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## Preparation and Characterization of Chitosan/ Polypyrrole/ Sepiolite Nanocomposites

S. Sezin Tarımsal Gülmen<sup>a</sup>, Esin Ateş Güvel<sup>b</sup>, Nilgün Kızılcın<sup>b\*</sup>

<sup>a</sup>Istanbul Technical University; Department of Polymer Science and Technology, Faculty of Science, Istanbul, 34469 Turkey

<sup>b</sup>Istanbul Technical University; Department of Chemistry, Faculty of Science, Istanbul, 34469 Turkey

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### Abstract

In this work, Chitosan / Polypyrrole/ Sepiolite (Cs/PPy/Sep.) Nanocomposites (NC) were synthesized with pyrrole and chitosan via redox polymerization in aqueous media with magnetic stirrer system in presence of ammonium cerium (IV) nitrate ( $Ce^{+4}$ ) and sepiolite 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/ Sepiolite Nanocomposites (Cs/PPy/Sep.NC) were prepared with the oxidant to pyrrole mole ratio 0.67:1 showed conductivity of  $3.7 \times 10^{-4}$  S/cm for 0.016 g chitosan, and  $3.0 \times 10^{-4}$  S/cm for 0.5 g chitosan. The oxidant to pyrrole molar ratio 0.8 is proposed to be the optimum stoichiometry for the better conductivity while the ratio for the highest yield was obtained for molar ratio of 1.0. The obtained results showed that ESEM micrograph for the surface of Chitosan/ Polypyrrole/ Clay Nanocomposite has average size of 28.63 nm. The yield of the product (polymer) and electrical conductivity of the product are investigated as physical characteristics. The electrical conductivities of Cs/PPy/Sep. NC were determined by four point probe technique. In addition, the resulting NC are characterized with spectroscopic method that is Fourier Transform Infrared Spectroscopy (FTIR), and also morphological method, which is Scanning Electron Microscopy (SEM).

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*Keywords:* Polypyrrole, Chitosan, Sepiolite, Nanocomposite.

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### 1. Introduction

Recently, polymer composites especially bio-composites and intrinsic conducting polymers (CPs) with conjugated double bonds have been attracted much attention. A composite material is made from two or more

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\* Corresponding author. Tel.: +90 212 2853242; fax: +90 212 285 63 86.

E-mail address: [kizilcan@itu.edu.tr](mailto:kizilcan@itu.edu.tr)

components with different physical or chemical properties that when combined produce a new material with different properties than the original components. Bio-composites are composite materials and formed by a resin and a reinforcement of natural fibers. Among those, bio-composites, which are made of chitosan (CS) (Fig. 1), are used for commercial applications because of favorable characteristics such as biocompatibility, biodegradability, and bio-functionality etc. (Yaçınkaya et al., 2010; Martinez-Camacho et al., 2010). Chitosan has both reactive amino and hydroxyl groups that can be used to modify its properties under mild reaction conditions (Lee et al., 2004). In addition, it is the second most abundant natural polymer on earth found mostly in the insect's cuticle, cell wall of fungi, and crustaceans' shells (Lavorna et al., 2014). Therefore, it has been used in many industrial application areas such as cosmetics, paper and textile industry, food packaging, wastewater treatment, photography, solid-state batteries, biomedical applications (wound healing and dressing, burn treatment, artificial skin, ophthalmology, biosensors), and separation membranes (Yaçınkaya et al., 2010; Martinez-Camacho et al., 2010; Lee et al., 2004; Lavorna et al., 2014; Kurita, 1998).

