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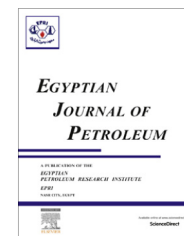
FULL LENGTH ARTICLE

Synthesis and characterization of hydrophilic chitosan-polyvinyl acetate blends and their sorption performance in binary methanol–water mixture

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Abstract Chitosan-polyvinyl acetate (CHI-PVA) blends were prepared throughout copolymerization reaction. Chitosan (CHI) as a hydrophilic molecule was added to modify the blend surface of polyvinyl acetate (PVA). The sorption effects of CHI-PVA blends were studied in the presence of binary feed mixture of methanol–water (MW). The obtained blends were investigated by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), microscopic analysis and conductivity measurements to investigate the chemical structure, crystallinity, surface morphology and electric property, respectively. Effect of water content on the swelling performance of CHI-PVA blends based on (methanol/water) ratio was discussed. CHI-PVA complexes show high swelling performance with 20% CHI based blends from 50% water content in methanol–water mixture.

1. Introduction

Graft copolymerization of synthetic polymers with natural biodegradable materials is of great interest due to their significant characterizations. The modification of synthetic polymers can enhance their properties such as flexibility, conductivity and sorption performance. Recently, one of the natural biopolymers that play a great role in this field is chitosan [1–3]. Chitosan (CHI) a cationic biodegradable polymer was prepared by the partial alkaline N-deacetylation of chitin. Chitin is a long-chain natural biopolymer of an N-acetyl

glucosamine, a derivative of glucose, found in the exoskeletons of crustaceans and also in the cell walls of certain fungi and algae [4–6]. Chitosan is one of the most common abundant basic substances currently used in life. Compared with synthetic polymers, chitosan has a very wide application range due to its biodegradability, biocompatibility, toughness and no toxicity [5,6]. Chitin is insoluble in many solvents, but chitosan can be dissolved in acidic media and becomes a cationic polymer due to the protonation effect of amino groups in its structure. Chitosan is known as an excellent adsorbent polymer for several purposes. The adsorbent mechanism of chitosan is mainly revealed to the chelation interaction between the primary amines of the chitosan along the backbone of the polymer [4–6]. Along with these advantages, it also has some pharmaceutical applications such as food protectives, anti-microbial, anti-oxidant, anti-tumor, hydrogels and

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nanoparticles [7–10]. Because of its high hydrophilic performance and good chemical resistance [11] it has acquired significant interest in membrane separation techniques like pervaporation dehydration [12–18] and gas separation [19–21]. Separation of alcoholic solvents such as methanol, ethanol, propanol and butanol from water is of vital importance in organic synthesis. Compared with other separation methods applied for this purpose, dehydration possesses high separation behavior and cheap technique [12]. For the separation method, it is very important to prepare good hydrophilic blends to realize high swelling degrees in aqueous media. For enhancing the efficacy of cationic chitosan blends, several techniques were used such as crosslinking [22–24] and polymer blending [25–27]. Many polymeric blends were used for dehydration of alcoholic solvents using polyvinyl alcohol, polysiloxane imide, nylon, cellulose and chitosan [28–30]. Miscibility of CHI with water will accelerates by breaking the hydrogen bonding inside the matrix of blends. The reaction mechanism and kinetics of the graft copolymerization of chitosan onto polyvinyl acetate have been explained in a previous paper [31]. In the current research, hydrophilic blends of CHI-PVA were prepared through grafting copolymerization process. These blends have ionic-rich structure which greatly improves its sorption performances. CHI-PVA blends were used to investigate the separation performance of binary feed concentrations of methanol–water (MW) mixture.

2. Experimental

2.1. Materials

Chitosan (CHI) with an average molecular weight of about 110,000 and a degree of deacetylation of about 85% was prepared locally through shrimp processing wastes [12,32]. Water soluble synthetic polyvinyl acetate (PVA) resin solution with high viscosity was obtained from Egyptian Chemical Co., Egypt. All other reagents were of analytical grade and used as received without further purification.

