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PREPARATION AND SWELLING PROPERTIES OF POLY(3,4–THYLENEDIOXYTHIOPHENE)/POLY(ACRYLIC ACID)/BENTONITE COMPOSITE HYDROGELS

Keziban Huner

Department of Chemistry, Faculty of Arts and Sciences, Yildiz Technical University, Istanbul, Turkey
khuner@yildiz.edu.tr

Abstract

In this study, poly(acrylic acid) (PAA)/bentonite (BNT) composites were synthesized through chemical crosslinking by a chemical polymerization using ammonium persulfate as initiator and N,N'-methylenebisacrylamide as crosslinker. Poly(3,4-ethylenedioxythiophene) (PEDOT) was synthesized by oxidative polymerization and then PEDOT/PAA/BNT composites were prepared by mixing PEDOT at 5%, 10% and 20% by mass into PAA/BNT composite. These hydrogel composites were characterized by FTIR, XRD and SEM. It was observed that water absorbency increased with the increase of PEDOT ratio of hydrogel composites.

Keywords: Hydrogel, poly(3,4-ethylenedioxythiophene), poly(acrylic acid), bentonite

1. Introduction

Hydrogels are multicomponent systems composed of hydrophilic polymers that swell in water [1]. Cross-linked polymers with a solvent uptake capacity of at least 20% of their own mass are defined as xerogels [2]. The relationships between the synthesis conditions, structures and properties of polymer gels have been the subject of intense research since the 1940s. Network structures determine the properties of polymer gels, for example the solvent absorption capacity. In recent years, hydrogels that absorb a thousand times their own mass in liquid have been synthesized [3]. Hydrogels are three-dimensional cross-linked hydrophilic network polymers [4, 5]. The network forming the hydrogel consists of polyelectrolyte chains linked by cross-links. These chains usually contain carboxylic acid groups as substituents. The negative charges on the polymer chains repel each other and expand. Carboxyl groups also interact with water by forming hydrogen bonds. The presence of cross-links allows polymer chains to swell in gel form without dissolving [5, 6].

One of the most important properties of hydrogels is their swelling in an aqueous medium. However, swelling and shrinkage behavior alone is not sufficient to deal with hydrogels. Recently, many researchers have prepared new hydrogels that can respond to a signal (swelling, shrinking, and deteriorating) by attaching some functional groups to hydrogels [7]. These hydrogels with attached functional groups are called smart gels. Intelligent gel syntheses are made from the monomer used in gel synthesis, which can respond to certain environmental stimuli, depending on their structure [8, 9]. Superabsorbent hydrogels are smart polymers made for this purpose. Superabsorbent hydrogels can be prepared by forming pores in the hydrogel structure, or by attaching suspended groups to the gel or by reducing the gel size. The best-known smart gels are those that can respond instantly to small changes in environmental conditions. For this reason, such gels are also known as environmentally sensitive gels. One of the unique properties of environmentally friendly gels is that they change their swelling rate very sharply in response to small changes in their environment. Smart, that is, environmentally sensitive gels; It can be divided into 5 classes as electrical and magnetic sensitive, pH sensitive, light sensitive, temperature sensitive, solvent sensitive [10]. The responses of smart polymer gels to environmental stimuli; they can be listed as shape, mechanical, surface energy, phase change, electrical field, reaction rate, precipitation rate, molecular arrangement [11-13]. Clay-based hydrogels are used in many application areas due to the unifying properties of both clays and polymers such as biodegradable, large surface area, biocompatible, high specificity, three-dimensional network, abundant raw material and swelling-deswelling properties.

Polymer composites have common areas of study to improve or differentiate the properties of polymers [14, 15]. Poly(3,4-ethylenedioxythiophene) (PEDOT), one of the most successful conductive polymers [16], has advantages such as optical transmittance in the conductive state, high stability in the doped state and low redox potential. Therefore, the aim of this study is to prepare the gel of PEDOT with PAA/BNT and to obtain composites with the desired properties. In this study, the water absorption capacity and morphology of PEDOT/PAA/BNT composites prepared with PEDOT synthesized by chemical polymerization of 3,4-ethylenedioxythiophene (EDOT), a derivative of thiophenes [16, 17], were investigated.

