

EFFECTS OF BLENDING CHITOSAN WITH PEG ON SURFACE MORPHOLOGY, CRYSTALLIZATION AND THERMAL PROPERTIES*

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Abstract Biodegradable blend films composed of chitosan and PEG with various composition ratios were prepared. The chemical structure of the blend films was characterized with FTIR and X-ray, which showed no chemical bond formations but certain interactions probably coming from the hydrogen bonds. Morphologies of these blend films were viewed using AFM and SEM, suggesting that pure chitosan film had a smooth surface structure and the blend films surface showed a plenty of holes with varying size. Through the DMA measurement, it was found that there existed differences in the peak area and position of the blend films, and the peak at the glass transition temperature became significantly weaker and was markedly wider with the increasing content of PEG. The obtained results showed that the crystallinity of chitosan was suppressed and partially destroyed; and this should have an influence on the thermal behaviors and dynamic mechanical properties of the blend films.

Keywords: Chitosan; Poly(ethylene glycol); Blend; Film.

INTRODUCTION

Chitosan [β -(1,4)-2-amino-2-deoxy-D-glucopyranose] is a natural polymer derived by deacetylation of chitin, which is the second most abundant biopolymer in nature next to cellulose^[1]. Compared with other polysaccharides, chitosan has several important advantages, including biocompatibility, biodegradability, no toxicity, good film-forming characteristics and excellent chemical-resistant properties. So, chitosan has been widely studied for use in clinics^[2], drug delivery systems^[3], solid polyelectrolytes^[4], surfactants^[5] and membranes on ultrafiltration, reverse osmosis and evaporation^[6].

However, its mechanical properties and other physical/chemical properties are not good enough to meet this wide range of applications. Incorporation with other natural or synthetic polymers is an effective approach for improving the physical/chemical properties of chitosan through the amino groups and hydroxyl groups on its backbone, including blending chitosan with other polymers^[7–9], introducing cross-linking structure to the membrane^[10, 11] and developing organic-inorganic hybrid membrane^[12]. Polymer blends have shown favorable results in terms of the targeted biological, mechanical or degradation properties in comparison to the individual components. Various reagents, including polycaprolactone^[13], polylactide^[14], poly(vinylpyrrolidone) (PVP)^[15], 3-(aminopropyl)siloxane oligomers (pAPS)^[16] and plasticizers^[17], *etc.* have been used to blend with chitosan. Among all the alternatives, poly(ethylene glycol) (PEG) is of particular interest owing to its useful properties such as low toxicity, immunogenicity, biocompatible and biodegradable performance. Alexeev *et al.* found the

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significant improvement in mechanical properties of chitosan upon blending with PEG^[18, 19]. Zhang *et al.* reported chitosan-PEG blend films had improved protein adsorption and cell growth^[20]. Kolhe concluded that PEG-blending is a more efficient way to improve ductility of chitosan than the copolymerization with PEG^[21].

The subject of this study is to investigate the molecular interaction between chitosan and PEG and variations generated by blending in crystal structure, surface morphology and thermal behaviors of the chitosan-PEG blend film. With this aim, a series of samples with different blending ratio of chitosan to PEG were prepared by solvent-blending, and then the resultants were systematically characterized by XRD, AFM, SEM, DSC and DMA measurements.

MATERIALS AND METHODS

Materials

Chitosan, degree of deacetylation (DD) $\geq 93\%$, viscosity < 0.1 Pa·s, was a product of Fluka. Pure PEG with $M_w = 1.0 \times 10^4$ was purchased from Tianjin Kermel Chemical Reagent Co., Ltd.

Sample Preparation

Appropriate amounts of chitosan and PEG were dissolved in a 2% solution of glacial acetic acid in water to obtain a 4% solution of blend. The solution was stirred for 0.5 h to obtain a clear solution and centrifuged at a speed of 5000 r/min for 30 min at 25°C to remove the air bubbles. Approximately 25 mL of this solution was added in a Petri dish, and a uniform gel was obtained. This gel was allowed to dry for 5 days and washed with ethanol and water to remove excess acetic acid. The resulting films had uniform thickness ranging from 13 μm to 25 μm . The compositions of blends (CS/PEG) employed subsequently were 8/2, 7/3, 6/4, and 5/5, respectively. The samples for AFM measurements were prepared on the newly cleaned silicon wafer.