2.2. Preparation of CHI-PVA blend

Hydrophilic blends of chitosan-polyvinyl acetate (CHI-PVA) were prepared throughout graft copolymerization reaction as described in the Schematic diagram (Fig. 1) [12]. Prior to use, a specific amount of chitosan (CHI) was dissolved completely into 200 ml of a 2% (w/w) acetic acid solution and then stored until it became clear. A water-soluble synthetic polyvinyl acetate (PVA) resin solution was used without further purification. CHI solution was blended onto PVA solution according to 10–90% mass fraction at quasi-steady rate under continuous stirring. By adding CHI solution to the PVA emulsion "contains some additives act as a catalyst", polymerization was started and a dispersion solution of CHI-PVA blend was obtained. As more CHI solution was added, the diffusion rate increased with more crosslinking. Then the different mass fraction solutions of CHI-PVA were poured, dried and stored for further investigation. For simplicity, CHI-PVA blends were cut as coupons in a dimension of $1 \times 1 \times 0.04$ cm (W $\times$ H $\times$ D).

2.3. Characterization

Fourier transform infrared spectroscopic (FTIR) technique of CHI, PVA and CHI-PVA blends were recorded on FTIR Spectrophotometer (Model 960M000g; ATI Mattson Infinity Series; USA). The spectra measurements of CHI, PVA and CHI-PVA samples were employed in a range of 4000–400 cm^{-1} with a scan resolution of 4 cm and scan rate of 32 cm min^{-1}. X-ray diffraction (XRD) analysis of CHI, PVA and CHI-PVA was carried out on X-ray diffractometer
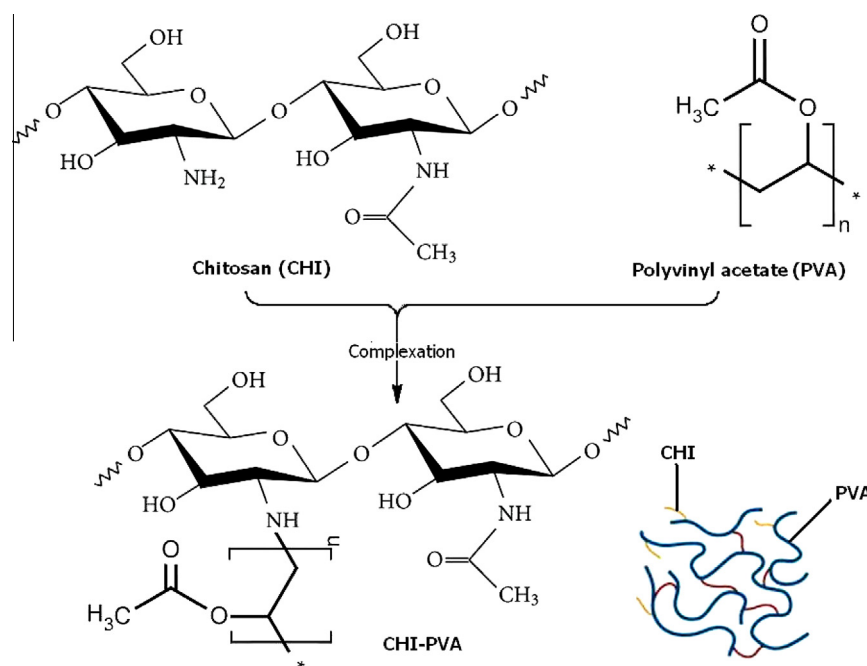
Figure 1   A Schematic diagram for preparing CHI-PVA blends.

using target Cu Kα 1.54 Å (Model D/Max2500VB2+/Pc, Rigaku Co., Japan). The X-ray measurements were employed by a diffraction angle of 2θ in a position range of 4–80 with a scan size of 0.02 2θ and scan step of 0.8 s. The surface morphology of the modified and unmodified blends was observed using Olympus Camedia digital camera C-5060 wide zoom. It has a fast startup time of 3 s, short shutter release time lag of 0.4 s, three frames per second in HQ mode and 4× optical zoom. DC conductivity values were measured by Keithley instrument (Model 6517A 5-1/2 digit Electrometer/High Resistance Meter) all samples were measured using micrometer.

2.4. Swelling performance

Prior to use, dry CHI-PVA blends were weighted (W_i) then immersed into a wide range of binary feed concentrations of methanol–water (MW) mixture at room temperature for 48 h. After that the blends were then taken out from the alcohol–water mixture and weighted again (W_f). The swelling degree (SD) was calculated using SD (%) = $(W_f - W_i)/W_i \times 100$.

