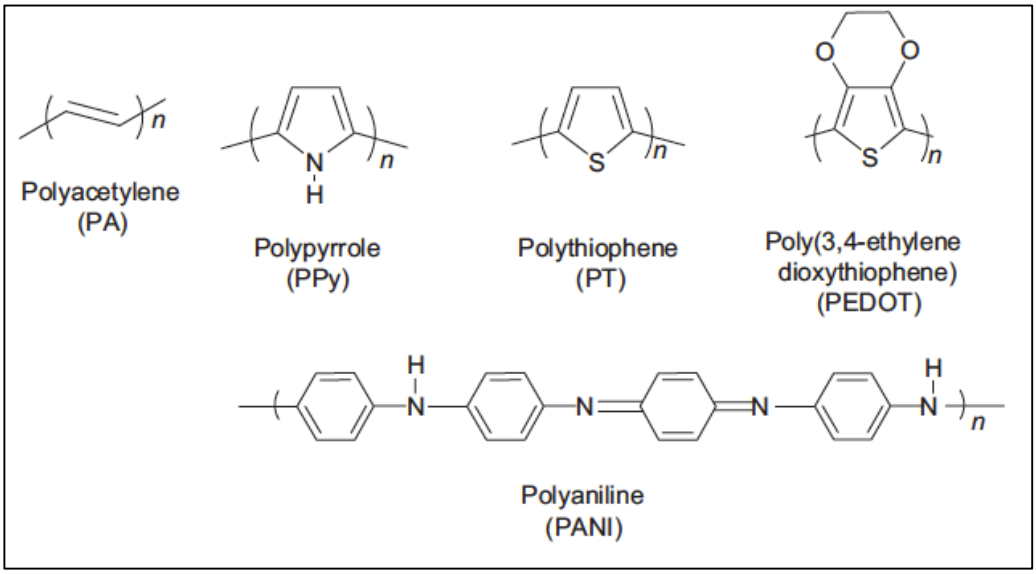

Figure 2.6: Conductive Polymers [37].

Table 2.4: Conductivity of common conductive polymers [37].

Conducting Polymer	**Maximum conductivity (S/cm)**	**Type of doping**
Polyacetylene (PA)	200-1000	n,p
Polyparaphenylene (PPP)	500	n,p
Polyparaphenylene sulfide (PPS)	3-300	p
Polyparavinylene (PPv)	1-1000	p
Polypyrrole (PPy)	40-200	p
Polythiophene (PT)	10-100	p
Polyisothionaphthene (PITN)	1-50	p
Polyaniline (PANI)	5	n,p

Synthesis of conducting polymers can be either chemically or electrochemically. Both of them has advantages and disadvantages as summarized in Table 2.5. Chemical synthesis methods include condensation polymerization (i.e., step growth polymerization) and addition polymerization (i.e., chain growth polymerization). At the condensation polymerization, small molecules like hydrochloric acid or water is loss to proceed. At the addition polymerization, radical, cation, and anion polymerizations can be done. Chemical synthesis method provides many different possible routes to synthesize a variety of CPs and also permits the scale-up of these materials which is not possible with using electrochemical synthesis method [37].

Table 2.5: Comparison of chemical and electrochemical CP polymerization [37].

Polymerization Approach	**Advantages**	**Disadvantages**
Chemical polymerization	- Larger-scale production possible - Post-covalent modification of bulk CP possible - More options to modify CP backbone covalently	- Cannot make thin films - Synthesis more complicated
Electrochemical polymerization	- Thin film synthesis possible - Ease of synthesis - Entrapment of molecules in CP - Doping is simultaneous	- Difficult to remove film from electrode surface - Post-covalent modification of bulk CP is difficult

Recently, conductive polymers have been extensively investigated because of their special properties and encouraging potential important applications such as electromagnetic interference shielding, biosensors, actuators, and field emission [9 - 13]. Table 2.6 shows that conducting polymers in biological applications with advantages and disadvantages [37]. In addition to that, lately modern researchers head towards to the fabrication of nano-architectures of these conducting polymers for improvement of different features. For example, one-dimensional nanostructures of CPs have offered many potential applications in various fields such as chemical sensor, gas separation membranes, neuron devices etc. [6].

Table 2.6: Conducting polymers in biological applications.

Application	Description of application	Advantages of conducting polymers	Limitations of conducting polymers
Tissue engineering	Biocompatible, biodegradable scaffolds containing stimuli to enhance tissue regeneration	- Biocompatibility - Good conductivity - Possible modification to include chemical cues	- Not biodegradable - Not highly porous - Hydrophobicity
Neural probes	Implantable electrodes for recording or stimulating neurons, primarily in the brain	- Biocompatibility - Good conductivity - Good stability - Electrochemical synthesis on metal electrodes - Increased surface area (decreased impedance)	- Decreased electrical contact at interface
Biosensors	Devices containing biomolecules as sensing elements, integrated with electrical transducers	- Ability to entrap biomolecules in films - Possible surface modification - Efficient electric charge transfer from bio-reactions - Electrochemical synthesis on metal electrodes	- Hydrophobicity can denature entrapped proteins - Diffusion barriers for entrapped enzymes
Drug Delivery	Devices for storage and controlled release for drugs	- Ability to entrap biomolecules - Controlled release with reduction	- Hydrophobicity can denature entrapped proteins - Rapid release
Bio-actuators	Devices to create mechanical force that could be used as ‘artificial muscle’-type actuators	- Biocompatibility - Good conductivity - Can control dopant uptake/release	- Short-term redox stability - Delamination of CP films - Response limited by ion mobility

2.2.1 Pyrrole

Polypyrrole (PPy) was one of the first studied conducting polymers (CPs) on mammalian cells to investigate its effects. According to the previous examinations, PPy has been reported that supports cell adhesion and growth of a number of different cell types [37]. PPy is the unique one among the family of conductive polymers owing to their high electrical conductivity at physiological pH, easy synthesis procedure, and cost effectiveness [6]. Relatively, its' environmental stability is good and also it has reversible doping and redox properties [41- 43]. In addition, it is biocompatible with mammalian cells [7, 8]. Both chemical and electrochemical polymerization is possible and it can cover over different kinds of substrates [14].

However, PPy has some drawbacks for example; poor cycling stabilities, low accessible degree of doping, high self-discharge rates, and mass transport limitations in thick polymer layers. Furthermore, it has limited large scale industrial applicability due to be brittle and also poor post- synthesis processability which are poor solubility in solvents, poor heat annealing properties, and poor compatibility affect that to produce coherent, self-standing films, wires, or other moulded or cast forms [14].

In situ polymerization of pyrrole (Py) monomers on various substrates has been widely used to give PPy with the chosen mechanical properties. According to that, both conductive, such as metals or carbon materials, and non conductive substrates such as synthetic or natural polymers, have been used [14]. Therefore, it has received great attention because of its wide application areas possibilities such as chemical sensors, biosensors, actuators, and dye sensitized solar cells [7].

Besides that, PPy in their nanoscale shows good electrical and electrochemical properties which allow their application in fabrication of wide range types of devices and still different kinds of nanoarchitectures of PPy have been investigated to find out them such as PPy nanoparticles, PPy nanowire, PPy nanotube, and PPy nanofiber [6].

2.2.1.1 Synthesis of Polypyrrole

Polypyrrole (PPy) can be formed either chemically or electrochemically through oxidative polymerization of pyrrole monomer (Figure 2.7) [44].

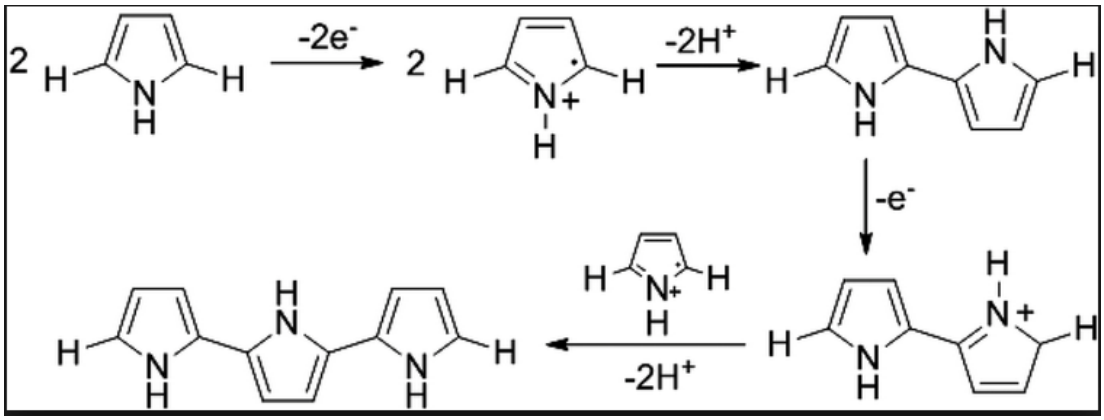

Figure 2.7: Oxidative polymerization of pyrrole to polypyrrole proceeds via a one electron oxidation of pyrrole to a radical cation [44].

PPy's resonance structures resemble the aromatic or quinoid forms (Figure 2.8). In the neutral state, PPy does not conduct electricity but it conducts only when it is oxidized [45].

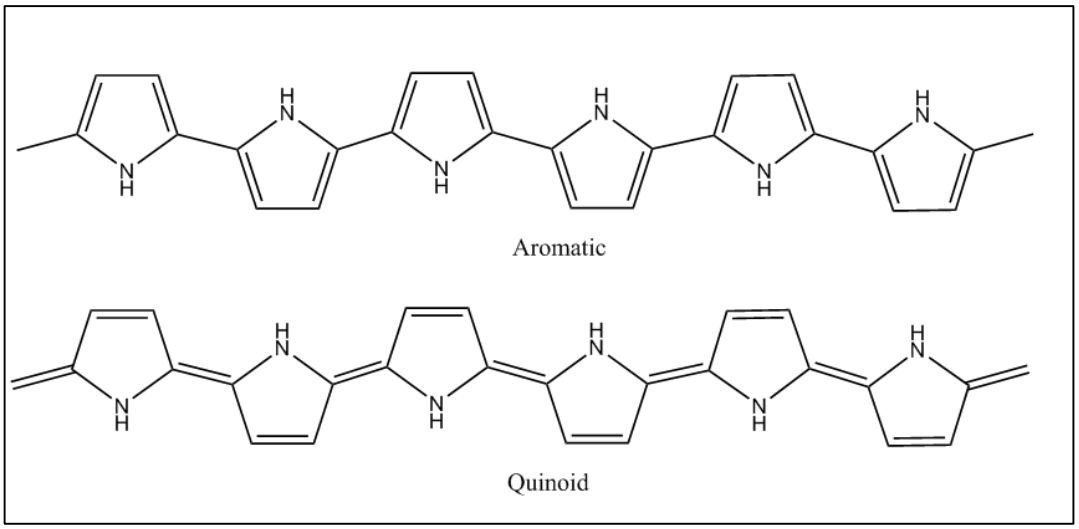

Figure 2.8: Aromatic and quinoid forms of polypyrrole chain [45].

The charge related with the oxidized state is typically delocalized over several units of this polymer and can form a radical cation, known as polaron, or a dication which is known as bipolaron [46,47]. The final chemical structure of polypyrrole, which has a long conjugated backbone, is shown in Figure 2.9. Resulting from chemical polymerization, polypyrrole's physical form is tough powder and also it gives insoluble films resulting of electropolymerization [48].

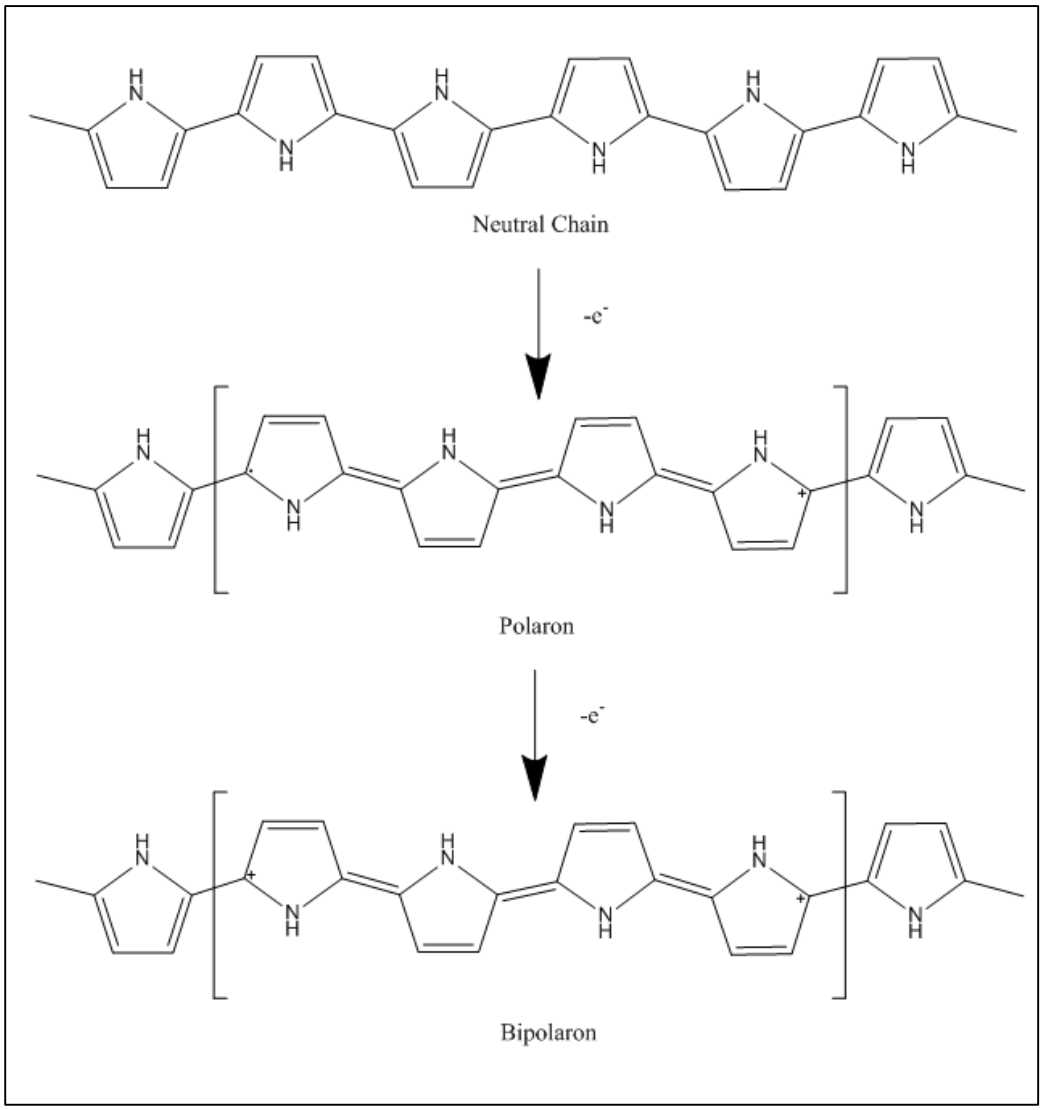

Figure 2.9: Chemical structures of polypyrrole in neutral chain, polaron and bipolaron forms [48].

2.2.1.2 Chemical Polymerization of Pyrrole

Chemical synthesis of polypyrrole is performed by the oxidation of pyrrole with an oxidant. The mechanism is similar with the electropolymerisation of pyrrole but conductivities are different. The resulting polymer, which is in its oxidized form, is conducting due to charge compensation afforded by dopant ion [49].

The concentration of acid affects the polymerization process. The conductivity of pyrrole increases when the synthesis temperature is reduced [50]. The density of polypyrrole is known as 1.48 g/cm^3 and 1.44 g/cm^3 [51, 52].

In the presence of an anionic surfactant, synthesized PPy samples have some advantages [53]. These are improved stability toward deprotonation, better thermal

stability [53], improved electrical parameters [54], reduced size polymer globules and more compact morphology [55], also higher solubility function [56]. However, these mentioned advantages are only achieved in the presence of an anionic surfactant, cationic or neutral surfactants are reported to be ineffective [53]. Therefore, in the form of free acid or salt, anionic surfactants can be used as stabilizers for these aims.

2.2.1.3 Pyrrole Copolymer With Ceric Ion

Significant progress about processibility and solubility of PPy has been made with polymerizing or producing functional groups on the carbon or nitrogen atoms of the pyrrole (Py) ring to get derivatives of polypyrrole [57]. The copolymerization of pyrrole with different monomers or oligomers produces copolymers that have various properties [58]. The polymerization of pyrrole with Ce^{+4} salts is produced by redox reaction between Py and Ce^{+4}. This redox reaction produces pyrrole radical cation (Py^{+}) which may dimerize with the expulsion of $2H^{+}$ and the polymerization process continues (polymer chains continue to grow) as long as Ce^{+4} ion and Py are present in the system [59].

2.2.2 Chitosan-Polypyrrole (CS-PPy) Copolymers

Recently, there have been attempts to synthesize various polypyrrole (PPy) composite materials to achieve a synergistic effect in regards to their properties.

Composites of chitosan and PPy have formed to investigate what combined biomimetric functionality can be obtained. According to previous experimental results, chemical polymerization of conducting polymer shows that direct interaction between the chitosan matrix and PPy, these materials can be dissolved as stable suspensions, coated on fabrics or fibers with antioxidant properties [15].

New type of conductive composites can be used possible applications in nerve repairs [8]. In addition, due to overcome some limitations in some industrial applications; such as biosensor production with incorporating a rigid conducting polymer into a flexible matrix like chitosan to combine the good processability of the matrix and electrical conductivity of polypyrrole [1].

2.3 Redox Polymerization

Redox polymerization has attracted the attention of scientist for many years. It is initiated by a reaction between an oxidizing and a reducing agent. Reduction-oxidizing process, the essence of redox initiation, is an oxidant such as Ce (IV) or Mn (III) produces firstly a complex by reacting simply with organic molecules which then decomposes unimolecularly to forms free radicals that start polymerization. Peroxides, persulphates, peroxydiphosphate, and the salts of transition metals are the commonly used oxidants which form effective redox systems for the aqueous polymerization of vinyl monomers with various reducing agents such as; alcohols, aldehydes, amines, thiols. The main properties of components constituting a redox pair for aqueous polymerization are their solubility in water, fast, and steady liberation of active radicals [60]. The polymerization reaction with redox systems can be done easily at low temperatures, also the reaction rate is easy to control by varying the concentration of metal ion or peroxide [61]. According to many literature reports, initiation by a redox process is the only a method to get these types of polymers on the block copolymer synthesis [62-65]. Unfortunately, initiation process has not been investigated widely in literature to figure out starting, which occurs due to polymer's functional end groups attached to the chains resulting from redox polymerization [66-67].