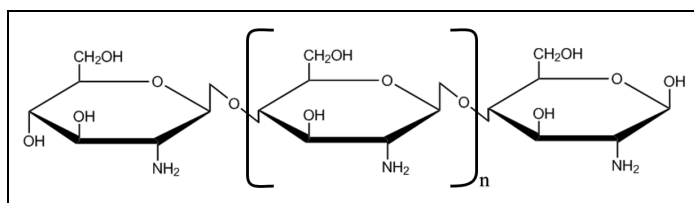


Fig. 1. Structure of Chitosan

Polypyrrole (PPy) is one of the most widely used conductive polymers (CPs) in commercial applications due to the capability to conduct electricity and its special characteristics, such as; good environmental stability, facile synthesis, and high conductivity (Sahoo et al., 2013). In addition, it is biocompatible with mammalian cells (Li et al., 2011; Lu et al., 2010). PPy can be used in production of biosensors, gas sensors, microactuators, wires, solid electrolytic capacitors, electrochromic windows and displays, anti-electrostatic coatings, polymeric batteries, functional membranes etc. (Zhang et al., 2004; Li et al., 2009; Brabec et al., 2001; Baker et al., 2008; Stewart et al., 2012). However, it has limited large-scale industrial applicability due to its brittle nature and poor post-synthesis processability including 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 (Mihriyan et al., 2012). 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 (Kiefer et al., 2014). Redox polymerization system is chosen 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 (Cakmak, 1993). In acidic media, ceric ions are used as oxidizing agents for many organic substrates to initiate the vinyl polymerization (Singh et al., 1979). To form ceric ions, ceric ammonium nitrate (CAN) may 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 (Darder, Aranda, & Ruiz-Hitsky, 2007). Sepiolite (Sep) 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. (Sabah & Celik, 2002).

## 2. Literature Review And Hypotheses

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 (Darder et al., 2006). Chitosan is a natural polysaccharide having amino and hydroxyl groups in its structure. According to interaction mechanism; amino groups in the structure of chitosan 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 hydroxyl groups of chitosan 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 ( $> 300 \text{ m}^2/\text{g}$ ). Therefore, new hybrid material may show microfibrinous morphology, improved mechanical properties, and attractive ion exchange behavior (Darder et al., 2006).

According to Fig. 2; 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  $1.1 \times 0.4 \text{ nm}^2$ . 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 sepiolite particles. Tunnels are filled with coordinated water molecules and zeolitic water. At the edges of octahedral sheets, water molecules are bonded to the  $\text{Mg}^{2+}$  ions. The zeolitic water is associated to the former by hydrogen bonding (Darder et al., 2006).

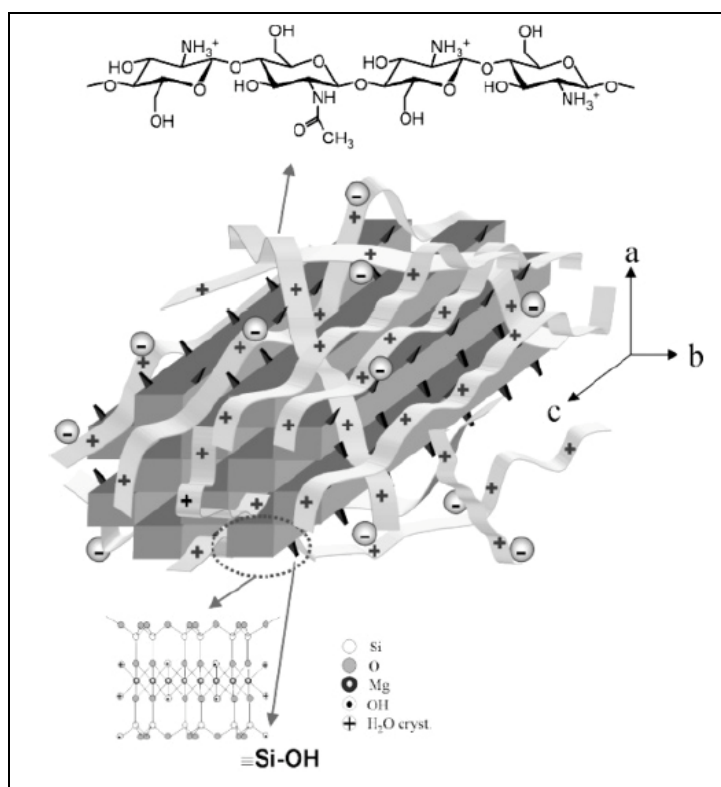


Fig. 2. Idealized Representation of Chitosan Adsorption on the Sepiolite Surface (Darder et al., 2006).