2. Material and method

2.1 Materials

EDOT, copper(II) nitrate and poly(styrene sulfonic acid) (PSSA) were supplied from Alfa Aesar. Acrylic acid (AA), N,N'-methylenebisacrylamide (MBAA), hydrogen peroxide (H_2O_2; 35%), ammonium persulfate (APS), sulfuric acid (H_2SO_4), sodium hydroxide (NaOH) and sodium hydrogen carbonate ($NaHCO_3$) were obtained from Merck. Synthesis was conducted under nitrogen and in all experiments deionized water was used.

2.2 Activation of BNT

BNT (9 g) was mixed with sodium hydrogen carbonate (2.7 g) in deionized water (108 g) overnight and then centrifuged 2 times. It was dried overnight at 70 °C after centrifugation. The dry bentonite was treated with sulfuric acid (8 N) at 90 °C for 7 hours and then washed with distilled water to neutralize it. The neutralized bentonite was dried at ~100 °C for 6 hours.

2.3 Synthesis of PAA/BNT composites

Acrylic acid (33.4 ml) was neutralized with NaOH solution. Activated bentonite (0.05 g) was added to the reaction vessel and mixed. MBAA (0.3 g) was added to the mixture and mixed under nitrogen gas at 30 °C for 30 minutes with a mechanical stirrer. APS (0.1 g) dissolved in water was injected into the mixture and stirred for ~3 hours at 60 °C. The resulting hydrogel was washed several times with distilled water, dried in an oven, and then ground with a grinder.

2.4 Synthesis of PEDOT

PEDOT were synthesized as in the literature [18]. The deionized water (10 ml) and PSSA (1.76 g) were added to the reaction vessel and stirred for 1.5 hours. At the same time, the EDOT monomer (0.11 g) and deionized water (10 ml) were added to a beaker and stirred for 1.5 hours with mechanical stirrer. And then the EDOT mixture was added dropwise to the reaction vessel and after 1 hour H_2O_2 (0.52 g) and $Cu(NO_3)_2$ (0.007 g) were added and the mixture was stirred with mechanical stirrer for 24 hours. The polymer mixture was dialyzed for 2 days and then dried on a hot plate at ~90 °C.

2.5 Preparation of PEDOT/PAA/BNT composites

5%, 10% and 20% by mass of PEDOT (of PAA/BNT) was mixed with PAA/BNT composite. The PEDOT/PAA/BNT composite was prepared by drying the mixture at ~100 °C overnight followed by grinding. Composites were called as 5% PEDOT/PAA/BNT, 10% PEDOT/PAA/BNT, and 20% PEDOT/PAA/BNT to indicate the percentage of PEDOT they contained.

2.6 Characterization

The fourier transform infrared-attenuated total reflection spectroscopy (FTIR-ATR, TENSOR27, Bruker Optic GmbH) was used for polymer characterization. The crystalline structure of composites were examined by X-ray diffraction (XRD, Rigaku D/MAX-Ultima+/PC). The morphology of nanofibers were investigated by Scanning electron microscopy (SEM, Zeiss EVO® LS 10).

The water absorbency of the composites was measured by immersion in 500 mL of distilled water. To achieve stability, the composites were allowed to fully swell for approximately 24 hours at room temperature. Swollen polymers were weighed and all composites were repeated 3 times for accuracy. To maintain accuracy, experiments were performed in triplicate for all formulations to obtain reproducible results. The % equilibrium water absorbency (swelling) was calculated using the following equation 1 [19]:

$$Swelling\ (\%) = \left(\frac{Mass\ of\ swollen\ polymer\ (Ws) - Mass\ of\ dry\ polymer\ (Wd)}{Mass\ of\ dry\ polymer\ (Wd)}\right) x\ 100 \quad (1)$$

3. Results and discussion

FTIR spectra of PAA/BNT, BNT, 5%, 10%, 20% PEDOT/PAA/BNT composites were given in Figure 1. A broad peak at about 1000 cm^{-1} and peaks at about 790 cm^{-1} prominently observed in BNT disappeared in the PAA/BNT composite. The peaks at 1400 and 1550 cm^{-1} in the PAA/BNT composite can correspond to the out-of-plane C–O–H binding of PAA and the CH_2 group asymmetric stretching of PAA, respectively [20, 21]. The characteristic bands of PEDOT

are the asymmetric stretching of the C=C bond at about 1490 cm^{-1}, the intertwining stretching of the C-C bond at about 1304 cm^{-1}, the C–O–C bending vibrational band in the ethylenedioxy group at around 1040, 1163 and 1280 cm^{-1} [22]. Accordingly, it can be said that the peaks around 1030 and 1165 cm^{-1} seen in all PEDOT/PAA/BNT composites are C-O-C bending vibrations in the ethylenedioxy group.

