Polymer Bulletin 41, 553–559 (1998)

Polymer Bulletin

Blend of chitosan acetate salt with poly(*N*-vinyl-2-pyrrolidone): Interaction between chain-chain

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Received: 1 June 1998/Revised version: 1 October 1998/Accepted: 13 October 1998

SUMMARY: Clear blends of chitosan acetate salt with poly (*N*-vinyl-2-pyrrolidone) (PVP) made from aqueous solutions look to be miscible on appearance. IR spectra investigated the carbonyl-hydroxyl hydrogen bonding between chain-chain in the blends and thus evidenced the compatibility of two polymers on a molecular level. The IR spectra, DSC also explored the interaction changing during the temperature increasing and indicated that a significant conformational change took place.

Introduction

Chitin is one of the most abundant natural polymers being second only to cellulose in the amount produced annually by biosynthesis[1]. It occurs in animals, particularly in crustaca, molluscs and insects, where it is an important constituent of the exoskeleton, and in certain fungi where it is the principal fibrillar polymer in the cell wall.

Chitosan is a product obtained by alkaline deacetylation of chitin and has good properties for forming membrane. In dehydration of solvents, e.g. ethanol, pyridine, the pervaporation performances were fully investigated and the results showed it was an excellent membrane[2,3]. But it has little permeability for MeOH/MTBE mixture, probably due to its rigid chain and close packing with presence of several different types of intermolecular and intramolecular hydrogen bonding in polymer matrix, and thus up to now there is no any report on this. But with poly (*N*-vinyl-2-pyrrolidone) (PVP) blending with chitosan, the obtained polyblend membrane showed good pervaporation permeation for methanol(MeOH)/methyl tert-butyl ether(MTBE) mixture[4]. The possible explanation should contribute to the structure characteristics of polyblends, particularly the interaction between chain-chain of two amorphous polymers[5,6].

A number of papers reported the miscibility behavior in blends composed of polymers with dissimilar chemical structures, which provide specific interactions between chains. Miscibility of blends containing donor and acceptor polymer like those containing acid and/or basic units has been reported. It has demonstrated that poly (*N*-vinyl-2-pyrrolidone) interacts strongly with polymers of a wide variety of polymers, e.g. poly(vinylidene fluoride)[7], polyvinlyalcohol[8], poly(2,6-dimethlyt-1,4-phenylene oxide)[9], poly (mono-n-alkylitaconates)[10], poly (*N*-1-alkyitaconamic acids)[11] , cellulose[12] etc. However, to our knowledge, no works dealing with blends containing chitosan acetate salt and poly (*N*-vinyl-2-pyrrolidone) have been reported.

Our earlier interest was the membrane pervaporation properties, but the membrane showed good permeability for MeOH/MTBE mixture, particularly compared with chitosan membrane. For this reason, the structure characteristics of polyblends of chitosan acetate salt and poly (*N*-vinyl-2-pyrrolidone), particularly the hydrogen-bonding interaction between chain-chain in polyblends, were investigated by IR, DSC.

Experimental

Materials

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Chitosan with a degree of deacetylation of 78% and an average molecular weight of 3-4x10^5 as a membrane material was supplied by Koyo Chemical Co., Japan. Poly (*N*-vinyl-2-pyrrolidone) (PVP) with an average molecular weight of 4x10^5 was from Aldrich Co.. The other reagents and solvents were analytical-grade from commercial sources and used without further purification.

Membrane preparation

The solution of poly (*N*-vinyl-2-pyrrolidone) (1.5wt.%) and chitosan solution (1.5wt%) in 1.0wt% aqueous acetic acid were mixed in different ratios. The casting solutions of both with different composition were poured on glass plate and evaporated at room temperature. The thickness of blending membrane is about 20μm. All the samples were dried under reduced pressure in a vacuum oven at 40°C for two days before tested.

FTIR measurements

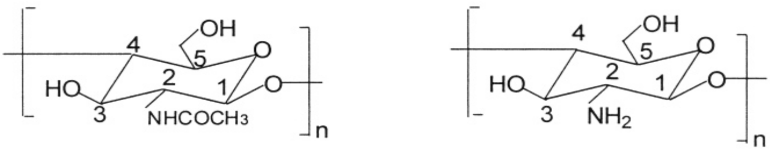
Infrared spectra of pure polymers and blends were recorded on Bruker Fourier Transform Infrared Vector 22 spectrophotometer. The spectra were recorded with a resolution of 2 cm^{-1}.

DSC Measurement

DSC curves were obtained using a Perkin Elemer DSC 7 thermal analysis system with a heating rate 20 °C/min under the nitrogen atmosphere. The samples were dried under reduced pressure in a vacuum oven at 30°C for two days.