### 3. Methodology

#### 3.1. Research Goal

Aim of sepiolite and chitosan combination is to develop nanostructured biohybrid materials presented with improved mechanical properties. Chitosan/ Polypyrrole/ Sepiolite Nanocomposites (Cs/PPy/Sep.NC) were prepared with the oxidant to pyrrole mole ratio 0.67:1 and also for comparison 0.8:1 and 1:1 mole ratios were used.

### 3.2. Sample and Data Collection

#### 3.2.1. 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<sub>3</sub>) were supplied by Merck and J.T. Baker, respectively. Sodium hydroxide (NaOH) pellets were purchased from Sigma-Aldrich. Sepiolite was supplied from ITU general chemistry laboratory.

#### 3.2.2. Methods

1 M HNO<sub>3</sub> was prepared and 4 ml of it freshly used, which includes dissolved 7.0 ml HNO<sub>3</sub> 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/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 1 and 2, 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<sub>3</sub>, 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. Fig. 3 represents the basic experimental procedure for all conducted experiments.

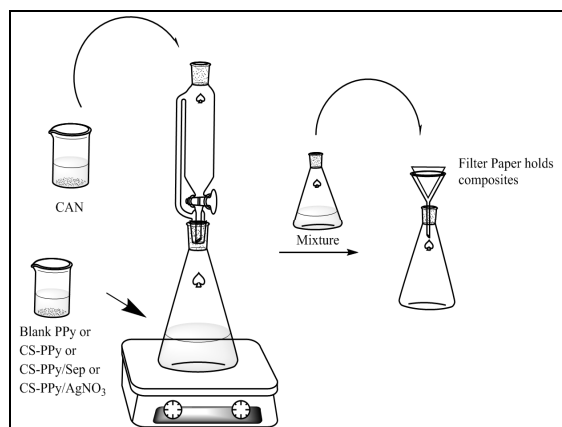


Fig. 3. Experimental procedure representation.

Table 1. Concentrations of Pyrrole and CAN and CAN/PPy molar ratios.

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

Table 2. Used amount moles and grams of Pyrrole, Chitosan, CAN, and Sepiolite.

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

### 3.3. Analyses and Results

#### 3.3.1. Analyses

Four-point probe technique was used to measure electrical conductivities of prepared pellets, which were copolymer powders. Fourier transform infrared (FTIR) spectra were 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.

#### 3.3.2. Equations

Compact thin pellets were prepared under 8-10 tons/cm<sup>2</sup> pressure to measure electrical conductivity ( $\sigma$ ). 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 (1):

$$\sigma = V^{-1} \cdot I \left( \frac{\ln 2}{\pi d_n} \right) \quad (1)$$

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

#### 3.3.3. Results

Table 3 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<sup>+4</sup> salt amount was increased however, above the value of [CAN]/[PPy]= 0.8 ratio, Ce<sup>+4</sup> amount became inversely proportional to conductivity. It could be due to termination step of the polymerization. Fig. 4 and 5 show the effect of [CAN] concentration on the polymerization yield and conductivity.

Table 3. Yield and conductivity results of PPy-CS/Sep composites.