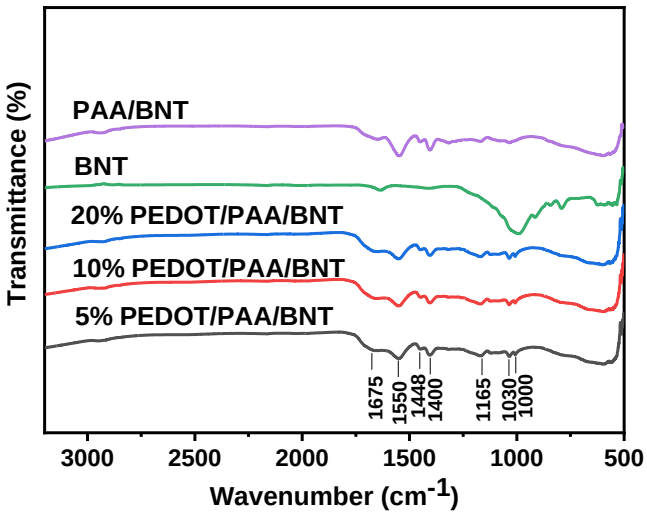

Figure 1. FTIR spectra of PAA/BNT, BNT, 5%, 10%, 20% PEDOT/PAA/BNT composites

XRD paterns were investigated to obtain information about the crystallinity and amorphous structure of the polymers. Figure 2 shows the crystallinity of 10% and 20% PEDOT/PAA/BNT composites. It can be said that the peaks between 2θ = 10° and 20° show the crystal structure of bentonite [23, 24]. The peak at 2θ = 45° is due to the crystalline nature of PEDOT [25]. Crystalline material always exhibits sharp diffraction peaks but is not amorphous. Accordingly, it can be said that 10% and 20% PEDOT/PAA/BNT composites have similar crystalline structures.

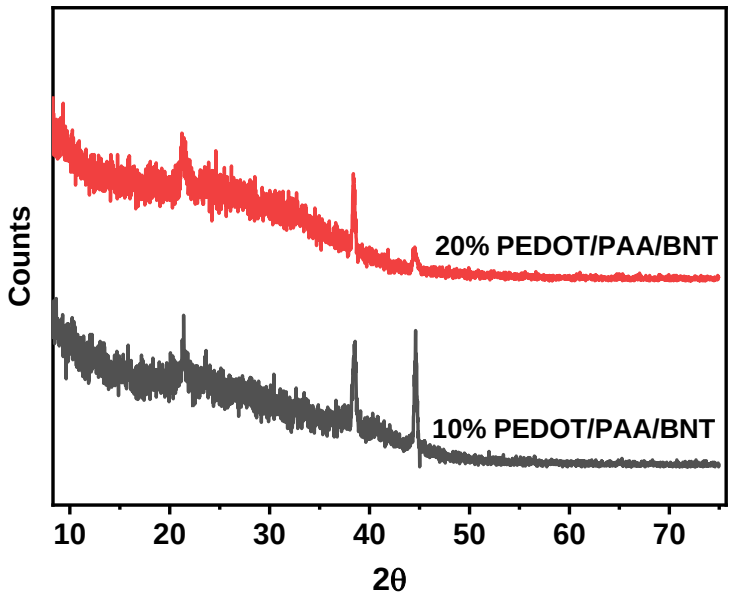

Figure 2. XRD patterns of 10% and 20% PEDOT/PAA/BNT composites

Swelling rate, swelling ratio and water retention capacity are known to be the three most important parameters for superabsorbent hydrogels. The swelling ratio is usually the inverse of the water retention capacity. A high swelling ratio usually means poor water retention and vice versa. The swelling ratio and water retention capacity of hydrogels are affected by many factors, such as the molecular weight of the polymers and the chemical structure of the repeating unit [26, 27]. Table 1 was given water absorbency of PAA/BNT and PEDOT/PAA/BNT composites. The water absorbency of the composite increased from 78 to 90%, while the PEDOT ratio in the composite increased from 5 to 20. PEDOT with functional pendant groups carrying double bonds had an enhancing effect on the water absorption of the composites. Since the water absorbency of the PEDOT/PAA/BNT composite containing the highest PEDOT ratio is the highest, it can be said that its water retention capacity may be the lowest.