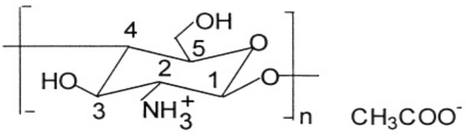
Results and discussion

Chitosan is practically insoluble in water and organic solvents due to its micelle structure, the close packing and the presence of several different types of hydrogen bonds. Chitosan gives water-soluble salts with acetic acid (Fig.1) and thus blends with PVP to form clear films. Their transparency is dependent on the polyblend composition.



Chitin

Chitosan



Chitosan acetate salt

Fig.1 The chemical structure of chitin, chitosan and chitosan acetate salt

The infrared spectra of pure PVP and chitosan have been obtained[12,13]. The main characteristic bands are the following:

3480cm^{-1} C$_6$-OH stretching band of chitosan
3447cm^{-1} C$_3$-OH stretching band of chitosan
3375cm^{-1} hydrogen bonding of amide
3264cm^{-1} N-H stretching band
1681cm^{-1} C=O stretching of PVP
1652cm^{-1} amide I band of chitosan
1558cm^{-1} amide II band of chitosan, overlaping with NH$_3^+$ band(1500cm^{-1})

The good identification of these peaks allows us to investigate the influence of chain-chain interaction between the polyblend on the basis of band positions and relative intensities.

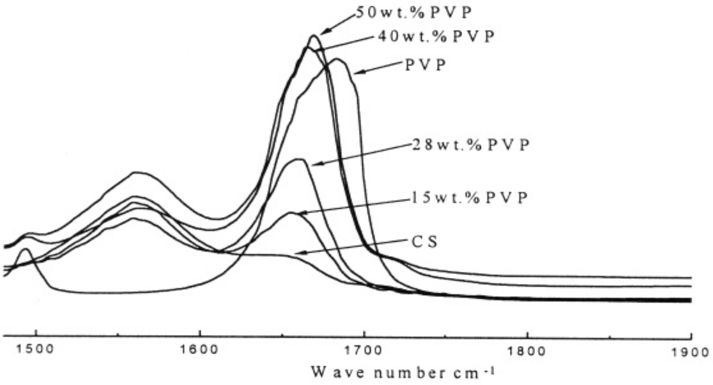


Fig.2 IR spectra of chitosan/PVP blends in region of 1300-1900cm^{-1}

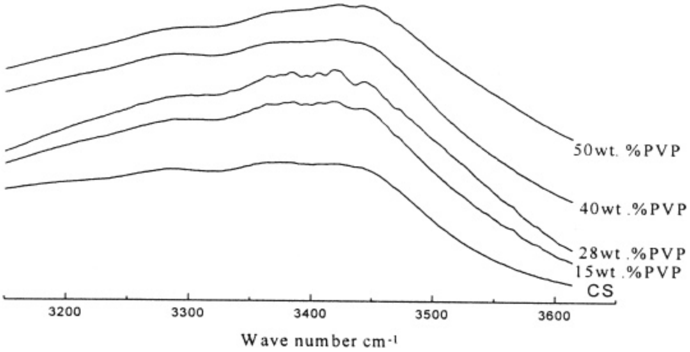


Fig.3 IR spectra of chitosan/PVP blends in region of 3150-3600cm^{-1}

The chain-chain interaction between two polymers can be deduced from the shifts of the vibration frequencies of the group involved in the hydrogen bonding, e.g., the frequencies of the PVP carbonyl (Fig.2) and those of the O-H bands of chitosan (Fig.3). When the PVP content increases, the carbonyl band shifts towards lower frequencies and finally overlaps with the amide I band, indicating that carbonyl of PVP takes part in hydrogen bonding with chitosan. With increasing the PVP content, strong NH_3^+ band overlapping with amide II band at 1558cm^{-1} exists in polyblends and has no obvious shift, indicating that the NH_3^+ does not participate the intermolecular bonding between chitosan and PVP. So the carbonyl of PVP should form hydrogen bonding with hydroxyl of chitosan. This result also proves that there is miscibility at a molecular level between two polymers, at least in some regions. The C-O stretching band of chitosan near 1100 cm^{-1} shifts steadily towards higher frequencies when the PVP content increasing (Fig.4). The possible explanation should be: in the pure chitosan film, the C-O-H groups involve in different types of self-associations; the C-O stretching frequency is lower than the frequency of a free C-O-H group. With the PVP incorporating into chitosan, many hydroxyl groups are involved in hydroxyl-carbonyl hydrogen bonding at the expense of hydroxyl-hydroxyl hydrogen bonding. As a result many oxygen atoms of C-OH are freed from hydrogen bonding. Meanwhile, a similar phenomenon may happen with the OH stretching band (Fig.3). These bands are usually assigned to the hydrogen-bonded hydroxyls. The splitting of the hydroxyl band of chitosan upon blending with PVP helps us to further insight into the interaction in the system. Since the bands in region of 3300-3500cm^{-1}are usually assigned to the inter- and intramolecular hydrogen bonding of hydroxyl groups, the occurrence of splitting in this region indicates that the carbonyl group of PVP take part in the hydrogen bonding with hydroxyl group and thus change the hydrogen bonding interaction results in matrix. This result correlate with pervaporation properties that the membrane performs high permeation with PVP added in chitosan to alternate the interaction in matrix. According to the splitting condition in Fig.3, it is supposed that there are existed the following forms of hydrogen bonding after blending with PVP (Fig.5): 1) hydroxyl groups associated by multiple hydrogen bonding in matrix, 2)hydroxyl groups whose proton is involved in hydrogen bonding with ca carbonyl group and an oxygen atom of another hydroxyl group, or with two carbonyl groups, 3)hydroxyl groups simply bonded to a carbonyl group.