PPy-CS/Sep	CS (g)	[PPy] (M)	[CAN] (M)	n(CAN)/n(PPy)	PPy (g)	Sep (g)	Yield (%)	Conductivity (S/cm)
#1	0.016	0.113	0.075	0.67	1.55	0.52	53	3.7 x 10 <sup>-4</sup>
#2	0.5	0.113	0.075	0.67	1.55	0.52	83	3.0 x 10 <sup>-4</sup>
#3	0.016	0.113	0.09	0.8	1.55	0.52	60	6.4 x 10 <sup>-4</sup>
#4	0.5	0.113	0.09	0.8	1.55	0.52	64	6.41 x 10 <sup>-4</sup>
#5	0.016	0.113	0.113	1	1.55	0.52	66	5.7 x 10 <sup>-4</sup>
#6	0.5	0.113	0.113	1	1.55	0.52	69	4.24 x 10 <sup>-4</sup>

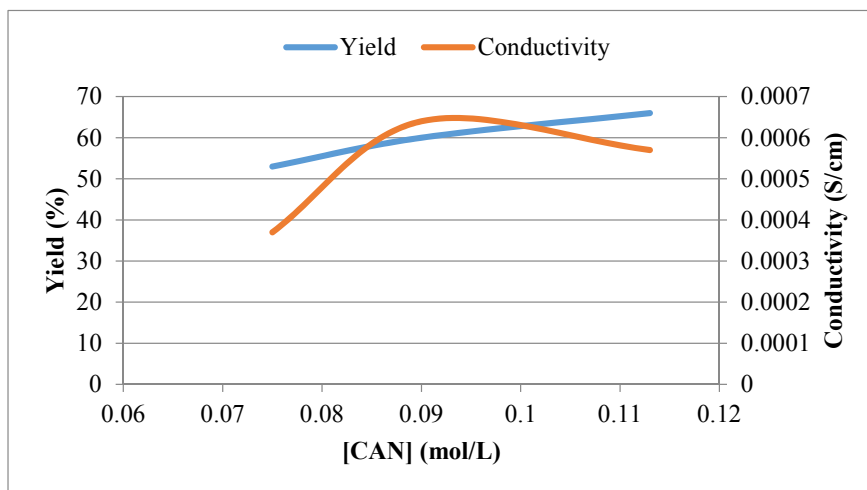


Fig. 4. The effect of [CAN] concentration on the polymerization yield and conductivity for 0.016 g chitosan.

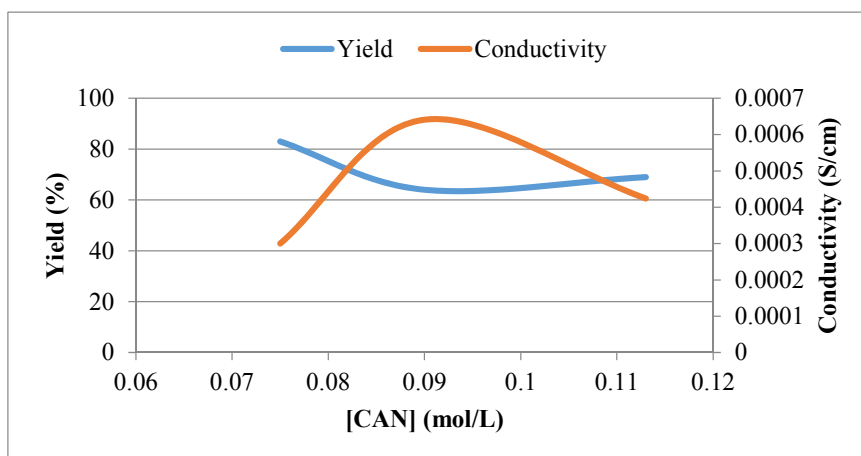


Fig. 5. The effect of [CAN] concentration on the polymerization yield and conductivity for 0.5 g chitosan.