Redox polymerization systems have many technical and theoretical advantages over other methods for synthesis of block copolymers. For example; they are applicable at low temperatures and have decreasing possibility of side reactions [16]. They have a very short induction period (almost negligible) and a relatively low energy of activation (10-20 kcal/mol) allow the redox polymerization to be carried out under milder conditions than thermal polymerization. Comparatively high molecular weight polymers with high yields can be obtained in a very short time. In addition that, they can provide valuable information regarding the mechanism details of the elementary steps such as; the transient radical intermediates which are generated by redox reactions and they can be used for identification of these radicals as end groups of polymers to find the new idea on the reaction mechanisms of redox reactions [68-70]. However, there are still some problems present in the redox systems; such inorganic salts in a medium have poor solubility feature, slightly colored products

can be formed, and short pot life are expected due to production at ambient temperature [71].

Redox polymerization of vinyl monomers is initiated by transition metal ions in their higher oxidation states in an aqueous medium [72]. Many redox systems use ceric, manganese, cupper, iron, vanadium ion, and hydrogen peroxide as a catalyst for synthesis block copolymers via redox polymerization. The most versatile one could be ceric-based catalyst systems also many of redox systems with various catalysts still have been investigated [73].

2.3.1 Ceric Ion Redox Polymerization Systems

In acidic media, ceric ions are well known oxidizing agents for many organic substrates. These ions can be used as initiators for vinyl polymerization either by themselves or in combination with reducing agents. In 1979, Singh et al. [17] firstly attempted to initiate polymerization with using Ce (IV) in organic solvents [74-81]. Also they observed that the solvent toluene inhibits the redox initiating process for the polymerization of acrylonitrile. Many suitable reducing agents was found and reported in the literatures, these are alcohols [82], polyoils [83], ketones [84], acids [85], amines [86], thiols [87], and thiourea [88]. According to experimental results shown below, kinetic reaction scheme is proposed by Nagarajan et al. [89] for vinyl radical polymerization.

Reaction of ceric ion with reducing agent:

$$Ce^{+4} + R \rightarrow R\cdot + Ce^{+3} + H^{+}$$

Where, R is reducing agent and R· is the organic free radical formed from the reducing agent.

Reaction of the radical with Ce^{+4} to give the oxidation products:

$$Ce^{+4} + R\cdot \overset{k_0}{\underset{fast}{\rightarrow}} Oxidation\ Products + Ce^{+3} + H^{+}$$

Initiation of polymerization by reaction of the free radical with monomer:

$$R\cdot + M \overset{k_i}{\rightarrow} RM.$$

Propagation:

$$RM. + M \overset{k_p}{\rightarrow} RM_{2\cdot}$$

.....

.....

$$RM_{\dot{n}-1} + M \overset{k_p}{\rightarrow} RM_{\dot{n}}$$

Mutual termination:

$$2\,RM_{n\cdot} \overset{k_{t2}}{\rightarrow} polymer + Ce^{+3} + H^{+}$$

2.3.1.1 Ceric Ammonium Nitrate (CAN)

Ceric ammonium nitrate (CAN) is the one of the important reagents, which have unique role in chemical reactions. CAN is available as an orange solid compound. It has been widely used in industry and academia due to commercial availability until 1980s. Many reviews have been proposed to explain the role, efficiency, and advantages of CAN. Also, it is discussed for using at versatile roles in different chemical transformations that are carbon-carbon bond formation, oxidative carbon-carbon bond cleavage, nitration, and protecting groups removing. Obtained information will be valuable for chemical synthesis of new compounds and materials.

CAN, new chemical agent, was invented in 1936 by Smith [90] and also known as ammonium cerium (IV) nitrate, ammonium hexanitratocerate (IV), or ammonium nitratocerate (IV). It is prepared with using fresh ceric hydrate or oxide in an excess amount of nitric acid and after that with adding a quantitative amount of ammonium salt. At low temperatures, crystallized CAN which is orange color can be gained by evaporation process. According to X-Ray crystallography of CAN, cerium (IV) presents at the center of the anion completed by six bidentate nitrate groups [91]. Therefore the formula can be written as $(NH4)_2[Ce(NO_3)_6]$. It is readily available in pure form and can be overcome easily due to be anon-hygroscopic solid. The solubility of CAN in water changes according to temperature; for example it is 1.41 g/ml at 25 °C and 2.27 g/ml at 80 °C [92]. In polar organic solvents (such as acetic acid), it is used for a minimize extent. In redox reactions, CAN plays role as an oxidant. Due to color change from orange to pale yellow or colorless, consumption of CAN can be understandable if the substrate and the product not strongly colored. Because it has limited solubility property in common organic solvents, so reactions

including CAN are often performed in mixed water-organic solvents such as aqueous acetonitrile. The toxicity of CAN has not been clarified yet.

In industry, solution of CAN in dilute perchloric acid is used as etchants for preparing printed circuits, metal samples, and also it can be used as surface cleaning first step to production by soldering. In addition to that, this blend is used for etching of alloys, monel, nichrome, and stainless steel. In academia, CAN is extensively used in organic reactions to figure out the outcomes. Some representative examples are oxidation - oxidation addition, photo oxidation, nitration, deprotection, and graft polymerization. In these reactions, formed intermediates may undergo oxidative fragmentation, rearrangement, or cleavages of C-H and C-C bonds.

In the third world, many researchers have developed significant useful transformations by application of this reagent. For instance; Chavan and Subbarao [50] advanced a CAN-mediated azidoalkoxylation of enol ethers and olefins (Figure 2.10). Polanc [52] created a selective conversion of hydrazides to esters with using CAN in the presence of alcohol (Figure 2.11). Marko [80] used CAN as a catalyst in the deprotection of acetals to give the parent ketones (Figure 2.12). Arslan and Hazer [93] noted a polymerization of methyl methacrylate initiated by CAN, which is used in combination with polytetrahydrofuran diol represented in Figure 2.13.

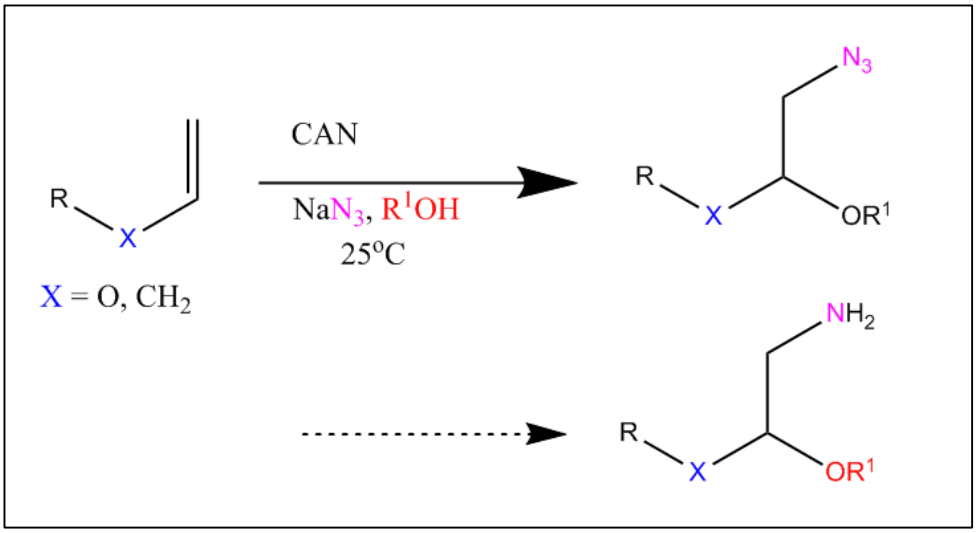

Figure 2.10: CAN-mediated azidoalkoxylation of enol ethers and olefins [50].

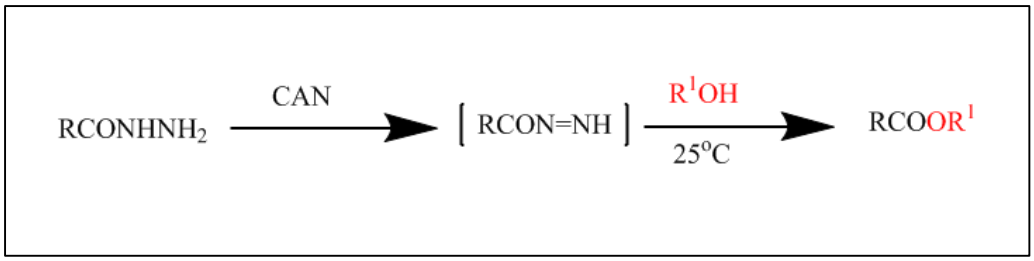

Figure 2.11: Selective conversion of hydrazides to esters [52].

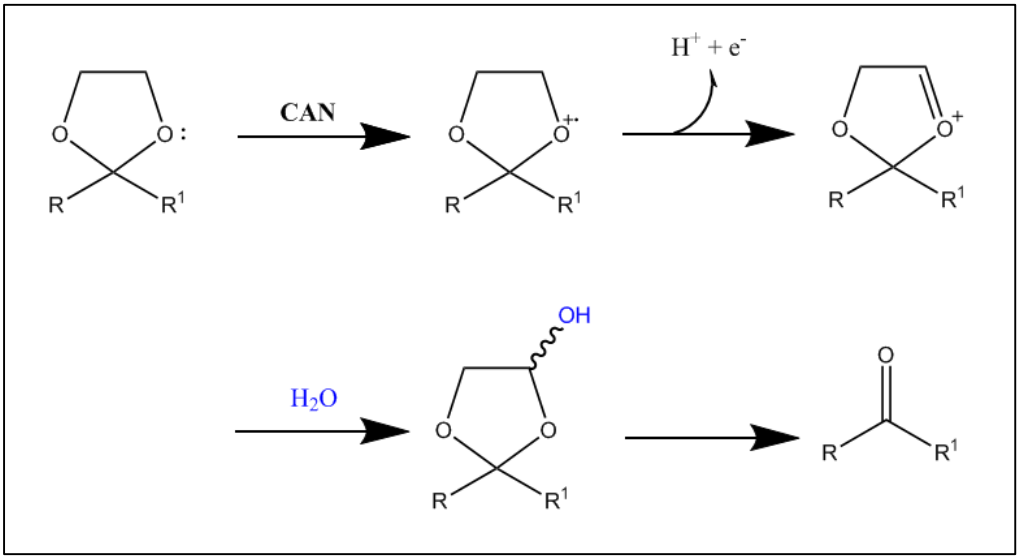

Figure 2.12: CAN as a catalyst in the deprotection of acetals [80].

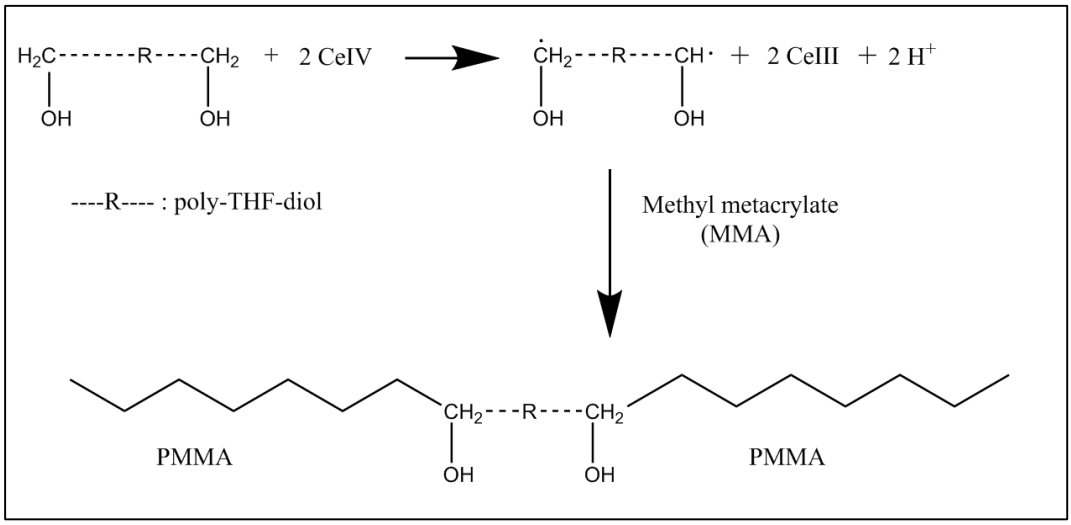

Figure 2.13: Methyl metacrylate initiated by CAN [93].

2.4 Polymer-Clay Nanocomposites

The preparation of polymers with clay minerals through different mechanisms due to the synergistic effect of them has been extensively studied topic in not only Clay Science but also in Polymer and Material Science [94]. The resulting materials are more commonly named as polymer-clay nanocomposites, or clay-polymer nanocomposites and also usually abbreviated as CPN [95]. CPN can show good modifications in their properties depending on the clay mineral and its interaction with the polymer. These modifications can be improved mechanical and barrier properties, thermal stability, high transparency, etc. In addition, CPN can actuate the inorganic counterpart as fillers in polymer matrix and if the polymer is natural one, the resulting materials are classified as a new group of hybrids, which are bionanocomposites [18]. Besides offering improved structural features, clay mineral-biopolymer nanocomposites usually give the biocompatible and biodegradable properties associated with the biopolymer. Also depending on the biopolymers' functional properties, they can be used in relevant areas as heterogeneous catalysts, chemical sensors, magnetic and electrochemical devices [94].

Most of the studies show that just bionanocomposites are related to polylacticacid (PLA), polycaprolactone (PCL), proteins and polysaccharides. However, recently using microfibrous clay minerals such as sepiolite and palygorskite show that good results in an interesting reinforcement of polymer as well as biopolymer matrices [96 -100].

2.4.1 Sepiolite

Sepiolite (Sep) is a clay mineral and it can be named inorganic solid [20]. It is an effective absorbent of organic species because of having some properties such as high specific surface area, high porosity, and high surface activity. Therefore, it can be used in many situations with utilizing its adsorptive, catalytic, and rheological properties. Due to having high specific surface area, it has absorption ability. This can be used in various industrial processes such as oil refining, wastewater treatment, the removal of odor, drug and pesticide carriers, paper and detergent manufacturing etc. Historically, scientist focused on especially adsorptive characteristic of sepiolite and therefore increasing the specific surface area of it [19]. Sepiolite is a good

alternative for low cost absorbents as clay minerals due to be abundant in nature and its unique ion exchange and intercalation properties [101].

Chivrac et al. [96] recognized that the fusion of sepiolite in a starch matrix results in a higher increase in Young's modulus and stress at break of the reinforced starch films than in bionanocomposites with the fusion of montmorillonite.

Sepiolite is a microcrystalline hydrated magnesium silicate, and its' theoretical unit cell formula is $Si_{12}O_{30}Mg_8(OH,F)_4(H_2O)_4*8H_2O$. It shows microfibrous morphology and a particle size in the 2-10 μm length range [20]. Natural magnesium silicates offer microporosity and large specific surface area around 320 m^2/g. The presence of OH groups at its external surface which can be functionalized to provide new properties [94]. Polymers not only interact with the external surface of sepiolite silicate, but they can also enter into the structural tunnels of it.

2.4.2 Chitosan-Polypyrrole-Sepiolite (CS/PPy/Sep) Nanocomposites

Chitosan and Sepiolite combination attracts special attention. Currently, material and polymer science researchers want to develop especially biomimetic or bioinspired materials based on the combination of natural polymers with inorganic solids. According to previous studies; chitosan- sepiolite composites can be used as components of electrochemical sensors [20].

Aim of sepiolite and chitosan combination is to develop nanostructured biohybrid materials presented with improved mechanical properties [20]. Chitosan is a natural polysaccharide having amino and hydroxyl groups in its structure. According to interaction mechanism; chitosan's amino groups in its' structure are protonated at slightly acidic pH to make this polysaccharide as a polymeric electrolyte which could be able to compensate the negatively charged sepiolite substrate. Also, hydrogen bonding can be established between the chitosan's hydroxyl groups and the silanol groups which are on the external surface of sepiolite.

Especially main reason for choosing sepiolite as a substrate for the preparation of new hybrid materials is the combination of amino group and hydrogen bonding interactions together with the increased specific surface area of silicate (> 300 m^2/g). Therefore, new hybrid material may show microfibrous morphology, improved mechanical properties, and attractive ion exchange behavior [20].

According to Figure 2.14; sepiolite shows an alternation of blocks and tunnels which grow up in the fiber direction. The blocks are formed by two layers of tetrahedral silica sandwiching a central magnesium oxide- hydroxide layer. The cross section tunnels are about 1.1 x 0.4 nm^2. The lack of continuity of the silica sheets leads to the presence of silanol groups (Si-OH) at the edges of the channels. These channels are the tunnels opened to the external surface of the sepioite particles. Tunnels are filled with coordinated water molecules and zeolitic water. At the edges of octahedral sheets, water molecules are bonded to the Mg^{2+} ions. The zeolitic water is associated to the former by hydrogen bonding [20].