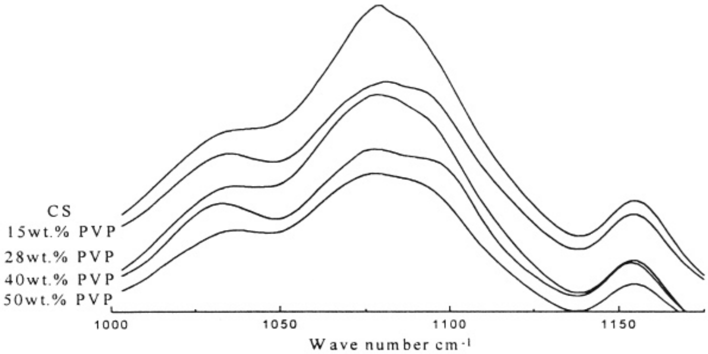


Fig.4 IR spectra of chitosan/PVP blends in region of 1000-1200cm^{-1}

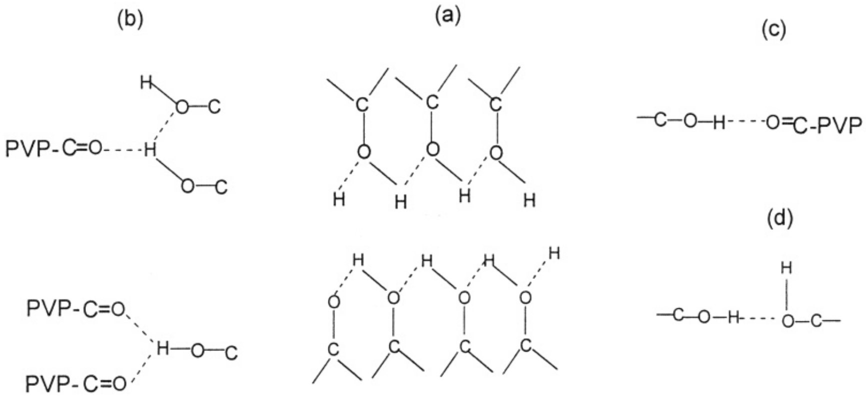


Fig.5 Different types of hydrogen bonding of hydroxyl groups of chitosan in the blends (a) Inter and intramolecular hydrogen bonding in matrix, (b) cross-interaction of hydroxyl group di-hydrogen bonded with two carbonyl groups or with one carbonyl and one oxygen atom of another hydroxyl group, (c) cross-interaction between a PVP carbonyl group and a chitosan hydroxyl group, (d) simple hydrogen bonding between two hydroxyl groups.

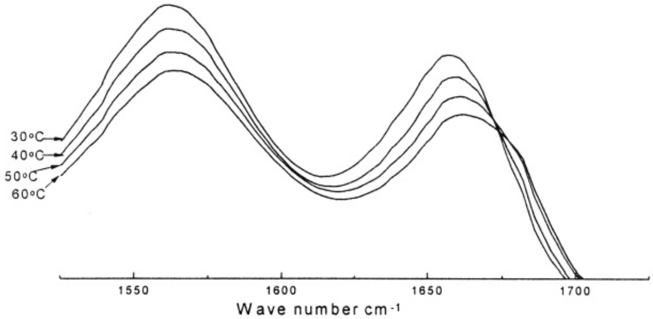


Fig.6 Influence of temperature on IR spectra of blend with 28wt.%PVP content in region of 1450-1700cm^{-1}