Figure 6 and 7 show the FTIR spectra of PPy-CS/Sep samples. According to Figure 6, the spectrum of chitosan indicates that the peaks at  $1654\text{ cm}^{-1}$  and  $1171\text{ cm}^{-1}$  could be assigned to carbonyl stretching vibration (amide I) and C-O stretching vibration of ether linkage of chitosan backbone. C-N stretching of the amino groups were found at  $1322$  and  $1328\text{ cm}^{-1}$ . Si-O-Si stretching vibration was at  $1001\text{ cm}^{-1}$ . The specific bands of the beta (1-4) glycoside bridge appeared at  $1171\text{ cm}^{-1}$ . Both  $991$  and  $995\text{ cm}^{-1}$  belong to sepiolite. The peak at  $3554\text{ cm}^{-1}$  can be attributed to the O-H stretching vibrations of chitosan and N-H stretching vibrations of polypyrrole.  $1549$ ,  $1551$ , and  $1535\text{ cm}^{-1}$  were observed as  $\text{NH}_3$ . Band at  $1294\text{ cm}^{-1}$  is for O-H bending vibrations.

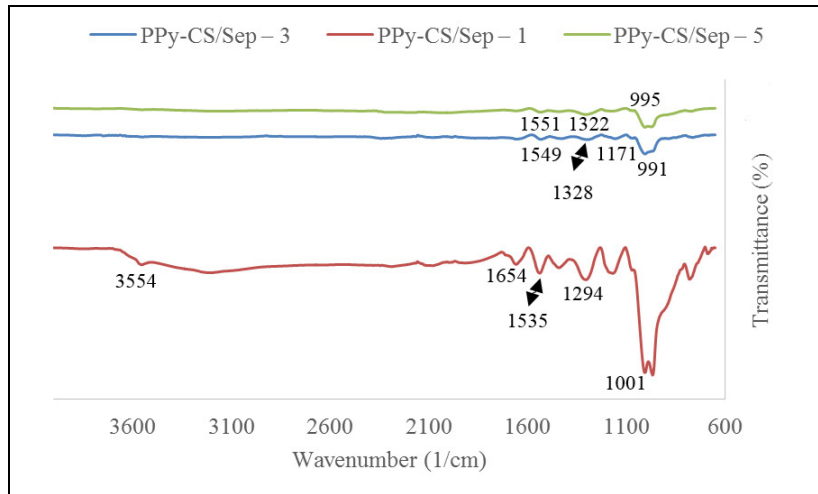


Fig. 6: FTIR spectrum of PPy-CS/Sep samples which includes 0.016 g chitosan.

According to Figure 7, the peak at  $3672\text{ cm}^{-1}$  can be attributed to the O–H stretching vibrations of chitosan. The peaks at  $1119, 1089,$  and  $1015\text{ cm}^{-1}$  assigned to Si–O–Si stretching.  $997\text{ cm}^{-1}$  could be sepiolite.  $3256\text{ cm}^{-1}$  was found as N–H stretching.  $1531\text{ cm}^{-1}$  correspond to C–C stretching. The characteristic peak at  $1615\text{ cm}^{-1}$  is assigned to the stretching vibrations of the –CONH– groups of chitosan. C–N stretching of the amino groups were found at  $1318\text{ cm}^{-1}$ .  $1338\text{ cm}^{-1}$  correspond to C–H.  $1352\text{ cm}^{-1}$  could be CAN due to a  $\text{NO}_3^-$  ligand incorporated into the polymer. Saccharide structure has peaks at  $1119, 831,$  and  $859\text{ cm}^{-1}$ .