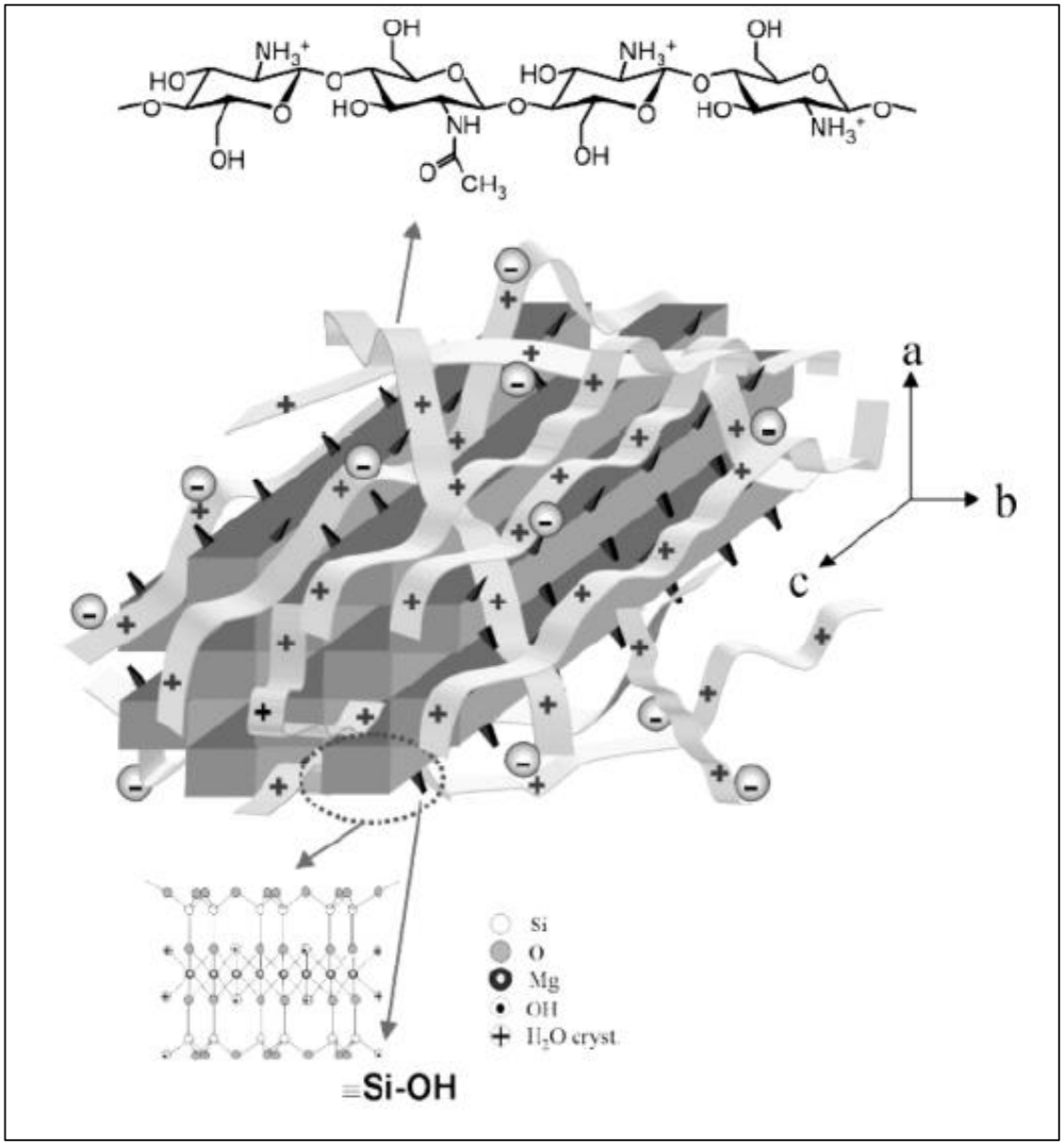

Figure 2.14: Idealized Representation of Chitosan Adsorption on the Sepiolite Surface [20].

2.5 Chitosan-Silver Nanocomposites

Recently, many scientists have focused on the use of biological materials like chitosan with combination of other inorganic agents such as Ag, Zn, CuO, TiO_2, and Fe to have higher antimicrobial activities than itself [21]. Resulted products, which include silver nanoparticles (AgnP), are able to exert bactericidal effects. The anti-microbial and multi-functional properties of Silver (Ag) ions have been investigated and attracted special attention because of their impact on the food and health care industries [22,23]. Tiam et al. [102] reported that Ag nanoparticles also have wound healing properties and it can help to restore burnt skin to the normal skin.

Chitosan has lots of amino and hydroxyl groups in the main chain and as a result of that it can coordinate well with metal ions and also can combine with metal ions via physical adsorption [103-105]. Thus, trying to load silver ion or silver containing compounds on chitosan has gotten attention day by day [106,107]. Yi et al. [108] found that the bacterial inhibition zone of silver loaded chitosan was 25% larger than silver nitrate at the same silver concentration. Rodriguez-Argüelles et al. [109] reported chitosan, which is loaded with silver nanoparticles showed broad-spectrum antibacterial activity against fungi, Gram-positive, and Gram-negative microorganisms. Due et al. [110] prepared silver loaded chitosan with minimum inhibitory concentration against *Escherichia coli* and *Staphylococcus aureus* in vitro, as a result of finding good synergistic antimicrobial effect of chitosan and silver.

Nano-silver, which is a particle of Ag element, is named as a new class of material because of it has different physical, chemical, and physicochemical characteristics such as increased optical, electromagnetic, and catalytic properties from bulk materials [111]. For producing silver nanoparticles, chemical reduction method is used which silver is dissolved in water with a reducing compound such as $NaBH_4$, citrate, glucose, hydrazine, and ascorbate [112].

Scientists have proposed different routes to synthesis of silver nanoparticles with incorporating into chitosan. For example; dispersion of silver powder in chitosan [113,114], reduction of $AgNO_3$ by $NaBH_4$ [115,116], dissolving $AgNO_3$ in chitosan solution [117]. As a result of silver interactions with OH and NH_2 groups of chitosan, the specific modifications in both chitosan and silver nanoparticles may affect inter- and intra- molecular hydrogen bonds in the biopolymer. Therefore,

biopolymer's physicochemical and electrical properties can be positively affected; in addition to that this may affect its antimicrobial characteristics [118]. Gonzalez-Campos et al. [118] hypothesize that the correlation is exist between electrical and antibacterial properties of CS/AgnP nanocomposites.

Silver ions can interact with a variety of microbial molecules such as DNA, cell wall components, sulfhydryl groups of metabolic enzymes etc. that cause the interruption of bacterial replication, membrane permeability, and different metabolic enzymes in the bacterial electron transport chain [119-124]. However, chitosan's poor mechanical properties and thermal stabilities are barrier for using it in a wider application areas so that researchers have focused on improving that with using combination of inorganic carriers such as montmorillonite, sepiolite, etc. [125]. Silver loaded chitosan–sepiolite blend can supply important improvement in mechanical and functional properties for using in different biological research and biomedical applications.

3. EXPERIMENTAL

3.1 Materials

Chitosan was supplied from Sigma – Aldrich. Product form is coarse ground flakes and powder. Its color is off-white beige and deacetylation ratio is 75%. Ceric ammonium nitrate was taken from Analar and dried in oven at 105 °C before used. Pyrrole and nitric acid (HNO_3) were supplied by Merck and J.T. Baker, respectively. Sodium hydroxide (NaOH) pellets were purchased from Sigma-Aldrich. Sepiolite was provided from Tolsa Group and Silver Nitrate ($AgNO_3$) were supplied from Sigma-Aldrich.

3.2 Analysis

Four-point probe technique was used to measure electrical conductivities of prepared pellets, which were copolymer powders. Fourier transform infrared (FTIR) spectra was obtained with a recording model FTS-600 Excalibur FTIR spectrometer with using Varian Resolutions Pro as software. They were obtained directly from the sample without KBr discs. The morphology of the products was examined by scanning electron microscopy (SEM; ESEM XL30 ESEM-FEG, Philips) and the samples for the SEM measurement were prepared by platinum coating.

3.3 Conductivity Measurement and Calculations

Compact thin pellets were prepared under 8-10 tons/cm^2 pressure to measure electrical conductivity (σ). After thickness of the pellets were measured, four-point probe technique was performed for conductivity measurements of copolymers and results were calculated according to the following equation (3.1):

$$\sigma = V^{-1} \cdot I\left(\frac{ln2}{\pi d_n}\right) \quad \textbf{(3.1)}$$

Parameters meaning are: *V* is the potential (V), *I* is the current (A), *dn* is the thickness of the samples (cm).

3.4 Preparation of Blank Polypyrrole (PPy) Composites

3.4.1 Choosing Ceric Ammonium Nitrate (CAN) stock solution type (Blank A Type vs. Blank B Type)

To understand the effect of CAN stock solution on the conductivity, two experiments were conducted. Blank A and Blank B types were compared according to conductivity results. Blank A type was prepared with 5.48 g ceric ammonium nitrate dissolved in 100 mL distilled water, and was used 91.2 mL of it. However; Blank B was prepared with 5.48 g ceric ammonium nitrate dissolved in 100 mL 1 M HNO_3, and used 91.2 mL of it. Both Blank A and Blank B types have the same procedure with the preparation of blank polypyrrole composites. Table 3.1 and Table 3.2 show the molar ratios of CAN and PPy, and also moles and used amount of them, respectively.

Table 3.1: Blank A Type vs. Blank B Type.

Sample Name	[Py] (M)	[CAN] (M)	CAN dissolved in	[CAN]/ [PPy]
Blank A Type	0.025	0.05	Distilled water	0.22
Blank B Type	0.025	0.05	Nitric acid (65 wt %)	0.22

Table 3.2: Used Pyrrole and CAN in moles and grams.

Sample Name	n(Py) (moles)	n(CAN) (moles)	PPy (mL)	CAN (g)	n(CAN)/ n(PPy)
Blank A Type	0.046	0.01	3.2	5.48	0.22
Blank B Type	0.046	0.01	3.2	5.48	0.22

1 M HNO_3 was prepared and 4 mL of it freshly used, which includes dissolved 7.0 mL $HN0_3$ in 100 ml distilled water. Differently prepared 0.1 M CAN stock solutions for Blank A and Blank B types were added drop-wise to the reaction mixture, which has 100 mL distilled water, 4 mL 1 M HNO_3, and 3.2 mL pyrrole monomer, and vigorous stirring, in about 25-30 min. while stirring under room condition at 25 °C. Reaction was completed in 1 hour when this time the flask was waited on the magnetic stirrer. After reaction was completed, polymerization solution was filtered and washed with distilled water several times. After copolymer was separated from

the filtering paper, taken part was dried at 40 °C in the drying oven until it was completely dry. Finally, it was ready for making compact thin pellets under pressure to measure conductivity and also using at other analysis. Figure 3.1 represents the basic experimental procedure for all conducted experiments.

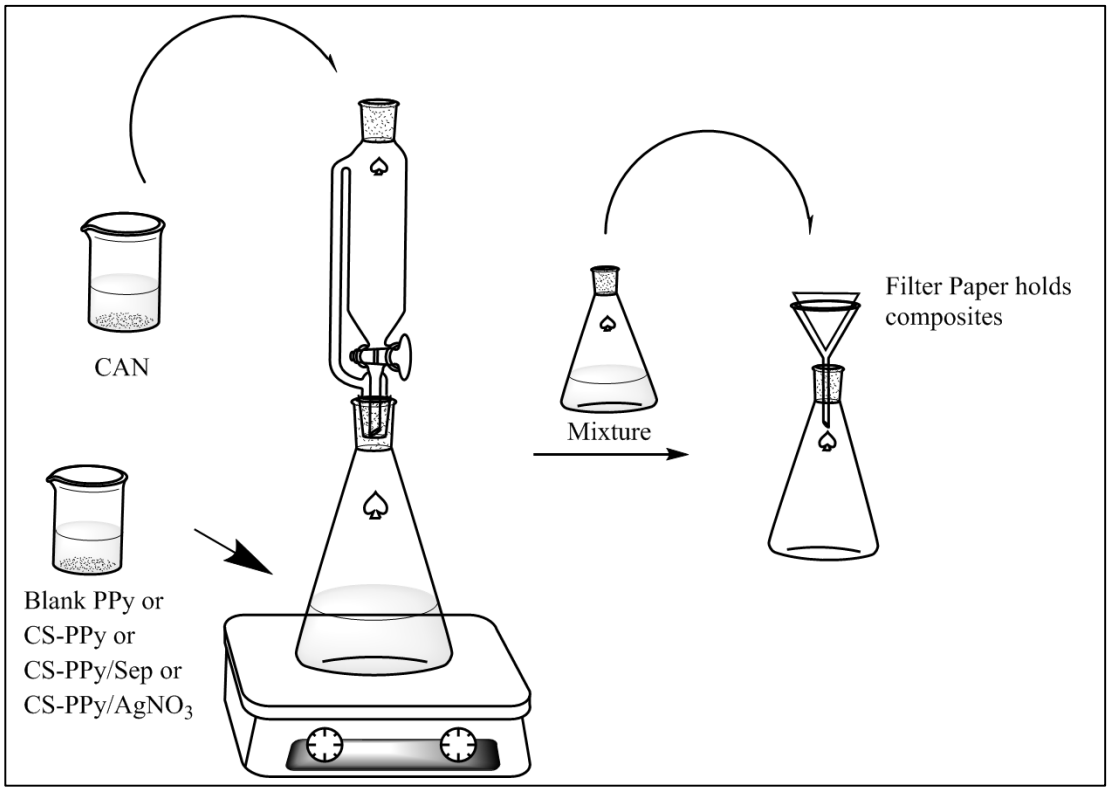

Figure 3.1: Experimental procedure representation.

3.4.2 Preparation of Blank Polypyrrole with Blank A Type

1 M HNO_3 was prepared and 4 mL of it freshly used, which includes dissolved 7.0 mL HNO_3 in 100 mL distilled water. 0.1 M CAN stock solution was prepared with dissolving calculated amount of ceric ammonium nitrate in 100 mL distilled water. According to n (CAN)/n(PPy) mole ratios which is varied from 0.67, 0.8, and 1.0 ; used ceric ammonium nitrate amount was changed. Variable molar ratios and used pyrrole and ceric ammonium nitrate amounts are shown in Table 3.3 and Table 3.4, respectively. For blank preparations; calculated amount of pyrrole monomer, ceric ammonium nitrate solution; and also 100 mL distilled water and 4 mL 1M HNO_3 were used. Blank types do not contain chitosan monomer. 100 mL distilled water, 4 mL 1 M HNO_3, and pyrrole monomer that is according to Table 3.4 were added with

vigorous stirring into the flask. After blend became homogenous approximately in 5 min., CAN stock solution was added drop-wise to the reaction mixture in about 25-30 min. while stirring under room condition at 25 °C. Reaction was completed in 1 hour when this time the flask was waited on the magnetic stirrer. After reaction was completed, polymerization solution was filtered and washed with distilled water several times. After copolymer was separated from the filtering paper, taken part was dried at 40 °C in the drying oven until it was completely dry. Finally, it was ready for making compact thin pellets under pressure to measure conductivity and also using at other analysis.

Table 3.3: Molar ratios of Pyrrole and CAN.

[Pyrrole] (M)	**[CAN] (M)**	**[CAN]/[PPy]**
0.113	0.075	0.67
0.113	0.09	0.8
0.113	0.113	1

Table 3.4: Used Pyrrole and CAN in moles and grams.

Sample Name	**n(Py) (moles)**	**n(CAN) (moles)**	**n(CAN)/n(PPy)**	**PPy (mL)**	**CAN (g)**
PPy – 1	0.023	0.015	0.67	1.6	8.41
PPy – 2	0.023	0.018	0.8	1.6	10.09
PPy – 3	0.023	0.023	1	1.6	12.6

3.4.3 Preparation of Blank Polypyrrole/ Sepiolite

1 M HNO_3 was prepared and 4 mL of it freshly used, which includes dissolved 7.0 mL HNO_3 in 100 mL distilled water. 0.1 M CAN stock solution was prepared with dissolving calculated amount of ceric ammonium nitrate in 100 mL distilled water. According to n(CAN)/n(PPy) mole ratios which is varied from 0.67, 0.8, and 1.0 ; used ceric ammonium nitrate amount was changed. Variable molar ratios and used pyrrole, sepiolite, and ceric ammonium nitrate amounts are shown in Table 3.5 and 3.6, respectively. For blank preparations; calculated amount of pyrrole monomer, sepiolite, and ceric ammonium nitrate solution were used according to Table 3.6. In addition, 100 mL distilled water and 4 mL 1M HNO_3 were used. Blank types do not

contain chitosan monomer. According to (Pyrrole)/(Sepiolite) = 3 (g/g) equation; sepiolite amount was calculated. Firstly, sepiolite and pyrrole were added into the flask with vigorous stirring. After they became integrated approximately in 5 minutes, 4 mL of 1 M HNO_3, and 100 mL distilled water added. After blend became homogenous approximately in 10 min., CAN stock solution was added drop-wise to the reaction mixture in about 25-30 min. while stirring under room condition at 25 °C. Reaction was completed in 1 hour when this time the flask was waited on the magnetic stirrer. After reaction was completed, polymerization solution was filtered and washed with distilled water several times. After copolymer was separated from the filtering paper, taken part was dried at 40 °C in the drying oven until it was completely dry. Finally, it was ready for making compact thin pellets under pressure to measure conductivity and also using at other analysis.

Table 3.5: Molar ratios of Pyrrole and CAN.

[PPy] (M)	**[CAN] (M)**	**[CAN]/[PPy]**
0.113	0.075	0.67
0.113	0.09	0.8
0.113	0.113	1

Table 3.6: Used Pyrrole, CAN, and Sepiolite in moles and grams.

Sample Name	**n(Py) (moles)**	**n(CAN) (moles)**	**n(CAN)/ n(PPy)**	**PPy (mL)**	**CAN (g)**	**PPy (g)**	**Sepiolite (g)**
PPy/Sep – 1	0.023	0.015	0.67	1.6	8.41	1.55	0.52
PPy/Sep – 2	0.023	0.018	0.8	1.6	10.09	1.55	0.52
PPy/Sep – 3	0.023	0.023	1	1.6	12.6	1.55	0.52

3.4.4 Preparation of Blank Polypyrrole/ $AgNO_3$

1 M HNO_3 was prepared and 4 mL of it freshly used, which includes dissolved 7.0 mL HNO_3 in 100 mL distilled water. 0.1 M CAN stock solution was prepared with dissolving calculated amount of ceric ammonium nitrate in 100 mL distilled water. According to n(CAN)/n(PPy)= 0.67 mole ratio; used ceric ammonium nitrate and polypyrrole amount were shown in Table 3.7. Used $AgNO_3$ amount was calculated according to n(Ag)/n(PPy) = 2.5 equation.

For blank preparations; calculated amount of pyrrole monomer, ceric ammonium nitrate solution; and also 100 mL distilled water, 10.8 g $AgNO_3$, and 4 ml 1M HNO_3 were used. Blank types do not contain chitosan monomer.

100 mL distilled water, 4 ml 1 M HNO_3, 10.8 g $AgNO_3$, and pyrrole monomer that is according to Table 3.8 were added with vigorous stirring into the flask. After blend became homogenous approximately in 10 min., CAN stock solution was added drop-wise to the reaction mixture in about 25-30 min. while stirring under room condition at 25 °C. Reaction was completed in 24 hour when this time the flask was waited on the magnetic stirrer. After reaction was completed, polymerization solution was filtered and washed with distilled water several times. After copolymer was separated from the filtering paper, taken part was dried at 40 °C in the drying oven until it was completely dry. Finally, it was ready for making compact thin pellets under pressure to measure conductivity and also using at other analysis.

Table 3.7: Molar ratio of Pyrrole and CAN

[PPy] (M)	**[CAN] (M)**	**[CAN]/[PPy]**
0.113	0.075	0.67

Table 3.8: Used Pyrrole, CAN, and $AgNO_3$ in moles and grams.