3. Results and discussion

3.1. FTIR analysis

FTIR spectra of CHI, PVA and CHI-PVA are shown in Fig. 2, respectively. In case of polyvinyl acetate (PVA) diagram, it can be clearly seen that there is absence of any OH groups and appears of strong absorption bands of C=O and C—O groups at 1727 cm^{-1}, 1370 cm^{-1} and 1220 cm^{-1}, respectively, where revealed to the existence of COOCH$_3$ groups. Compared with PVA, the chitosan (CHI) diagram shows common broad absorption bands of OH and NH$_2$ groups appeared at 3460 cm^{-1} in the absence of C=O group bands. From the diagram spectra of CHI-PVA complex, it was observed that the strong absorption band of NH$_2$ groups at 3450 cm^{-1} reduced dramatically as a result of the complexation between CHI and PVA. The ester group still appeared with common absorption peaks at 1725 cm^{-1}, 1369 cm^{-1} and 1290 cm^{-1}, respectively. Also there are two new absorption bands appearing clearly at 2011 cm^{-1} and 2165 cm^{-1}, indicating that there are double or triple bond categories existing between C and N throughout the blending process. This behavior due to some NH$_2$ groups on the CHI structure was protonated to the corresponding NH groups by the complexation with PVA. Based on this manner, the variation between the band intensities may refer to the crosslinking degree of CHI-PVA [12,33].

3.2. XRD analysis

Fig. 3 shows the XRD patterns of CHI, PVA and CHI-PVA, respectively. There are significant peaks recorded at diffraction angles of 10° for CHI and at 20° for both CHI and PVA, indicating the partial crystallinity of CHI and PVA. This structure of CHI is mainly described as the formation of partial crystalline phases through two types of hydrogen bonding. These hydrogen bonds happened between NH$_2$ groups and OH groups and also between OH groups itself. However, the band intensity at diffraction angles of 20° and 40° for CHI-PVA is reduced, indicating the ionic crosslinking interactions between CHI and PVA, breaking of hydrogen bonds and decreasing of crystallinity. Consequently, it was shown that the signals of NH$_2$ groups disappeared after the ionic complexation which restrict the chain mobility of both CHI and PVA, and hence reduce the crystallinity of PVA [12].

3.3. Morphological analysis

Fig. 4a–c exhibits the optical microscopic images of different ratios of CHI-PVA blends at room temperature. Microscopic images obtained from pure PVA do not manifest any fractal
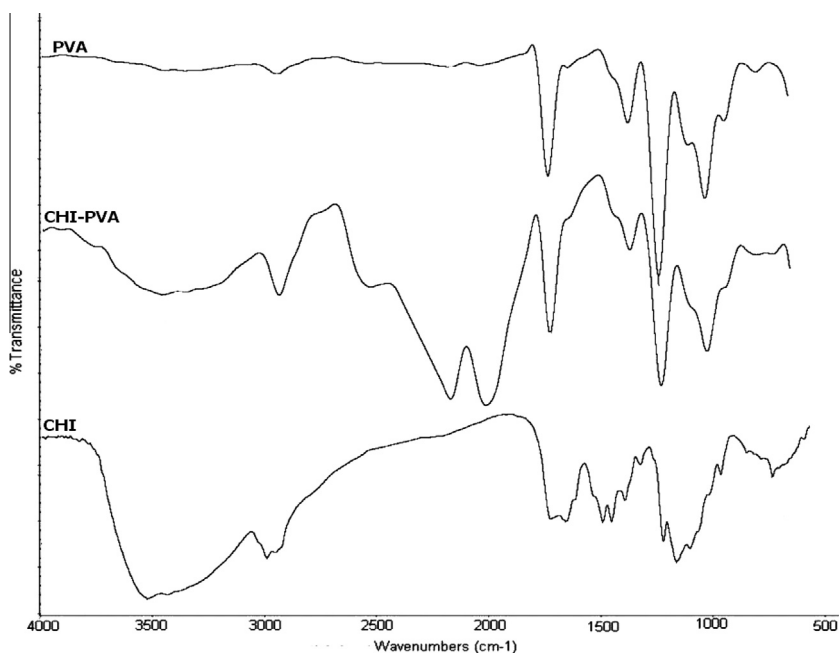