Table 1. Water absorbency of PAA/BNT and PEDOT/PAA/BNT composites.

Samples	**% Water absorbency**
PAA/BNT	75 (±11.5)
5% PEDOT/ PAA/BNT	78 (±18.0)
10% PEDOT/ PAA/BNT	82 (±7.5)
20% PEDOT/ PAA/BNT	90 (±10.2)

Figure 3 shows SEM image of hydrogel composites and BNT. It can be said that PEDOT/PAA/BNT composites have a porous and rough morphology (Fig.3a-b), while PAA/BNT composite has a morphology containing BNT particles on a hard and smooth surface (Fig.3c). It is seen that BNT is mostly composed of particles between 1-2 micrometers, as well as containing few large particles (Fig.3d).

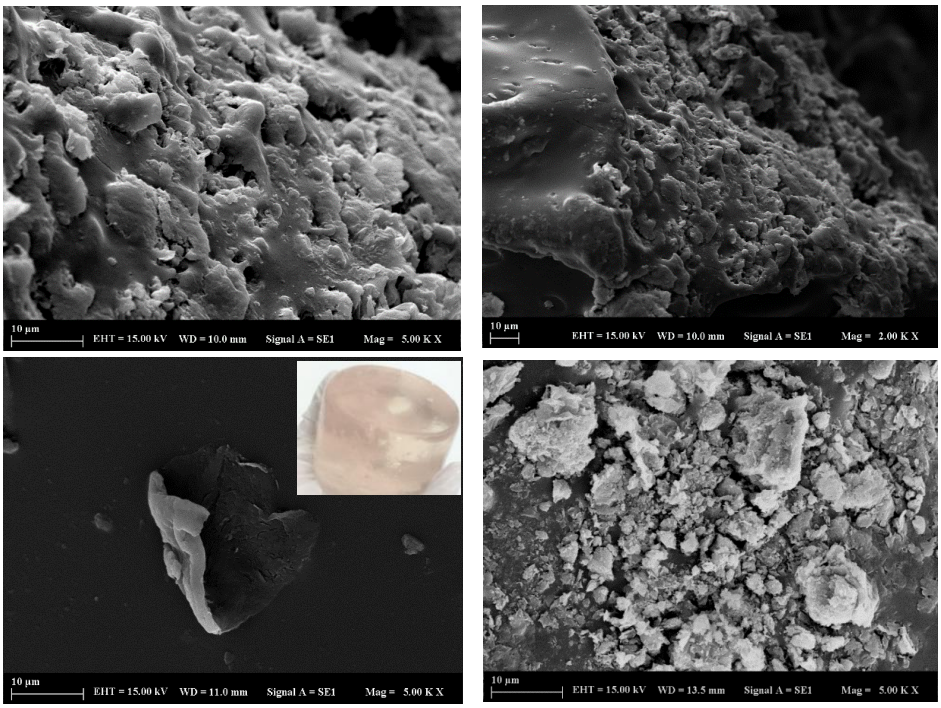

Figure 3. SEM image of a) 20% PEDOT/PAA/BNT b) 10% PEDOT/PAA/BNT c) PAA/BNT (inside photo: PAA/BNT composite obtained after polymerization) d) BNT

4. Conclusions

PAA/BNT composite and PEDOT were successfully synthesized. PEDOT/PAA/BNT composites were obtained by mixing PEDOT at different ratios, keeping the PAA/BNT ratio constant. The structure of the composites was investigated by FTIR spectroscopy and the crystalline structure of PEDOT/PAA/BNT composite was investigated by XRD. The surface morphology of bentonite and its composites was investigated by SEM. As the PEDOT ratio increased in the composite, the water absorption capacity of the gel increased slightly. This study is promising for further analysis to obtain PEDOT/PAA/BNT hydrogels with electrical conductivity, high swelling and water retention capacity.

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