Sample Name	**n(Py) (moles)**	**n(CAN) (moles)**	**n(CAN/ n(PPy)**	**PPy (mL)**	**CAN (g)**	**n($AgNO_3$) (moles)**	**$AgNO_3$ (g)**
PPy/Ag	0.023	0.015	0.67	1.6	8.41	0.06	10.8

3.5 Preparation of Chitosan/ Polypyrrole Copolymers

1 M HNO_3 was prepared and 4 mL of it freshly used, which includes dissolved 7.0 mL HNO_3 in 100 ml distilled water. 0.1 M CAN stock solution was prepared with dissolving calculated amount of ceric ammonium nitrate in 100 mL distilled water. According to n(CAN)/n(PPy) mole ratios which is varied from 0.67, 0.8, and 1.0; used ceric ammonium nitrate amount was changed. Variable molar ratios and used pyrrole, chitosan, and ceric ammonium nitrate amounts are shown in Table 3.9 and 3.10, respectively. Calculated amount of chitosan was dissolved in 100 mL distilled water with adding 4 mL of 1M HNO_3 to solve it easily. Then, calculated amount of pyrrole monomer was added with vigorous stirring into the flask. After blend became

homogenous approximately in 10 min., CAN stock solution was added drop-wise to the reaction mixture in about 25-30 min. while stirring under room condition at 25 °C. Reaction was completed in 1 hour when this time the flask was waited on the magnetic stirrer. After reaction was completed, polymerization solution was filtered and washed with distilled water and also methanol several times. After copolymer was separated from the filtering paper, taken part was dried at 40 °C in the drying oven until it was completely dry. In addition to that, due to the solution was so much liquid to filter, NaOH was added until getting its pH ≈ 7 to get chitosan easily from the filtering paper. Finally, it was ready for making compact thin pellets under pressure to measure conductivity and also using at other analysis.

Table 3.9: Molar ratios of Pyrrole and CAN.

[PPy] (M)	**[CAN] (M)**	**[CAN]/[PPy]**
0.113	0.075	0.67
0.113	0.09	0.8
0.113	0.113	1

Table 3.10: Used Pyrrole, CAN, and Chitosan in moles and grams.

Sample Name	**CS (g)**	**n(Py) (moles)**	**n(CAN) (moles)**	**n(CAN)/n(PPy)**	**PPy (mL)**	**CAN (g)**
PPy/CS – 1	0.016	0.023	0.015	0.67	1.6	8.41
PPy/CS – 2	0.5	0.023	0.015	0.67	1.6	8.41
PPy/CS – 3	0.016	0.023	0.018	0.8	1.6	10.09
PPy/CS – 4	0.5	0.023	0.018	0.8	1.6	10.09
PPy/CS – 5	0.016	0.023	0.023	1	1.6	12.6
PPy/CS – 6	0.5	0.023	0.023	1	1.6	12.6

3.6 Preparation of Chitosan/ Polypyrrole/ Sepiolite Nanocomposites

1 M HNO_3 was prepared and 4 mL of it freshly used, which includes dissolved 7.0 mL HNO_3 in 100 mL distilled water. 0.1 M CAN stock solution was prepared with dissolving calculated amount of ceric ammonium nitrate in 100 mL distilled water. According to n(CAN)/n(PPy) mole ratios which is varied from 0.67, 0.8, and 1.0; used ceric ammonium nitrate amount was changed. Variable molar ratios and used

chitosan, pyrrole, sepiolite and ceric ammonium nitrate amounts are shown in Table 3.11 and 3.12, respectively. According to (Pyrrole)/(Sepiolite) = 3 (g/g) equation; sepiolite amount was calculated. Firstly, 0.52 g sepiolite and 1.6 mL pyrrole were added into the flask with vigorous stirring. After they became integrated approximately in 5 minutes, variable amounts of chitosan according to sample names, 4 mL of 1 M HNO_3, and 100 ml distilled water added. After blend became homogenous approximately in 15 min., CAN stock solution was added drop-wise to the reaction mixture in about 25-30 min. while stirring under room condition at 25 °C. Reaction was completed in 1 hour when this time the flask was waited on the magnetic stirrer. After reaction was completed, polymerization solution was filtered and washed with distilled water and methanol several times. After copolymer was separated from the filtering paper, taken part was dried at 40 °C in the drying oven until it was completely dry. In addition to that, due to the solution was so much liquid to filter, NaOH was added until getting its pH ≈7 to get chitosan easily from the filtering paper. Finally, it was ready for making compact thin pellets under pressure to measure conductivity and also using at other analysis.

Table 3.11: Molar ratios of Pyrrole and CAN

[PPy] (M)	**[CAN] (M)**	**[CAN]/[PPy]**
0.113	0.075	0.67
0.113	0.09	0.8
0.113	0.113	1

Table 3.12: Used amount moles and grams of Pyrrole, Chitosan, CAN, and Sepiolite.

Sample Name	**CS (g)**	**n(Py) (moles)**	**n(CAN) (moles)**	**n(CAN)/ n(PPy)**	**PPy (mL)**	**CAN (g)**	**PPy (g)**	**Sep(g)**
PPy-CS/Sep – 1	0.016	0.023	0.015	0.67	1.6	8.41	1.55	0.52

Table 3.12 (Continued): Used amount moles and grams of Pyrrole, Chitosan, CAN, and Sepiolite.

Sample Name	CS (g)	n(Py) (moles)	n(CAN) (moles)	n(CAN) /n(PPy)	PPy (mL)	CAN (g)	PPy (g)	Sep(g)
PPy-CS/Sep – 2	0.5	0.023	0.015	0.67	1.6	8.41	1.55	0.52
PPy-CS/Sep – 3	0.016	0.023	0.018	0.8	1.6	10.09	1.55	0.52
PPy-CS/Sep – 4	0.5	0.023	0.018	0.8	1.6	10.09	1.55	0.52
PPy-CS/Sep – 5	0.016	0.023	0.023	1	1.6	12.6	1.55	0.52
PPy-CS/Sep – 6	0.5	0.023	0.023	1	1.6	12.6	1.55	0.52

3.7 Preparation of Chitosan/ $AgNO_3$ Nanocomposites

1 M HNO_3 was prepared and 4 mL of it freshly used, which includes dissolved 7.0 mL HNO_3 in 100 mL distilled water. 0.1 M CAN stock solution was prepared with dissolving calculated amount of ceric ammonium nitrate in 100 mL distilled water. According to n(CAN)/n(PPy) = 0.67 mole ratio; used ceric ammonium nitrate and pyrrole amount were shown in Table 3.13. Used $AgNO_3$ amount was calculated according to n(Ag)/n(PPy) = 2.5 equation.

Calculated amount of pyrrole monomer, chitosan, sepiolite, and ceric ammonium nitrate solution; and also 100 mL distilled water, 10.8 g $AgNO_3$, and 4 mL 1M HNO_3 were used.

100 mL distilled water, 4 mL 1 M HNO_3, 10.8 g $AgNO_3$, chitosan, sepiolite, and pyrrole monomer that is according to Table 3.14 were added with vigorous stirring into the flask. After blend became homogenous approximately in 15 minutes, CAN

stock solution was added drop-wise to the reaction mixture in about 25-30 min. while stirring under room condition at 25 °C. Reaction was completed in 24 hour when this time the flask was waited on the magnetic stirrer. After reaction was completed, polymerization solution was filtered and washed with distilled water and methanol several times. After copolymer was separated from the filtering paper, taken part was dried at 40 °C in the drying oven until it was completely dry. In addition to that, due to the solution was so much liquid to filter, NaOH was added until getting its pH ≈7 to get chitosan easily from the filtering paper, except PPy-Sep/Ag sample. Finally, it was ready for making compact thin pellets under pressure to measure conductivity and also using at other analysis.

Table 3.13: Molar ratios of Pyrrole and CAN.

[PPy] (M)	**[CAN] (M)**	**[CAN]/[PPy]**
0.113	0.075	0.67

Table 3.14: Used amount moles and grams of Chitosan, Sepiolite, Pyrrole, and $AgNO_3$.

Sample Name	**CS (g)**	**Sep (g)**	**n(Py) (moles)**	**n(CAN) (moles)**	**n(CAN) /n(PPy)**	**n($AgNO_3$) (moles)**	**$AgNO_3$ (g)**
PPy-Sep/Ag	0	0.52	0.023	0.015	0.67	0.06	10.8
PPy-CS/Ag	0.016	0	0.023	0.015	0.67	0.06	10.8
PPy-CS-Sep/Ag	0.016	0.52	0.023	0.015	0.67	0.06	10.8

4. RESULTS AND DISCUSSION

The goal of this study is to discover and produce high conductivity biodegradable, biocompatible, and biofunctional composites and nanocomposites which can be used in biomedical applications. Polypyrrole/Chitosan composites, Polypyrrole-Chitosan/Sepiolite and Polypyrrole/Silver Nitrate nanocomposites were formed. The yield of the composite products and electrical conductivities were calculated and listed in tables according to experiment titles that are below. For calculating electrical conductivities four probe technique was used. Also the resulting nano-composites were characterized with spectroscopic method that was Fourier Transform Infrared Spectroscopy (FTIR), and also morphological method, which was Scanning Electron Microscopy (SEM).

4.1 Blank Polypyrrole

According to the proposed chemical polymerization of pyrrole (Py) monomer; two mechanistic possibilities are available. First one is the oxidation of Py by Ce (IV) that forms radical cations (Py^+) which can dimerize with the expulsion of $2H^+$. The second possibility in the initial step is the formation of Py radical cations with proton loss and these radicals can dimerize. In the propagation step, the polymer chains continue to grow as long as Py and Ce (IV) are available in the medium. In the termination step, the growing PPy chains may combine with other PPy chains to produce PPy and terminate it with combination method. Initiation step can be shown in Figure 4.1 and also Figure 4.2 is for propagation and termination steps.

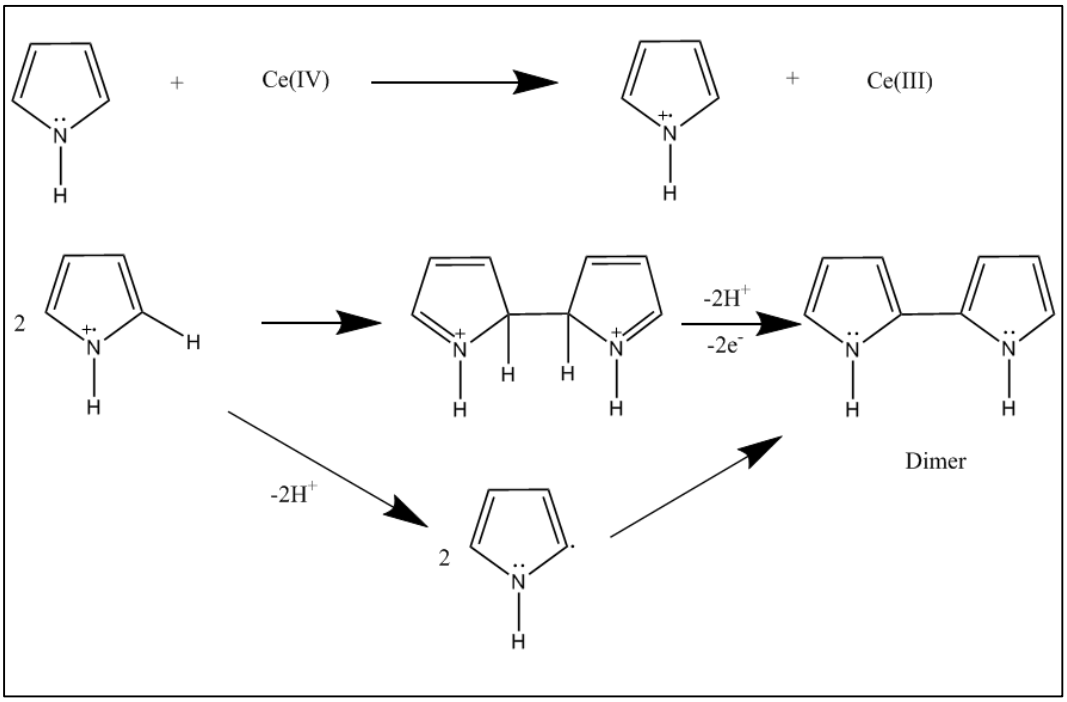

Figure 4.1: Initation Reaction of PPy.

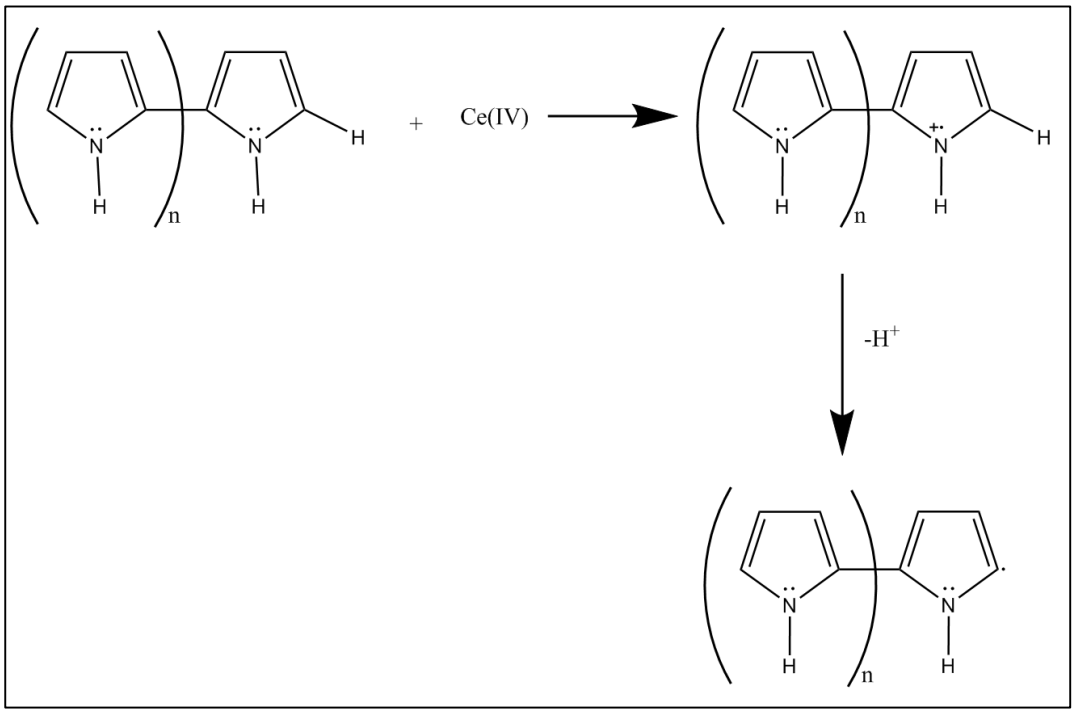

Figure 4.2: The propogation and termination reaction of PPy.

4.1.1 Blank A Type vs. Blank B Type

The effect of dissolving medium for ceric ammonium nitrate (CAN) was examined with conducting experiments. Conductivity and yield results are shown in Table 4.1. Blank A type and Blank B type were prepared with the same molar ratio of [CAN]/[PPy]; however CAN was dissolved in distilled water at Blank A type and the other was prepared with dissolving in nitric acid. According to the results, Blank A type has higher conductivity than Blank B type, but it has low yield. Therefore, Blank A type method, which CAN was dissolved in distilled water, was chosen to conduct all next experiments due to high conductivity.

Table 4.1: Yield and conductivity measurements of Blank A and Blank B.

Sample Name	**[Py] (M)**	**[CAN] (M)**	**CAN dissolved in**	**[CAN]/ [PPy]**	**Yield (%)**	**Conductivity (S/cm)**
Blank A Type	0.025	0.05	Distilled water	0.22	8.33	9.1×10^{-1}
Blank B Type	0.025	0.05	Nitric acid (65 wt %)	0.22	10	1.2×10^{-1}

4.1.2 Blank Polypyrrole With Blank A Type

The effect of concentration on the conductivity was examined with three different molar ratios of [CAN]/[PPy] which are 0.67, 0.8, and 1. Table 4.2 shows the molar ratios and yield and conductivity results of them. According to these data, when used Ce^{+4} salt amount was increased, yield increased. In addition, conductivity measurements increased with respect to the increased CAN molarity. However, above [CAN]/[PPy]= 0.8 ratio, Ce^{+4} amount became inversely proportional to conductivity. It could be due to termination step of the polymerization. In addition, yield increased but after [CAN]/[PPy]= 0.8 ratio it decreased too. Figure 4.3 shows the effect of [CAN] concentration on the polymerization yield and conductivity.

Table 4.2: Yield and conductivity results of blank PPy composites.

Sample Name	[Py] (M)	[CAN] (M)	[CAN]/[PPy]	Yield (%)	Conductivity (S/cm)
PPy-1	0.113	0.075	0.67	46	$5x\ 10^{-3}$
PPy-2	0.113	0.09	0.8	60	$8x\ 10^{-3}$
PPy-3	0.113	0.113	1	36	$1.3\ x\ 10^{-5}$

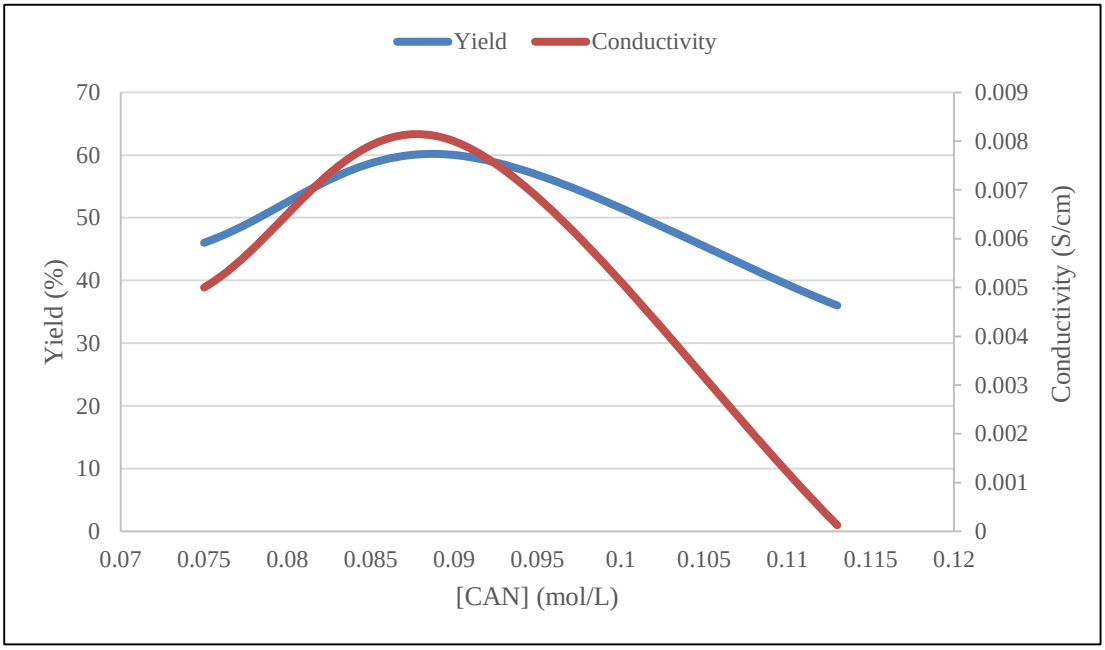

Figure 4.3: The effect of [CAN] concentration on the polymerization yield and conductivity.