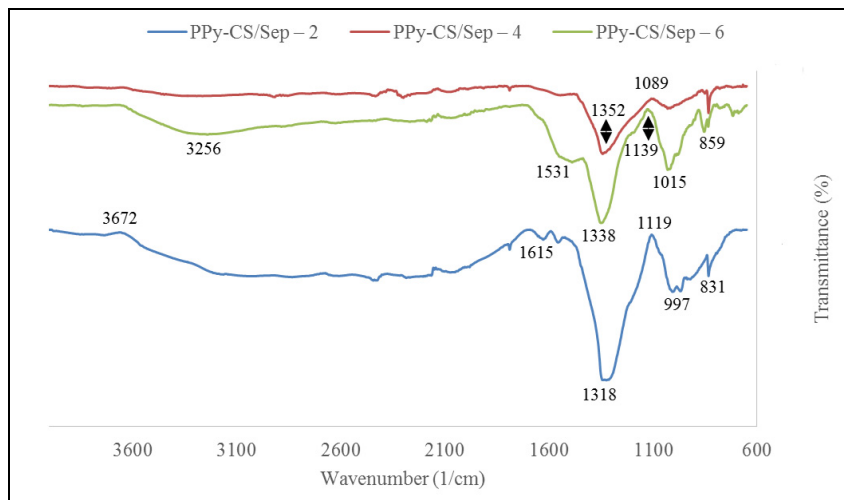


Fig. 7: FTIR spectrum of PPy-CS/Sep samples which includes 0.5 g chitosan.

Figure 8, 9, and 10 show the SEM pictures of PPy-CS/Sep-1. According to Figure 8, the obtained results showed that ESEM micrograph for the surface of Chitosan/ Polypyrrole composite has average size of  $28.63\text{ nm}$ . Circular shaped chitosan particles and rod shaped sepiolite were detected easily.

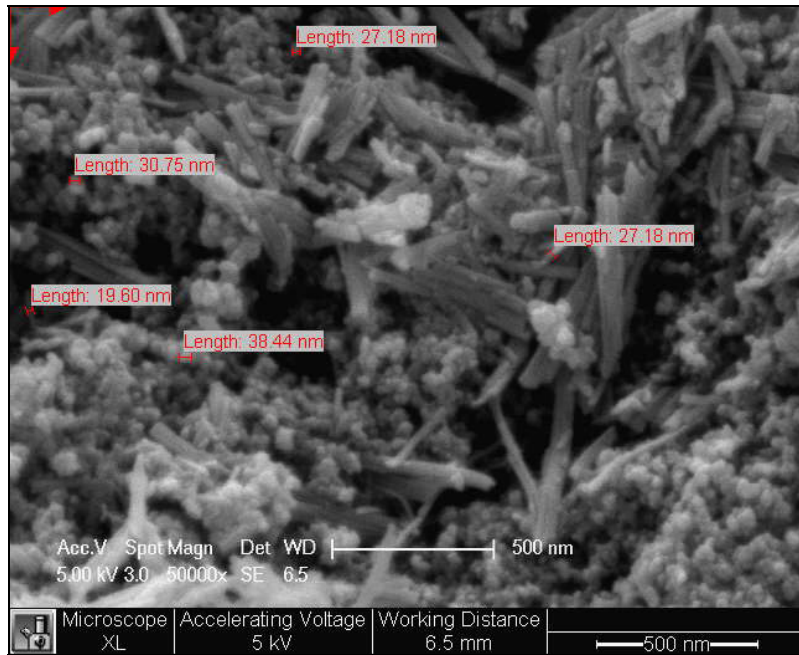


Fig. 8. SEM picture of Chitosan/Polypyrrole-Sepiolite Composite (PPy-CS/Sep-1) in 500nm.