Additionally, it is also found that the blending membrane is sensitive to the temperature (Fig.5). When the temperature increasing from 30 to 60°C, it is the carbonyl band of the PVP, not the amide I band of chitosan because the amide II band and the amide hydrogen bonding (3375cm^{-1}) have no any shift, which shifts to higher frequencies. This phenomenon indicates that the hydrogen-carbonyl hydrogen bonding is reducing with improving the chain motion. In fact, with the temperature increasing, the changing of the peaks in 3000-3600cm^{-1} region also confirms the above conclusion (Fig.6). The peaks at 3264cm^{-1} and 3375cm^{-1} don't obviously change, but the relatively intensities of peaks at 3447cm^{-1} and 3480 cm^{-1} have some change. Generally these bands are assigned to hydroxyl groups associated by multiple hydrogen bonds with hydroxyl groups, carbonyl groups ect[8]. So this temperature dependence is indicative of bands that reflect conformational sensitivity and suggests that a significant rearrangement of bond structure may be taking place within the blending membranes. In fact, DSC results of blending membrane with 28wt.% PVP content showed that there

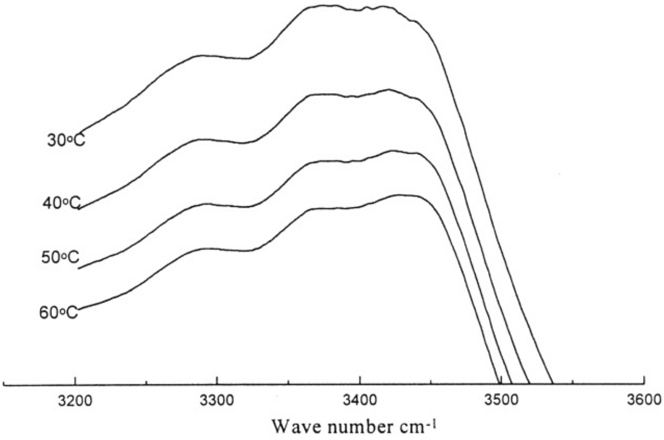


Fig.7 Influence of temperature on IR spectra of blend with 28wt.%PVP content in region of 3250-3500cm^{-1}

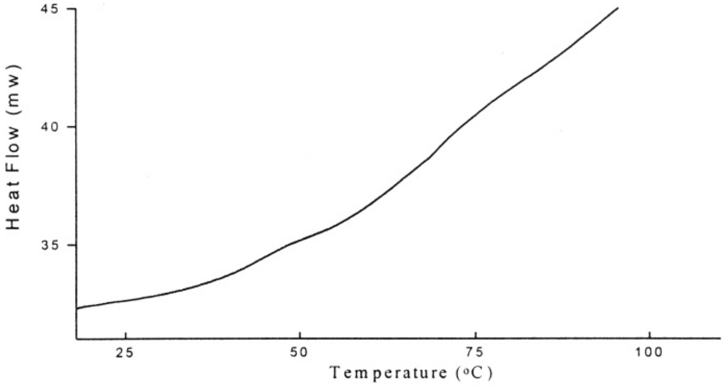


Fig.8 The DSC curves of blend membrane with 28wt.% PVP content

exited two second transition at 40.4°C and 56.2°C, respectively (Fig.7). Undoubtedly, these second transitions should contribute the chain conformational change during the temperature increasing and thus result in the interaction changing.

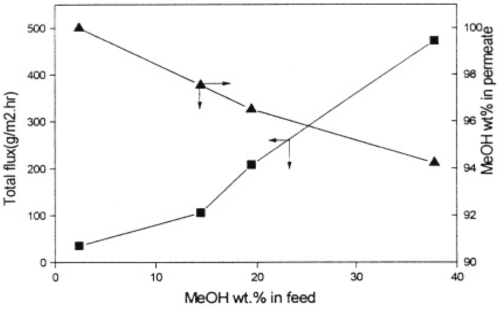


Fig.9 The pervaporation properties of blend membrane with 28wt.%PVP content

The above mentioned showed that the structure of membrane has been changed after the PVP added in matrix, particularly the hydrogen bonding forms. The blending membrane with 28wt.%PVP content was evaluated for separation of MeOH from MTBE. The pervaporation results are given in Fig.9 as function of the MeOH content in feed. It is shown that the blend membrane performed good permeability, especially compared with chitosan(almost no permeation). The possible explanation should be that the blending changed the rigid chain and close packing structure in membrane. Meanwhile, the carbonyl groups of PVP also form hydrogen bonding with MeOH in feed and thus act on sorption sites in pervaporation process. As a result, the blend membrane showed MeOH preferential permeation.

Acknowledgements This work was supported by Natural Science Foundation of China. The authors also thank Dr.Zhang Shimin for helpful discussions.

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