Figure 4.4 and Figure 4.5 show Scanning Electron Microscope (SEM) pictures of PPy-1 and also nano scale PPy particles can be seen easily.

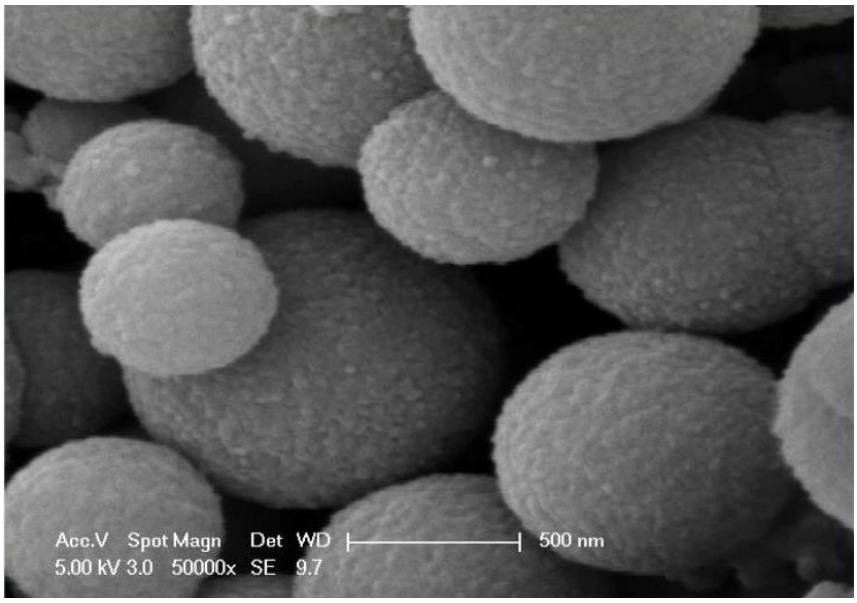

Figure 4.4: SEM picture of Blank Polypyrrole (PPy-1) in 500 nm.

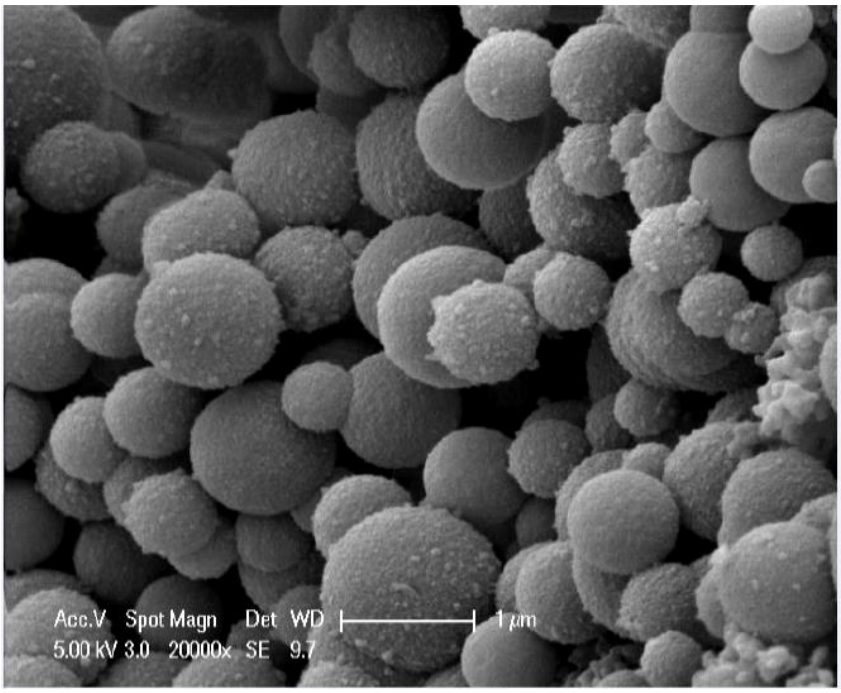

Figure 4.5: SEM picture of Blank Polypyrrole (PPy-1) in 1µm.

4.1.3 Blank Polypyrrole/ Sepiolite

Table 4.3 shows the results of conductivities and yields. According to that, yield increased when molar ratio of [CAN]/[PPy] was increased, of course this is expected. Also conductivity increased when Ce^{+4} salt amount was increased however, after

[CAN]/[PPy]= 0.8 ratio, Ce^{+4} amount became inversely proportional to conductivity. It could be due to termination step of the polymerization. Figure 4.6 shows the effect of [CAN] concentration on the polymerization yield and conductivity.

Table 4.3: Yield and conductivity results of blank PPy/Sep.

Sample Name	[PPy] (M)	[CAN] (M)	[CAN]/[PPy]	Yield (%)	Conductivity (S/cm)
PPy/Sep-1	0.113	0.075	0.67	56	5.8×10^{-4}
PPy/Sep-2	0.113	0.09	0.8	63	8.3×10^{-4}
PPy/Sep-3	0.113	0.113	1	71	5.04×10^{-4}

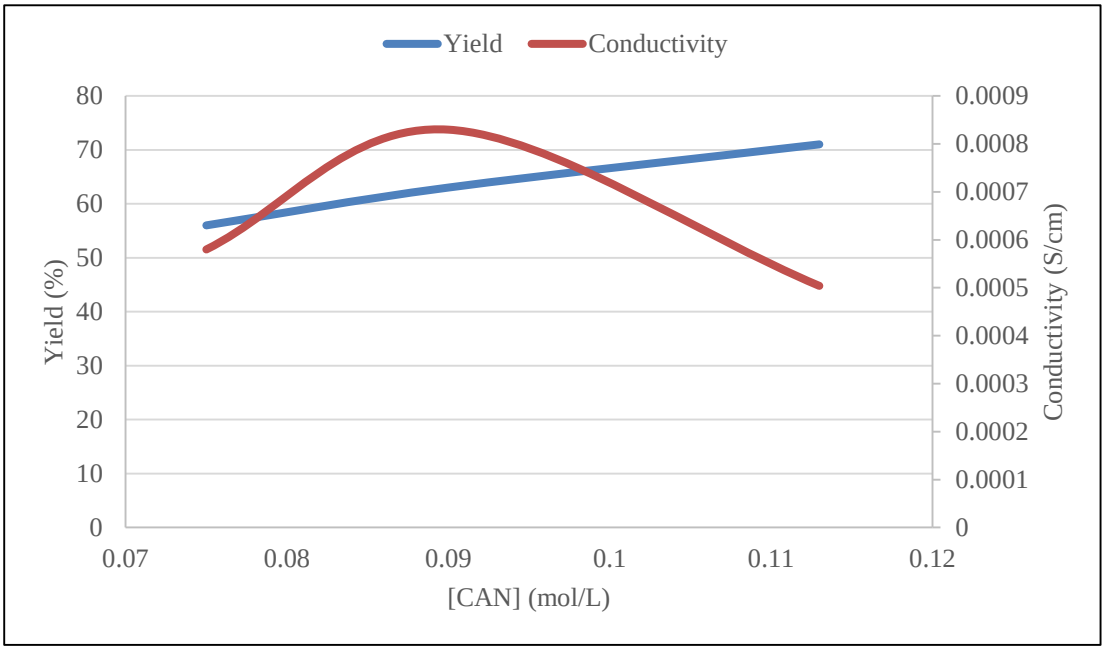

Figure 4.6: The effect of [CAN] concentration on the polymerization yield and conductivity.

Figure 4.7 shows the FTIR spectra of PPy/Sep-2 sample. The peak at 1528 cm^{-1} belong to C-C stretching of pyrrole. The characteristic peaks at 1157 and 1011 cm^{-1} correspond to sepiolite which is Si-O-Si.

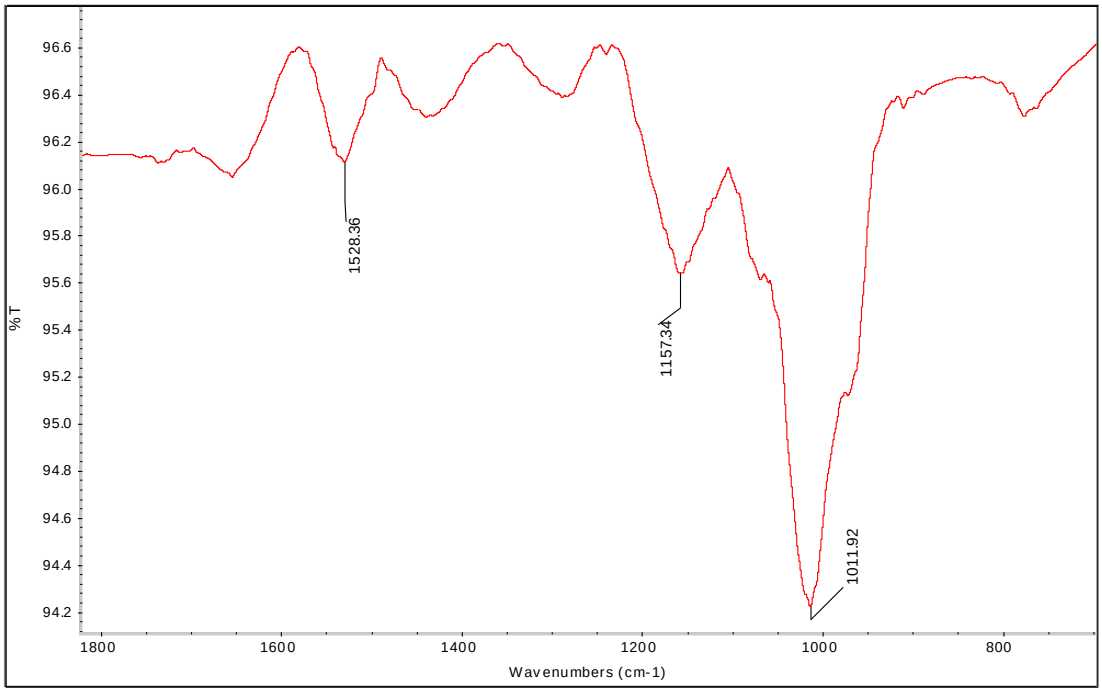

Figure 4.7: FTIR spectrum of PPy/Sep-2 Sample.

Figure 4.8, 4.9 and 4.10 show SEM pictures of PPy/Sep-1 and nano scale Sepiolite particles can be seen easily. In Figure 4.9, PPy particles can be seen at 20.000x magnitude.

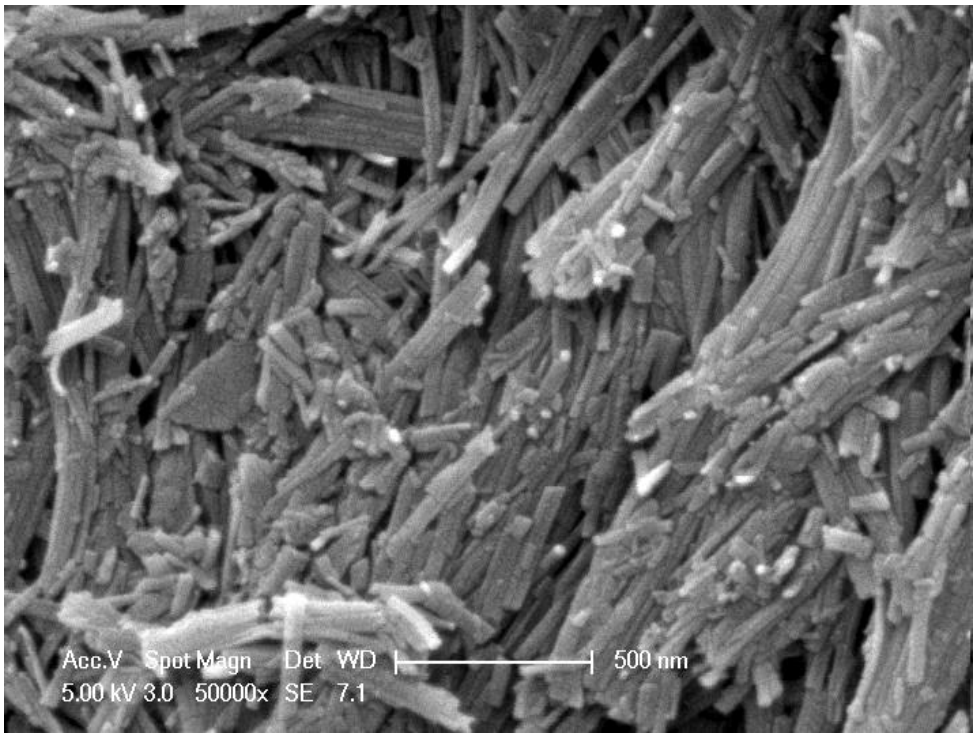

Figure 4.8: SEM picture of Blank Polypyrrole/Sepiolite (PPy/Sep-1) in 500nm.

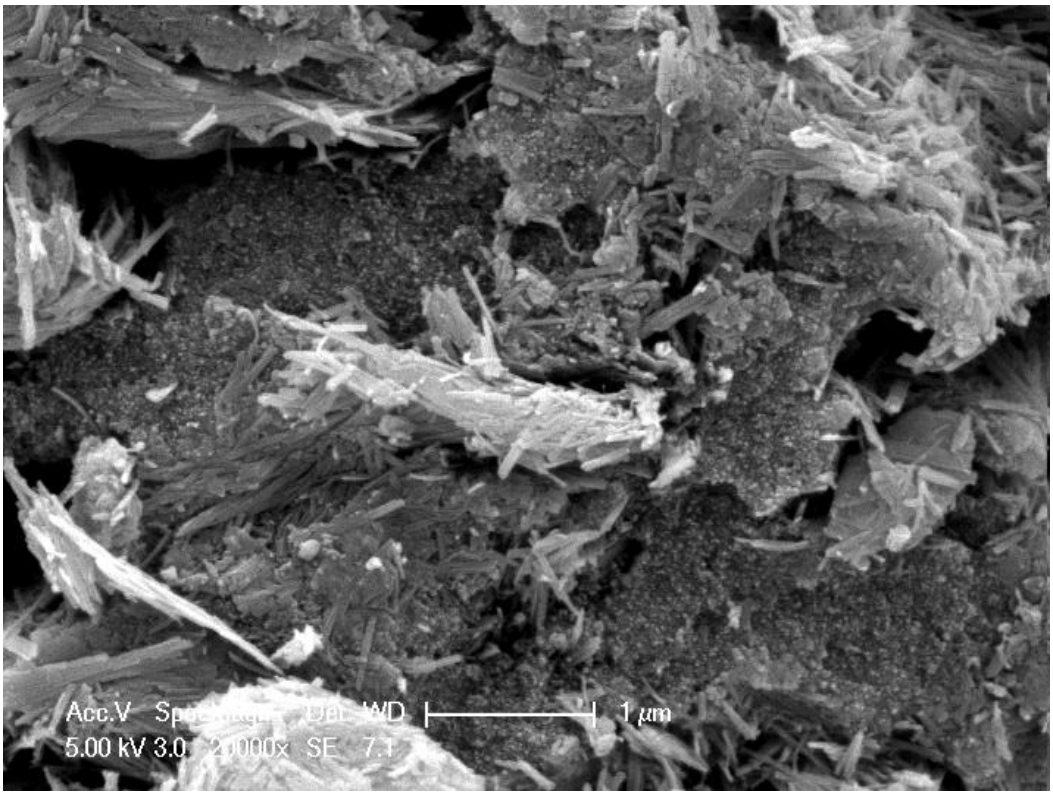

Figure 4.9: SEM picture of Blank Polypyrrole/Sepiolite (PPy/Sep-1) in 1 μm.

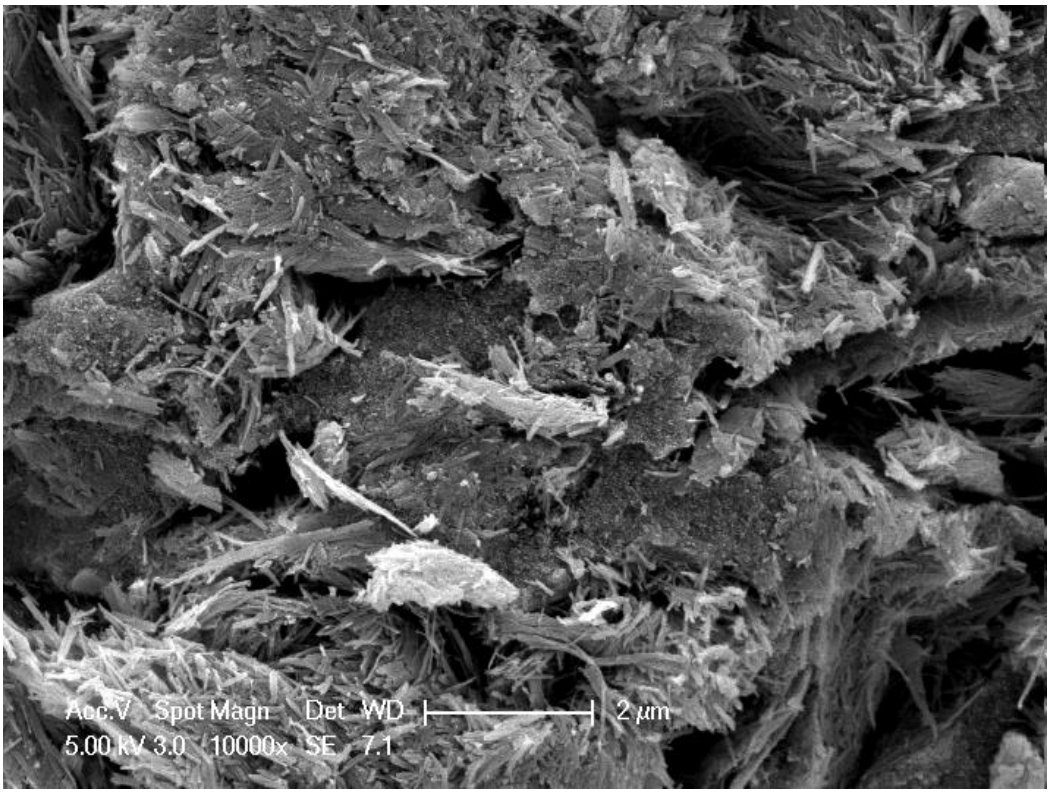

Figure 4.10: SEM picture of Blank Polypyrrole/Sepiolite (PPy/Sep-1) in 2 μm.