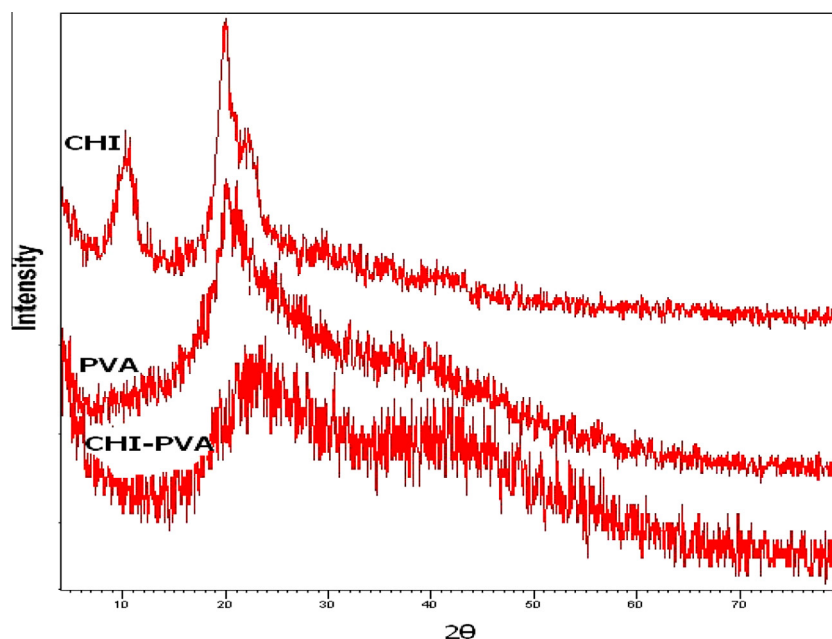**Figure 2**   FTIR spectra of CHI, PVA and CHI-PVA, respectively.

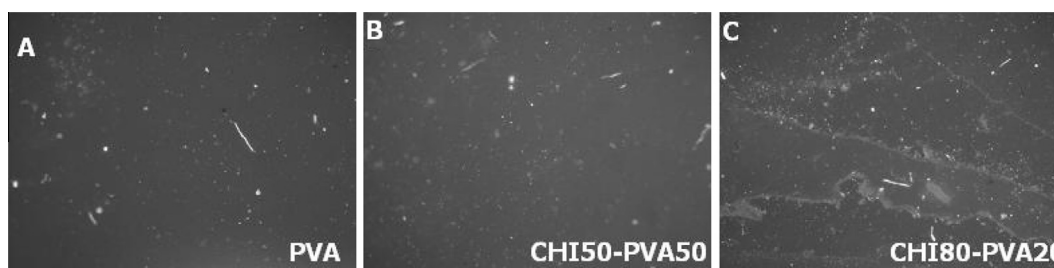**Figure 3** XRD diagrams of CHI, PVA and CHI-PVA, respectively.

Figure 4 Optical microscopic images of different ratios of prepared CHI-PVA (a) 00–100%, (b) 50–50% and (c) 80–20%, respectively.

structures (Fig. 4a), whereas those formed from the interaction of CHI with PVA manifest appearance of small embedded spots as shown in Fig. 4b. With the addition of CHI to PVA chains, the embedded CHI has several branched structures as observed clearly in CHI-PVA image (Fig. 4c) at room temperature. Clear dispersal structures of CHI-PVA (Fig. 4c) may relate to the chelate formation. The diffusion structure of CHI-PVA image obtained at room temperatures may attribute to the complex formation degree, the CHI concentration and the period required for drying. The major formation mechanism which detects the expansion of the morphological structures from CHI is based mainly on the concept of molecular diffusion. There are several techniques used to characterize the dimensions of CHI structures as function of concentration such as box counting method [34].

3.4. Conductivity

Fig. 5 shows conductivity diagrams for CHI-PVA blends, respectively. From the obtained results, it can be seen that conductivity values of CHI-PVA samples raise with increasing temperature, like the typical polyelectrolyte behavior, which is mainly due to the ionization of NH_2 groups "releasing of

H ions" in CHI structure. The high σ values of CHI-PVA are probably because the ionic crosslinking between CHI and PVA is powerful and not cracked [12]. Moreover, the conductivity measurements increase with elevating temperatures which strongly confirm that blends were dissolved due to the ionization of NH_2 groups through the blending solution and partial dissociation of the ionic complexation between CHI and PVA. The variations of conductivity between the different blends at the same conditions are probably due to the changing of the ionic crosslinking degree [12].