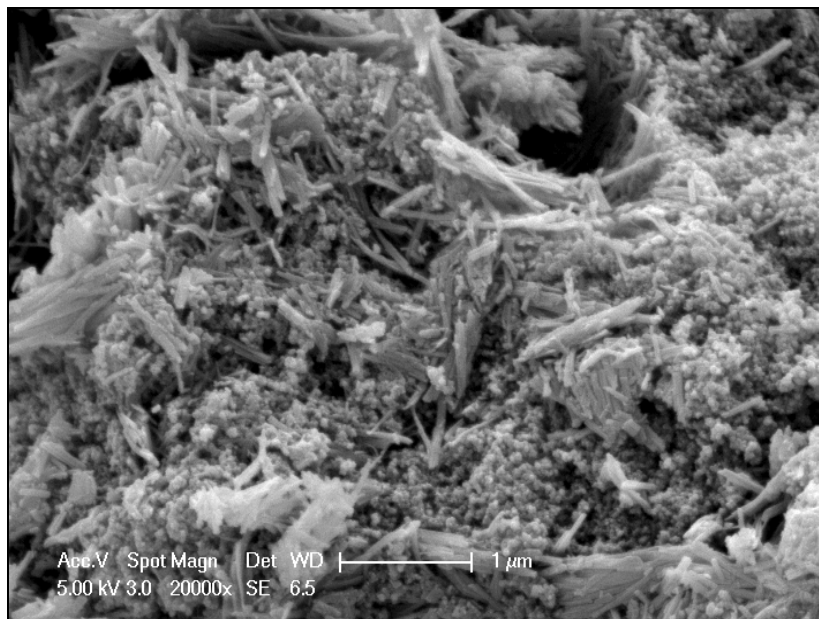


Fig. 9. SEM picture of Chitosan/Polypyrrole-Sepiolite Composite (PPy-CS/Sep-1) in 1 μm.



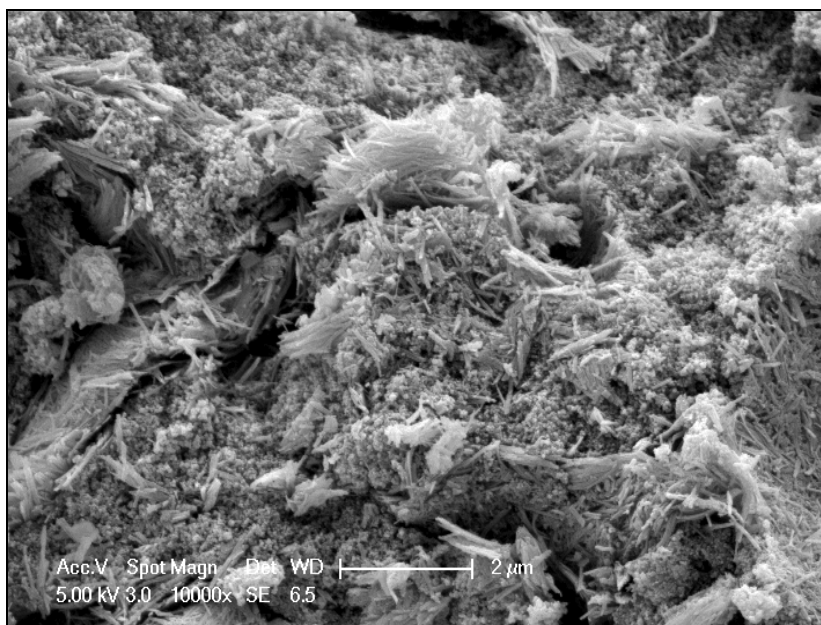


Fig. 10. SEM picture of Chitosan/Polypyrrole-Sepiolite Composite (PPy-CS/Sep-1) in 2  $\mu\text{m}$ .

#### 4. Conclusion

The aim of this research is the production of conductive biodegradable, biocompatible, and biofunctional composites production using chitosan and also determining optimum conditions for effective conductivity. Polypyrrole-Chitosan/Sepiolite nanocomposites were formed for this study. The effect of concentration on the conductivity and yield of the composite samples 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  $[\text{CAN}] = 0.09 \text{ M}$ , conductivities decreased, because of high  $\text{Ce}^{+4}$  concentration probably caused the oxidative chain termination and linear termination of polymerization. Polypyrrole-Chitosan/Sepiolite (PPy-CS/Sep) nanocomposite polymers showed conductivity between  $3.0 \times 10^{-4}$  and  $6.41 \times 10^{-4} \text{ S/cm}$ . According to this, 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. 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/Sep-1 sample has average size of 28.63 nm. Chitosan and sepiolite were 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/Sep in tissue engineering, biosensors, bioactuators and many other biomedical applications which will be very important in next century.

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