4.1.4 Blank Polypyrrole/ Silver Nitrate

Yield and conductivity results of blank PPy/ Ag sample are shown in Table 4.4.

Table 4.4: Yield and conductivity results of blank PPy/ Ag Sample.

Sample Name	[PPy] (M)	[CAN] (M)	[CAN]/[PPy]	Yield (%)	Conductivity (S/cm)
PPy/Ag	0.113	0.075	0.67	52	1.2 x10^{-1}

Figure 4.11 shows the FTIR spectra of PPy/Ag sample. 785 cm^{-1} was attributed to =C-H bending and also Ag-O bond vibration. 1042 and 962 cm^{-1} could be assigned to C-C. At 1296 was attributed to CAN. 1182 cm^{-1} were assigned to C-N stretching. The characteristic peak at 1548 cm^{-1} correspond to the stretching vibration of N-O.

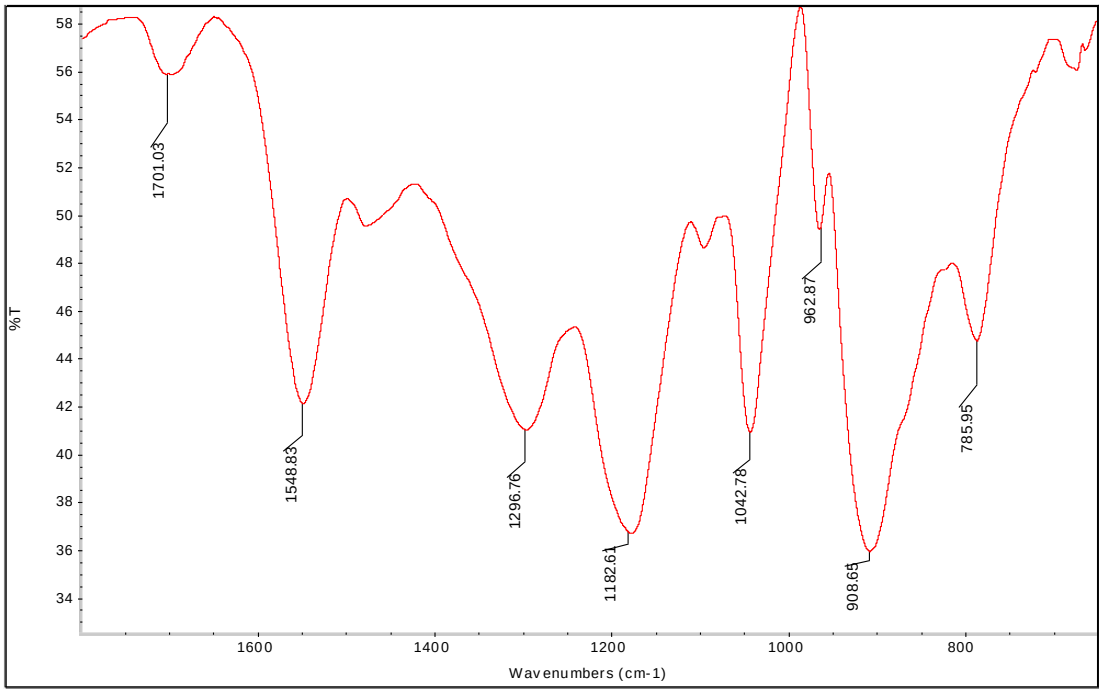

Figure 4.11: FTIR spectrum of PPy / Ag Sample.

4.2 Chitosan – Polypyrrole Copolymers

Figure 4.12 represents the proposed chemical polymerization of pyrrole (Py) monomer which is synthesized with Ce^{+4} and chitosan via redox polymerization in aqueous media. The polymer chains continue to grow as long as Py and Ce (IV) are available in the medium. The termination could be occur as combination method.

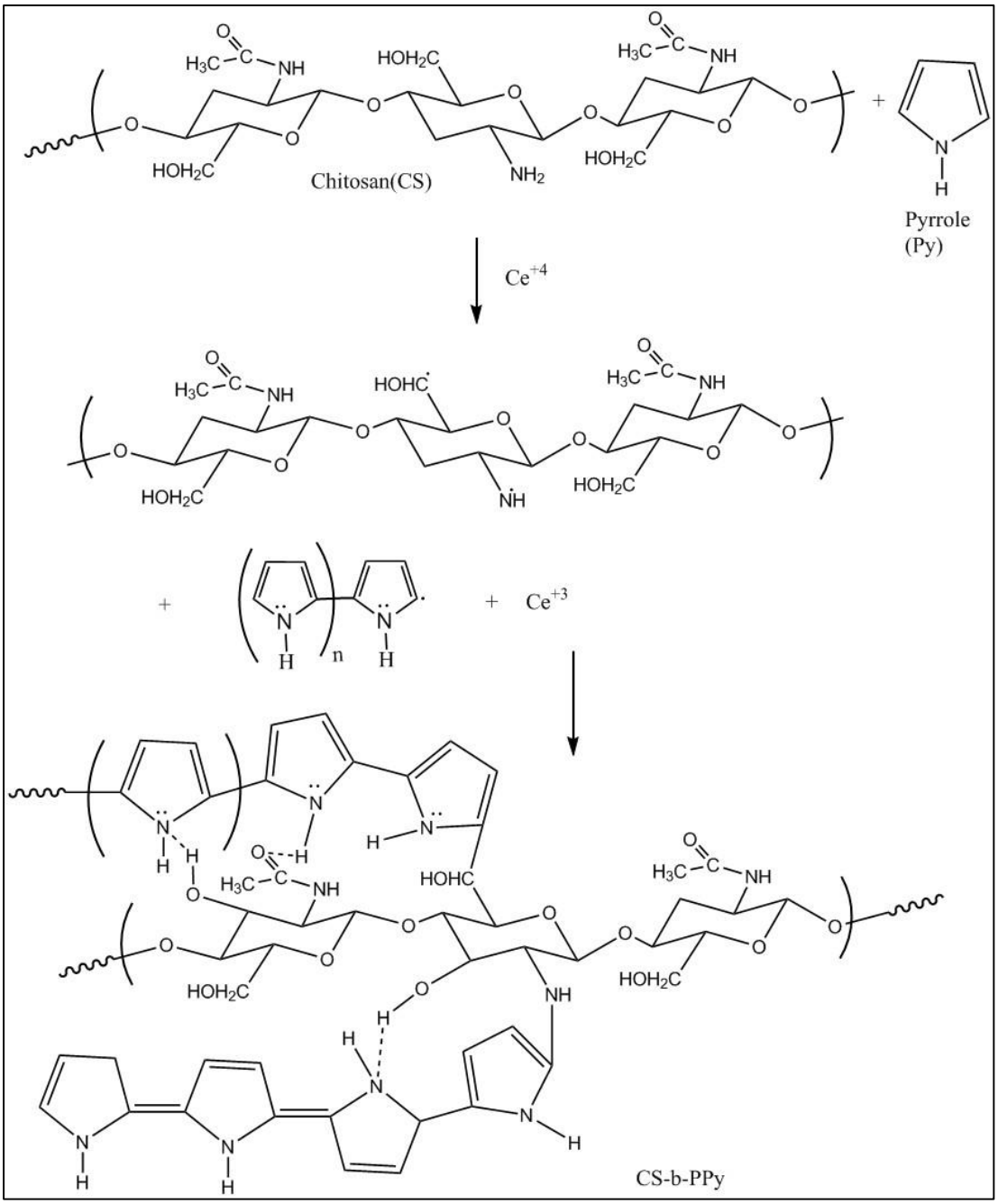

Figure 4.12: Proposed reaction mechanism for chemical polymerization of chitosan and polypyrrole.

Table 4.5 shows the results of conductivities and yields. According to that, yield increased when molar ratio of [CAN]/[PPy] was increased. Also conductivity increased when Ce^{+4} salt amount was increased however, above the value of [CAN]/[PPy]= 0.8 ratio, Ce^{+4} amount became inversely proportional to conductivity. It could be due to termination step of the polymerization. Some yield fluctuations were observed, because of chitosan solubility and acquring problems. PPy/CS- 6 was

not acquired from filter paper; it was dried in the petri dish and then it became film. Its' conductivity was not measured successfully by four point probe technique due to not done pellet and also yield couldn't be calculated.

Table 4.5: Yield and conductivity results of PPy/CS copolymers.

Sample Name	CS (g)	[PPy] (M)	[CAN] (M)	[CAN]/[PPy]	Yield (%)	Conductivity (S/cm)
PPy/CS- 1	0.016	0.113	0.075	0.67	42	$7.8x\ 10^{-6}$
PPy/CS- 2	0.5	0.113	0.075	0.67	50	2.1×10^{-3}
PPy/CS- 3	0.016	0.113	0.09	0.8	42	8.1×10^{-6}
PPy/CS- 4	0.5	0.113	0.09	0.8	20	1.4×10^{-2}
PPy/CS- 5	0.016	0.113	0.113	1	82	1.8×10^{-6}
PPy/CS- 6	0.5	0.113	0.113	1	-	-

Figure 4.13 and Figure 4.14 represent the effect of [CAN] concentration on the polymerization yield and conductivity.

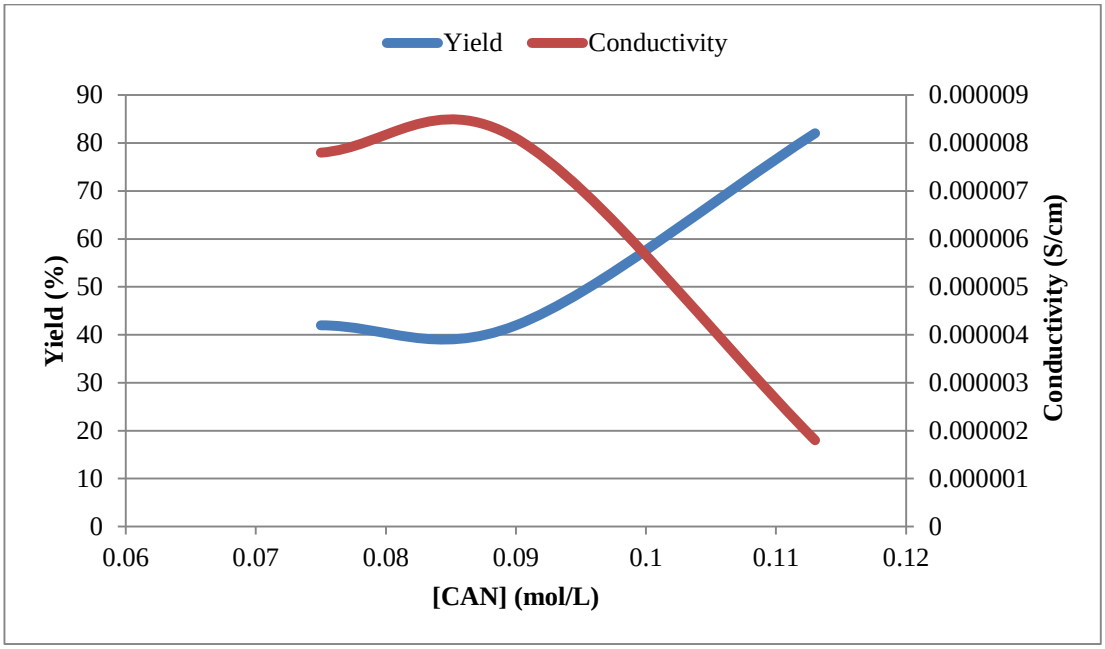

Figure 4.13: The effect of [CAN] concentration on the polymerization yield and conductivity for 0.016 g chitosan.

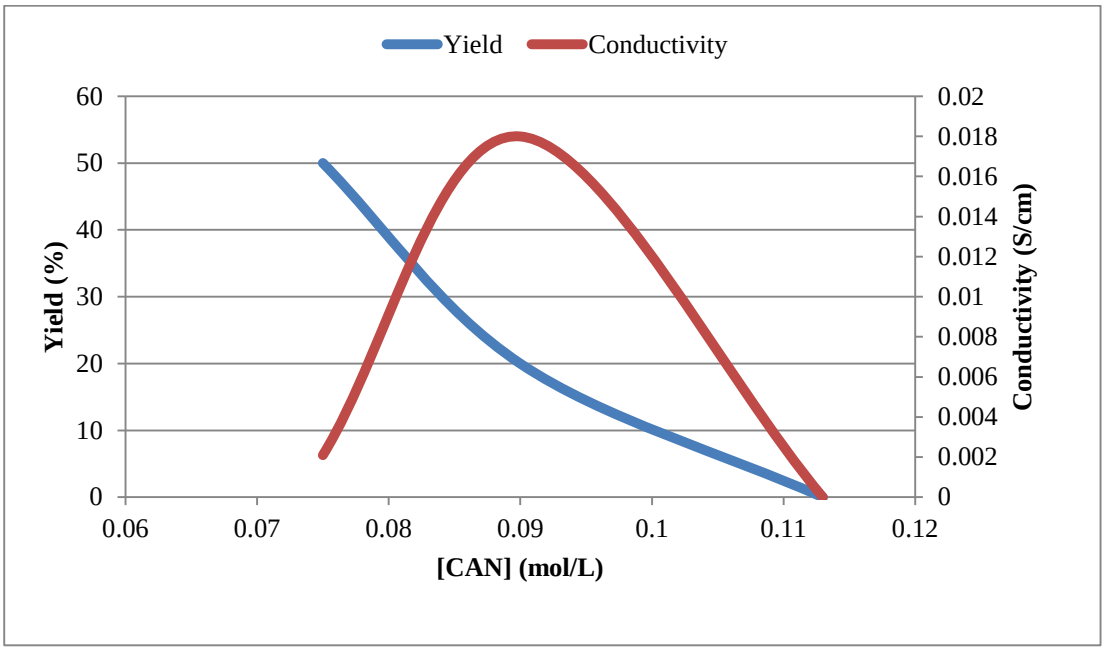

Figure 4.14: The effect of [CAN] concentration on the polymerization yield and conductivity for 0.5 g chitosan.

In addition, Figure 4.15 shows film forming result on the petri dish and Figure 4.16 shows that film forming example on the filter paper and its' separation problem.

Figure 4.15: Film forming sample on the petri dish.

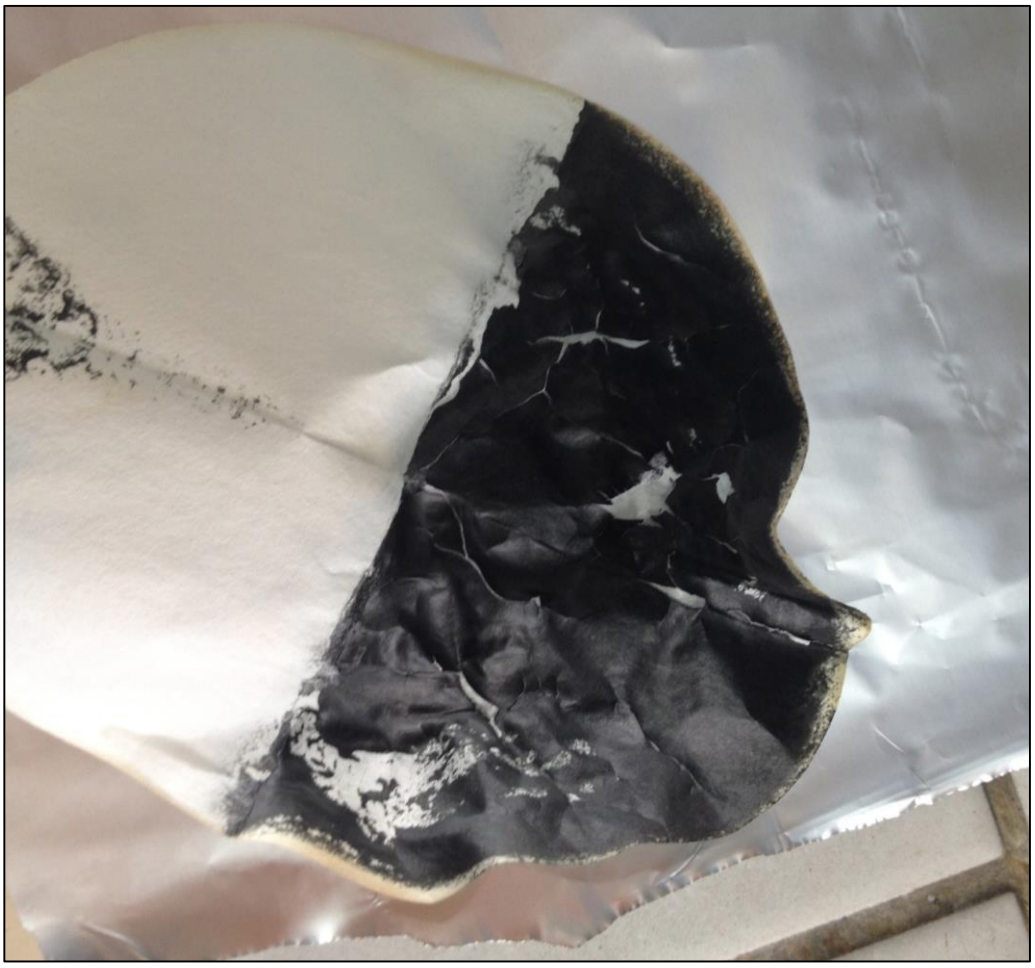

Figure 4.16: Film forming example on the filter paper.

According to Figure 4.17, the peak at 3399 cm^{-1} can be attributed to the O–H stretching vibrations of chitosan and N–H stretching vibrations of polypyrrole. The characteristic peak at 1643 cm^{-1} is assigned to the stretching vibrations of the –CONH– groups of chitosan. The characteristic peaks at 1311 and 1040 cm^{-1} are attributed to the C–N stretching vibration of the secondary amine and C–H in-plane bending vibration of pyrrole rings, respectively. 815 and 738 cm^{-1} were attributed to =C-H stretching.