3.5. Swelling performance

The swelling performance (Fig. 6) of different mass ratios of CHI-PVA in methanol–water (MW) mixtures, respectively, is mainly dependent on the blends hydrophilicity. Swelling degree of CHI-PVA in MW mixture increased with increasing water concentration followed by steady state at a higher water content. It should be mentioned that the degree of swelling of CHI-PVA in pure water was found higher than in pure alcohol. Flexibility of CHI-PVA increased gradually with increasing water content which develops more interactions with blends than alcohol. This behavior is due to the molecules in
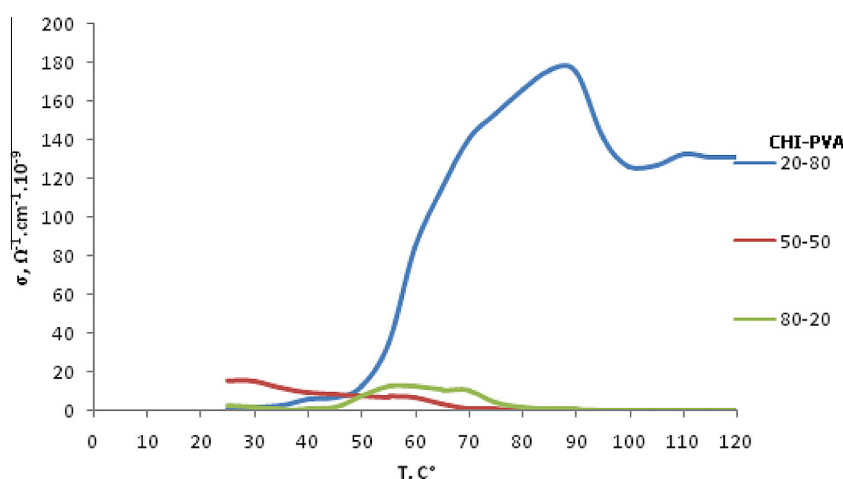
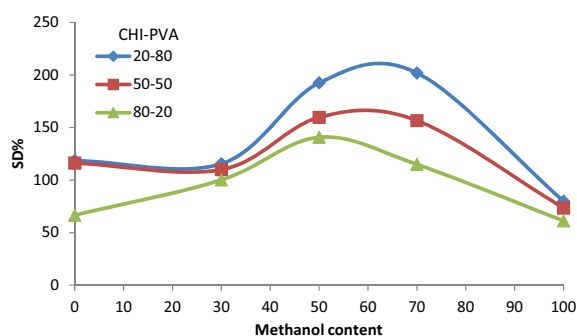**Figure 5** Conductivity diagrams of different ratios of CHI-PVA blend.

Figure 6 Swelling degree of different ratios of CHI-PVA in methanol–water mixture for 48 h at room temperature.

the outer layer of CHI-PVA firstly undergoing relaxation followed by diffusion of solvent molecules into the bulk [12]. However, the degree of swelling in pure alcohol is too low but when a small amount of water exists in alcohol, water molecules accelerate the relaxation of CHI-PVA which have hydrophilic polar groups. This is the main reason for the high swelling degree of the blends in alcohol–water mixture to that in pure alcohol. In general, the maximum change of swelling degree in all methanol–water mixtures was observed in the range of 50–70% at 20% CHI content. This result is attributed to the combined influence of alcohol and water. Up to 50% water content in MW mixtures, the permeation of alcohol and water through the blends at a compatible rate. After that, as water content in feed is the major, the swelling degree increased slightly. The swollen blends reduce the resistance to permeation due to the maximum relaxation of the hydrophilic blends. As the swelling of blends increases with increasing water ratio, more alcohol molecules are permeating together with water molecules due to the sorption coupling process [35].

4. Conclusion

Different ratios of hydrophilic CHI-PVA complexes were prepared through blending process. FTIR and XRD spectra show composition and crystallinity of the CHI-PVA blend which reduced greatly due to the crosslinking chains between CHI

and PVA. The difference between the diffusion structures of CHI-PVA images obtained at room temperatures may attribute to the complex formation, the CHI content and the drying period. Conductivity values of blend decrease with increasing temperature which strongly confirms that blends were dissolved due to the ionization of NH_2 groups through the blending solution and partial dissociation of the ionic complexation between CHI and PVA. Swelling degree of CHI-PVA blends in methanol–water mixtures increased gradually with increasing water content in feed.

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