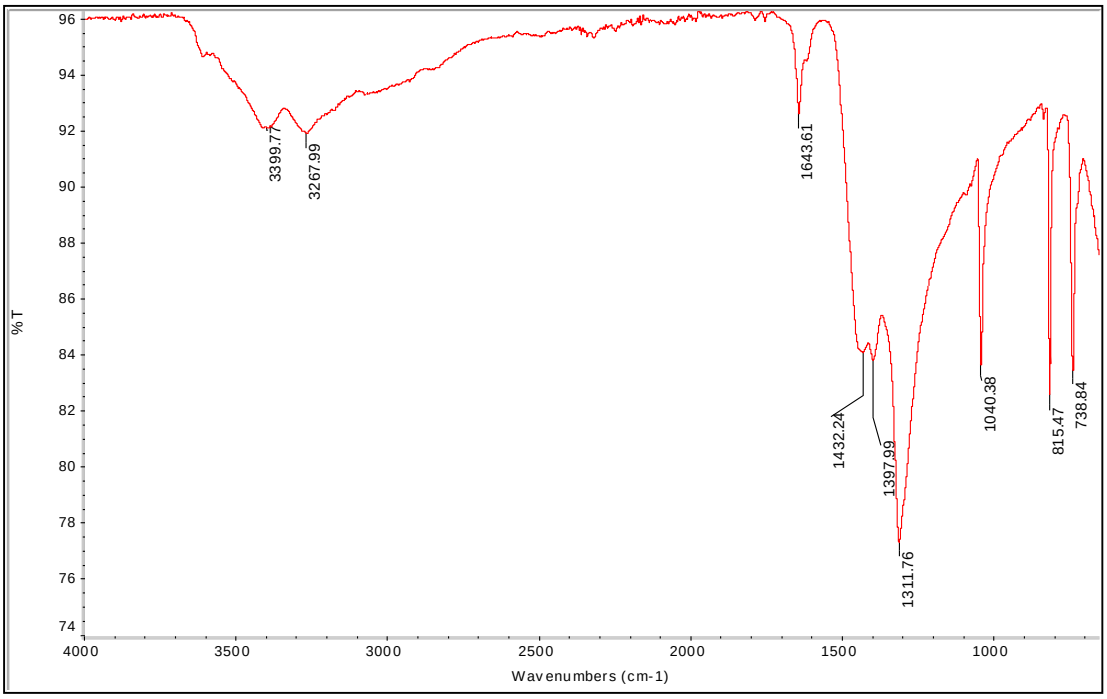

Figure 4.17: FTIR spectrum of PPy / CS - 2 sample includes 0.5 g chitosan.

Figure 4.18, 4.19, 4.20 show the SEM pictures of PPy/CS-1. According to Figure 4.18, the obtained results showed that SEM micrograph for the surface of Chitosan/ Polypyrrole composite has average size of 29.8 nm. Circular shape chitosan particles were detected easily.

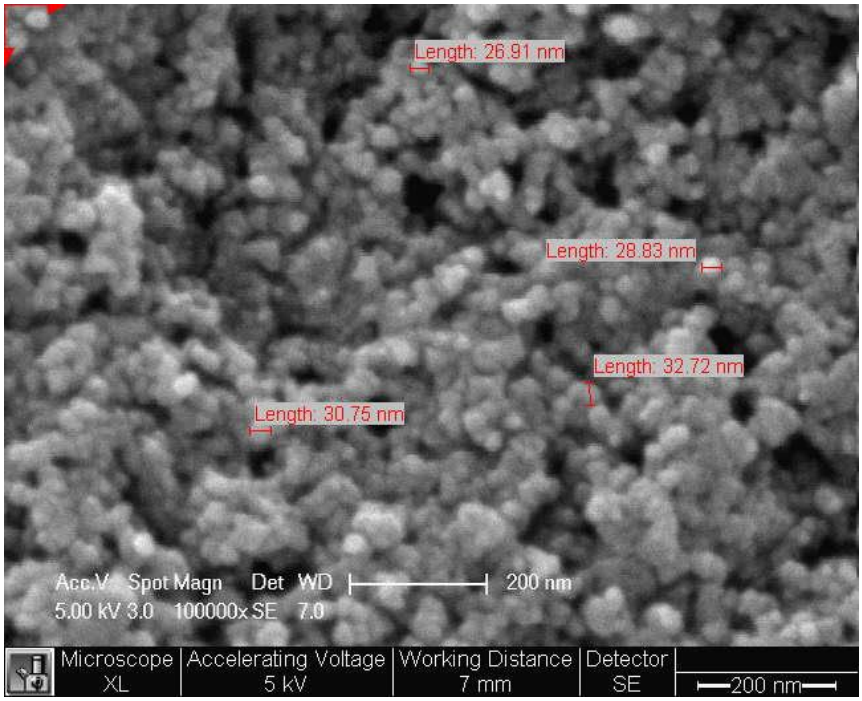

Figure 4.18: SEM picture of Chitosan/Polypyrrole Composite (PPy/CS-1) in 200nm.

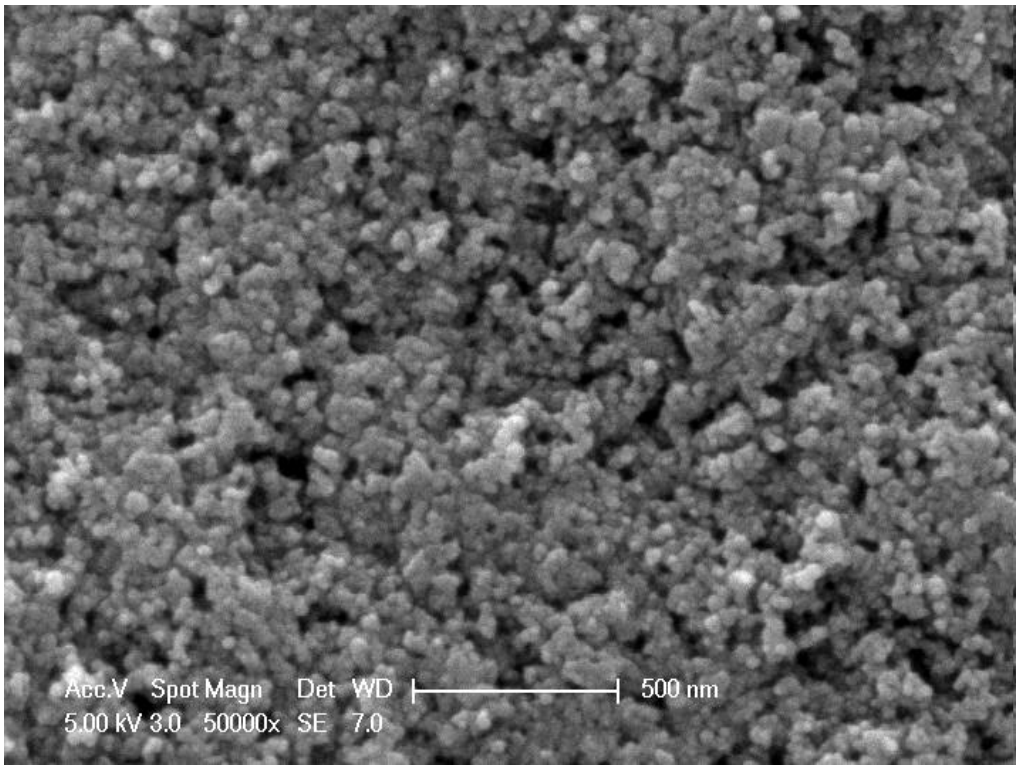

Figure 4.19: SEM picture of Chitosan/Polypyrrole Composite (PPy/CS-1) in 500nm.

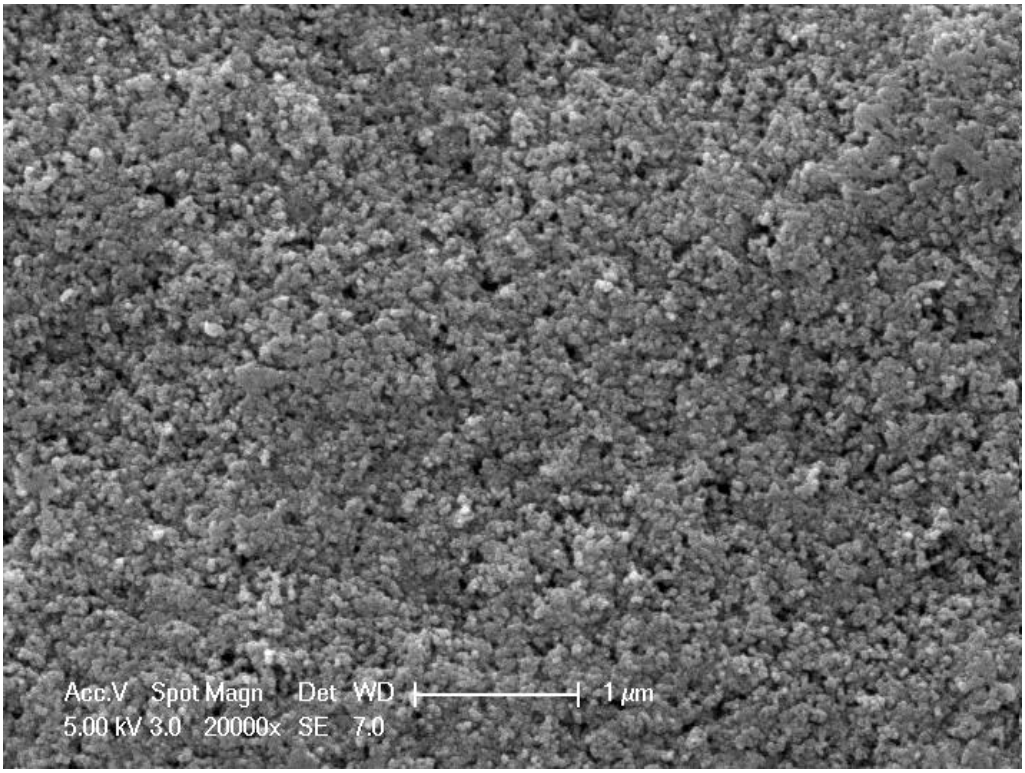

Figure 4.20: SEM picture of Chitosan/Polypyrrole Composite (PPy/CS-1) in 1μm.

4.3 Chitosan–Polypyrrole/ Sepiolite Nanocomposites

Table 4.6 shows the results of conductivities and yields. According to that, yield increased when molar ratio of [CAN]/[PPy] was increased. Also conductivity increased when Ce^{+4} salt amount was increased however, above the value of [CAN]/[PPy]= 0.8 ratio, Ce^{+4} amount became inversely proportional to conductivity. It could be due to termination step of the polymerization.

Table 4.6: Yield and conductivity results of PPy-CS/Sep nanocomposites.

Sample Name	**Chitosan (g)**	**[PPy] (M)**	**[CAN] (M)**	**n(CAN)/ n(PPy)**	**PPy (g)**	**Sepiolite (g)**	**Yield (%)**	**Conductivity (S/cm)**
PPy-CS/Sep-1	0.016	0.113	0.075	0.67	1.55	0.52	53	3.7×10^{-4}
PPy-CS/Sep-2	0.5	0.113	0.075	0.67	1.55	0.52	83	3.0×10^{-4}
PPy-CS/Sep-3	0.016	0.113	0.09	0.8	1.55	0.52	60	6.4×10^{-4}
PPy-CS/Sep-4	0.5	0.113	0.09	0.8	1.55	0.52	64	6.41×10^{-4}
PPy-CS/Sep-5	0.016	0.113	0.113	1	1.55	0.52	66	5.7×10^{-4}
PPy-CS/Sep-6	0.5	0.113	0.113	1	1.55	0.52	69	4.24×10^{-4}

Figure 4.21 and 4.22 show the effect of [CAN] concentration on the polymerization yield and conductivity.

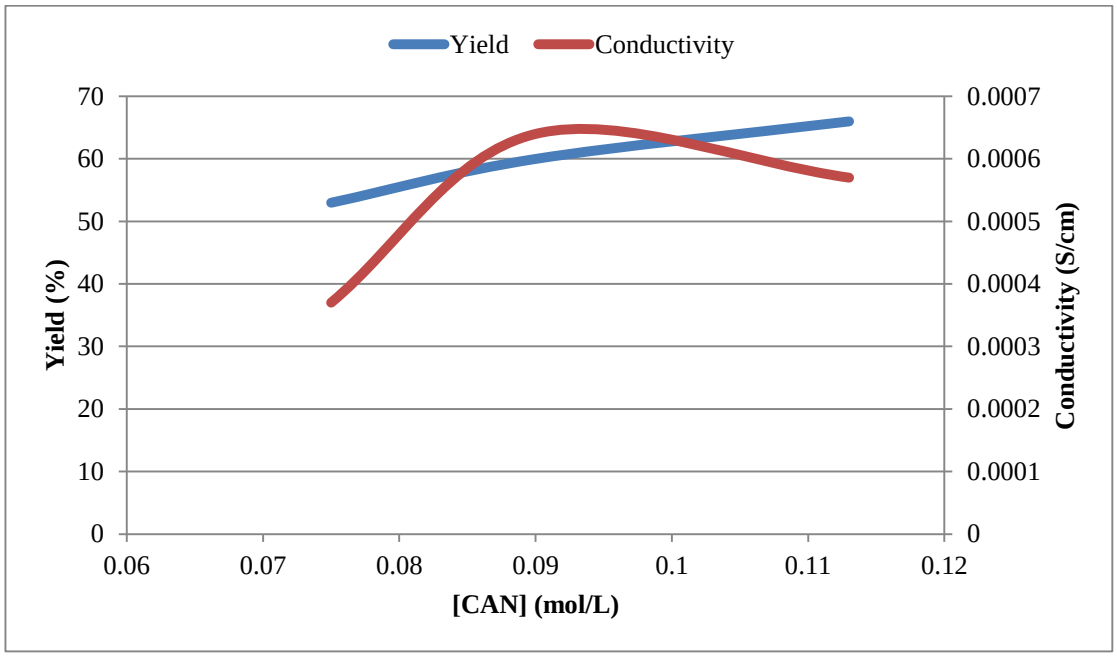

Figure 4.21: The effect of [CAN] concentration on the polymerization yield and conductivity for 0.016 g chitosan.

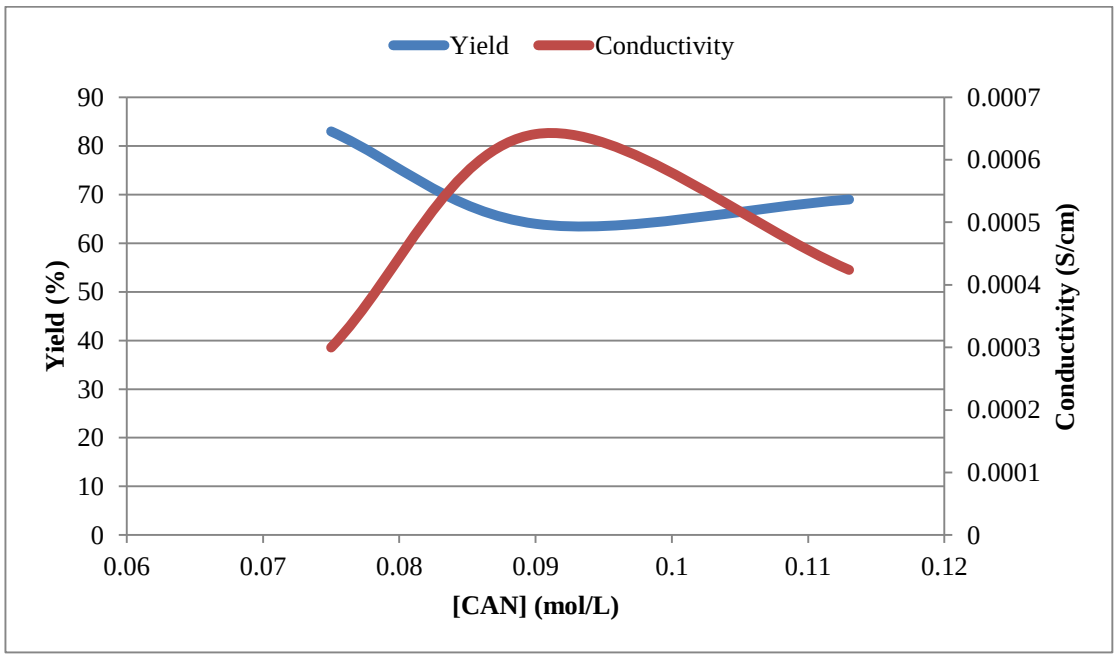

Figure 4.22: The effect of [CAN] concentration on the polymerization yield and conductivity for 0.5 g chitosan.

According to Figure 4.23, the spectrum of chitosan indicates that the peak at 1624 cm^{-1} could be assigned to carbonyl stretching vibration (amide I). C–N stretching of the amino groups were found at 1312 cm^{-1}. Si-O-Si stretching vibration was at 1000 cm^{-1}. Both 967 and 920 cm^{-1} belong to sepiolite.

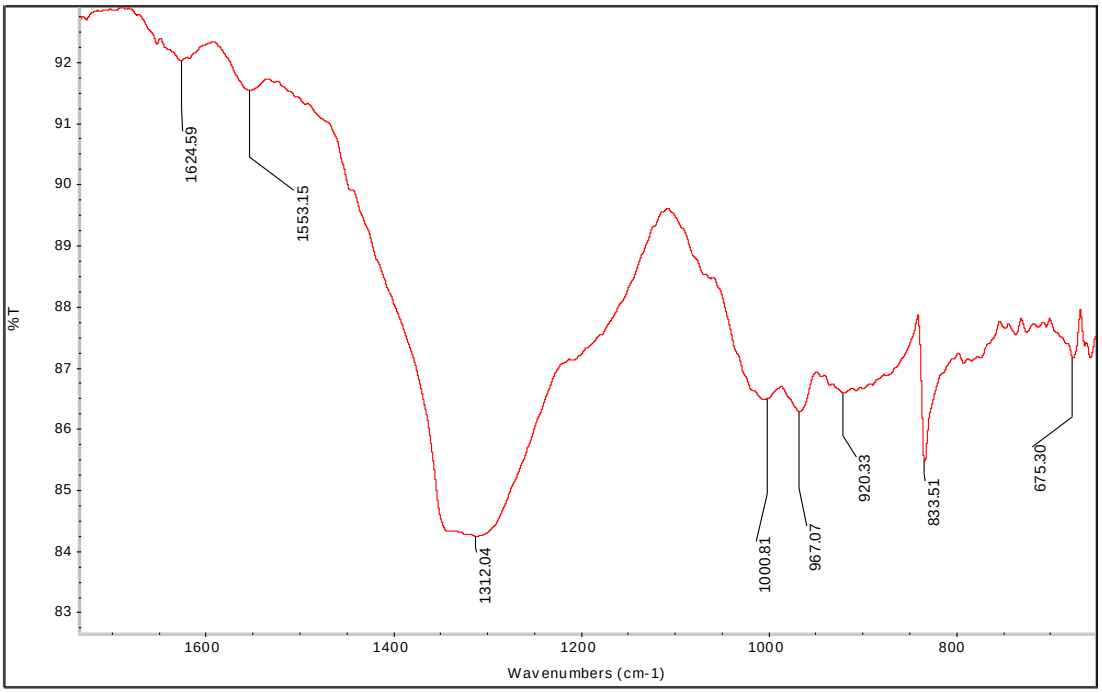

Figure 4.23: FTIR spectrum of PPy-CS/Sep - 2 sample which includes 0.5 g chitosan.

Figure 4.24, 4.25, 4.26 show the SEM pictures of PPy-CS/Sep-1. According to Figure 4.24, the obtained results showed that ESEM micrograph for the surface of Chitosan/ Polypyrrole composite has average size of 28.63 nm. Circular shape chitosan particles and rod shape sepiolite were detected easily.

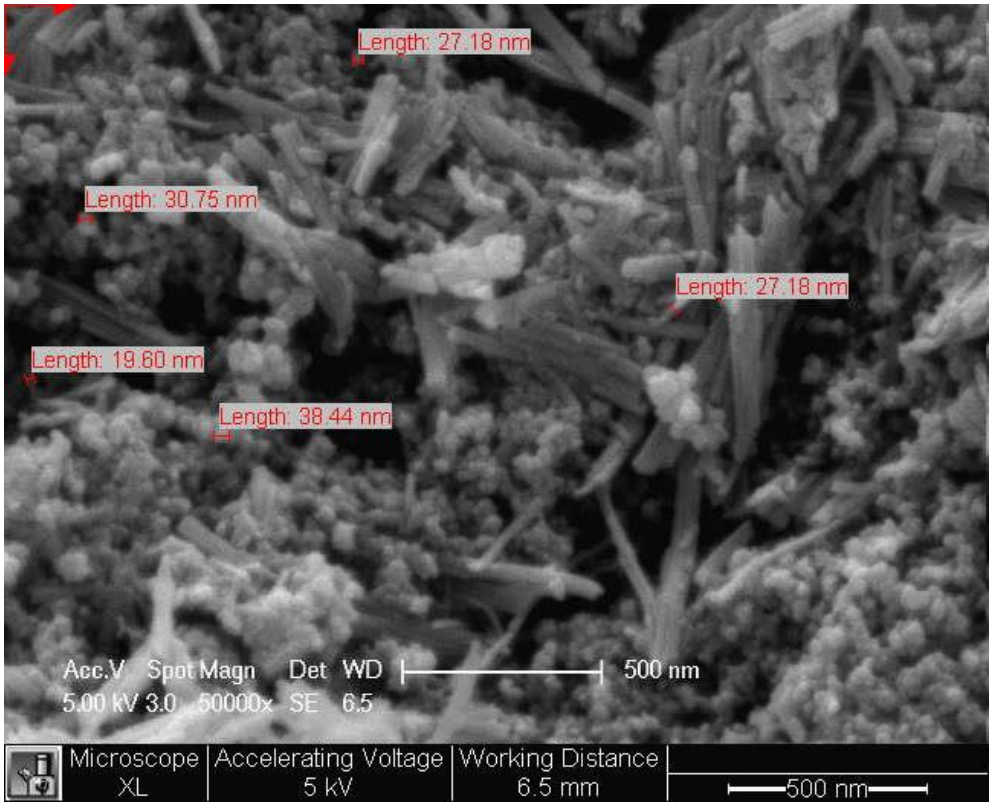

Figure 4.24: SEM picture of Chitosan/Polypyrrole-Sepiolite Nanocomposite (PPy-CS/Sep-1) in 500nm.

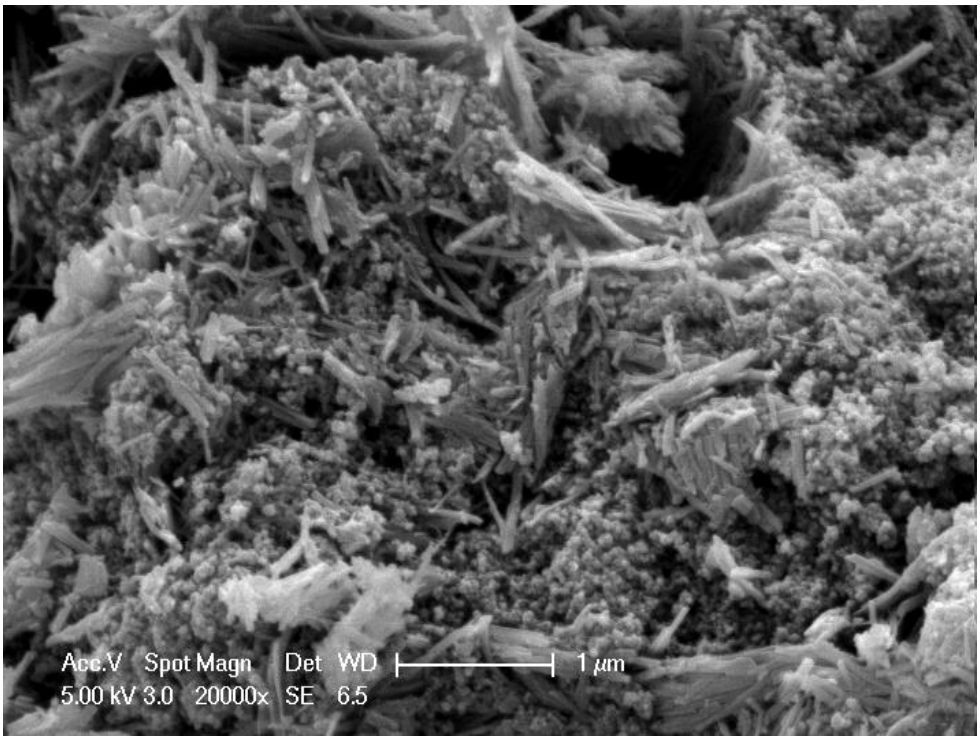

Figure 4.25: SEM picture of Chitosan/Polypyrrole-Sepiolite Nanocomposite (PPy-CS/Sep-1) in 1 µm.

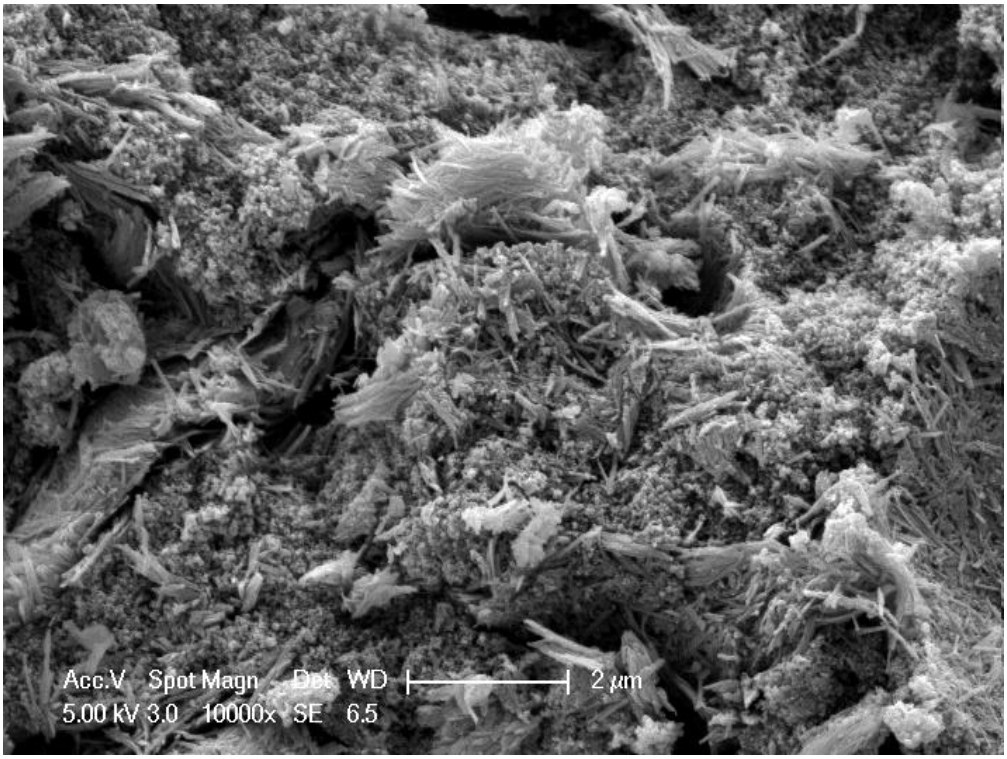

Figure 4.26: SEM picture of Chitosan/Polypyrrole-Sepiolite Nanocomposite (PPy-CS/Sep-1) in 2 μm.

4.4 Chitosan – $AgNO_3$ Nanocomposites

Table 4.7 shows the results of conductivities and yields. These three experiments has same [CAN]/[PPy] ratio which is equal to 0.67. Only either chitosan or sepiolite was variable. Therefore, PPy-Sep/Ag has not chitosan so that it has good yield due to not having solubility and separation problem from filter. PPy-CS/Ag has chitosan but not sepiolite so that its's yield is lower than PPy-Sep/Ag but higher than PPy-CS-Sep/Ag which has both chitosan and sepiolite. Figure 4.27 shows the yield and conductivity results on the graph.

Table 4.7: Yield and conductivity results of chitosan/silver nitrate nanocomposites.

Sample name	**CS (g)**	**Sep (g)**	**[PPy] (M)**	**[CAN] (M)**	**n(CAN)/ n(PPy)**	**n(AgNO3) (moles)**	**AgNO3 (g)**	**Yield (%)**	**Conductivity (S/cm)**
PPy-Sep/Ag	0	0.52	0.113	0.075	0.67	0.06	10.8	74	1.51
PPy-CS/Ag	0.016	0	0.113	0.075	0.67	0.06	10.8	26	7.55×10^{-1}
PPy-CS-Sep/Ag	0.016	0.52	0.113	0.075	0.67	0.06	10.8	23	7.2

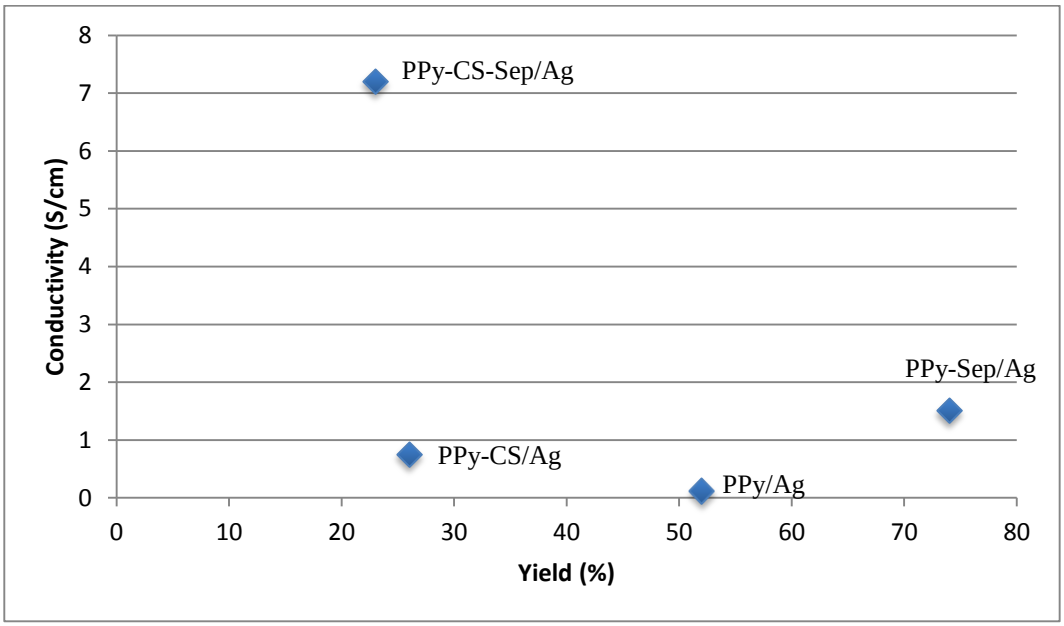

Figure 4.27: Yield and conductivity results of silver nitrate nanocomposites.

Figure 4.28 shows the FTIR spectra of chitosan/sepiolite/silver nitrate nanocomposite sample. 1009 and 958 cm^{-1} correspond to Si-O-Si stretching. 1527 cm^{-1} attributed to N-H bending.1133 cm^{-1} could be C-O. 1274 cm^{-1} was attributed to C-N stretching vibration of secondary amine. 846 cm^{-1} could be beta (1-4) glucoside bridge or Ag-O bond vibration.

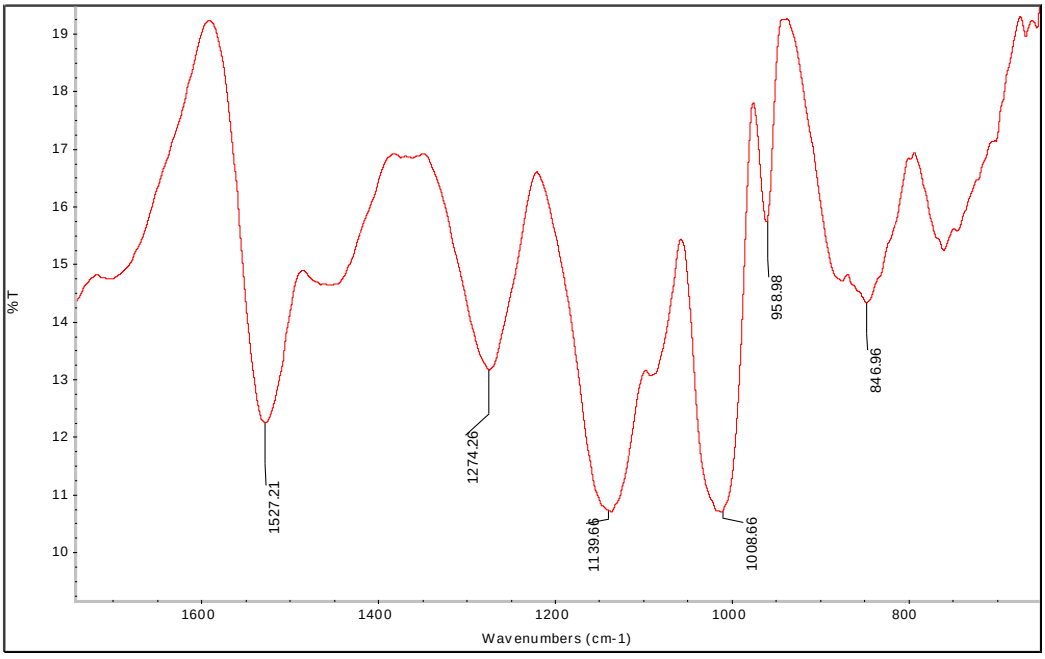

Figure 4.28: FTIR spectrum of Chitosan/Sepiolite-$AgNO_3$ nanocomposites.

5. CONCLUSIONS AND RECOMMENDATIONS

The aim of this research is the conductive biodegradable, biocompatible, and biofunctional composites production with using chitosan and also determining optimum conditions for effective conductivity. Polypyrrole/ Chitosan composites, Polypyrrole-Chitosan/Sepiolite and Polypyrrole/Silver Nitrate nanocomposites were formed for this study.

The effect of concentration on the conductivity and yield was examined with three different concentrations of CAN on the composite samples. According to acquired results with using four point probe technique, the conductivities increased with respect to the CAN concentration. However, generally above the value of [CAN] = 0.09 M, conductivities decreased, because of high Ce^{+4} concentration probably caused the oxidative chain termination and linear termination of polymerization. Polypyrrole/Chitosan (PPy/CS) composite polymers showed conductivity between $1.8x10^{-6}$ and $1.4x10^{-2}$ S/cm. Polypyrrole-Chitosan/Sepiolite (PPy-CS/Sep) nanocomposite polymers showed conductivity between $3.0x10^{-4}$ and $6.41x10^{-4}$ S/cm. Polypyrrole/$AgNO_3$ nanocomposite polymers had a conductivity between 0.755 and 7.2 S/cm. According to these results, PPy/CS samples had wide range of conductivity which may be used in different applications. However, PPy-CS/Sep samples had consistent results which may narrow the application areas while adding some special characteristics and advantages Sepiolite brings into these type of composites. As expected, adding silver nitrate increased conductivity dramatically. Also it may be used in anti-microbial applications because silver can transport into cell membrane resulting in damage.

Regarding to the serial experiments, polymerization yield seemed not exactly depend on the CAN concentration. It usually increased with increasing CAN concentration but sometimes it was not correspond with this hypothesis. The fluctuations may depend on the difficulty when collecting the samples from filtering paper or petri dish.

FTIR analysis was performed for characterization of composite samples and

respective peaks were examined. In addition SEM analysis was performed for the determination of morphology of samples. According to SEM results, PPy/CS-1 sample has average size of 28.90 nm and PPy-CS/Sep-1 sample has average size of 28.63 nm. Chitosan and sepiolite was easily detected from SEM pictures.

Conductive polymers have been used in a wide variety of application areas from photovoltaic devices to nerve regeneration. CPs are organic in nature so that they are biocompatible, furthermore the presence of conjugated backbone within the polymer offers it with the ability to conduct electrons. Not only they have highly desirable properties but also they can be prepared and modified easily which make them a popular choice for many applications. In future, many applications will benefit from conductive materials like PPy/CS, PPy-CS/Sep and PPy/Ag in biosensors, bioactuators and many other biomedical applications which will be very important in next century.

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CURRICULUM VITAE

Name Surname: Sevinc Sezin Tarımsal Gülmen

Place and Date of Birth: Ankara – 06.09.1989

Address: Huzur Mah. Oto Sanayi Sitesi. Menderes Cad. No: 8 / 4. Levent – İst.

E-Mail: sezintarimsal@gmail.com

B.Sc.: Istanbul Technical University & Montana State University - Bioengineering