Film Characterization

IR spectra were collected with a TENSOR 27 FTIR spectrometer (Bruker) in absorption mode with 32 scans at a resolution of 2 cm^{-1} intervals. An X-ray diffractometer (XRD, Bruker, D8) was used to inspect the diffractograms of the blend films at 25°C. The X-ray source was Ni-filtered Cu K α radiation (30 kV, 30 mA). The dry films were mounted on aluminum frames and scanned at a speed of 0.5 ($^\circ$)/min from 5° to 40° (2 θ). Surface analysis of films was done by atomic force microscopy (AFM) using a DI Nanoscope IIIA Multimode Scanning Probe Microscope (Digital Instruments, Veeco Metrology Group, Santa Barbara, CA) at ambient conditions. Topographic images were obtained in tapping mode using commercial silicon microcantilever probes (M1, Nanotools, Germany) with a tip radius of *ca.* 10 nm and spring constant *ca.* 42 N/m. The samples were coated with gold, and the cross-sections of the samples were viewed using a scanning electron microscope (SEM, Japan, JSM-5600LV) with an accelerating voltage of 25 kV. Differential scanning calorimetry (DSC) measurements were carried out on DSC Q100 (TA Instruments). Dynamic mechanical analysis (DMA) measurements were conducted to obtain the curve of stress-strain and observe T_g of the blend films. The storage modulus E' , loss modulus E'' and mechanical damping tangent ($\tan\delta$) of the blend films were recorded on a dynamic mechanical analyzer (DMA Q800, TA Instruments) from 30°C to 300°C at a frequency of 1 Hz and a heating rate of 3 K/min.

RESULTS AND DISCUSSION

FTIR Characterization

The infrared data of pure chitosan and the blend films in certain frequency ranges are displayed in Fig. 1. The typical absorption peaks of the functional groups presented in chitosan^[22] were also observed in all of the blend interferograms with varying intensities based on their composition. On the other hand, with increasing content of PEG, most of the characteristic peaks of PEG (1468, 1281, 1096, 963 and 841 cm^{-1})^[21] become more distinguishable compared to the pure chitosan spectrum. Since no appearance of new peaks or disappearance of peaks of individual components, it means that there was no chemical reaction between chitosan and PEG.

However, with increasing content of PEG, the O—H stretching vibrations (3184 cm^{-1}) and amide I band (1636 cm^{-1}) from chitosan were shifted to low wavenumbers. Depending on the blend ratios, the 3184 cm^{-1} band could shift 1 to 8 cm^{-1} , while the amide I band would shift 3 to 10 cm^{-1} . Furthermore, C—O stretching vibration from C—O—H of chitosan (1151 cm^{-1}) was shifted to low wavenumber by 3 to 4 cm^{-1} . All these imply the existence of an attractive intermolecular interaction between chitosan and PEG, as suggested in the literature^[23]. It is known that the chemical structure of chitosan is very similar to cellulose with ample of side hydroxyl on the 3 and 6 locations, and is abundant of C—O groups and two end hydroxyl. Hence, the intermolecular interaction between chitosan and PEG should be ascribed to the hydrogen bond. Namely, it is the hydrogen bond interaction between chitosan and PEG that leads O—H stretching vibrations and amide I band from chitosan to shift to lower wavenumbers.

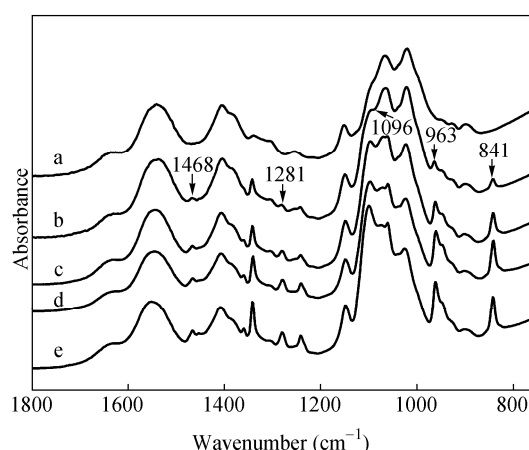


Fig. 1 FTIR spectra for chitosan and blend films with different mass ratios
a) Chitosan; b) CS/PEG (8/2); c) CS/PEG (7/3); d) CS/PEG (6/4); e) CS/PEG (5/5)

X-ray Diffraction

WAXD analyses were used to follow the evolution of structure for chitosan and PEG and the results were given in Fig. 2. The corresponding readable diffraction angles (2θ) matched with those of chitosan, and the calculated crystallinity is listed in Table 1. As indicated, pure chitosan diffractograms showed a strong reflection at 8.75° , 11.87° and 18.67° associated with the crystalline regions. With increasing content of PEG, the reflections for PEG (19.5° , 23.4° , 26.38° , 32.82° and 36.54°) in the blends are enhanced gradually. Conversely, the reflections for chitosan are diminished, and the crystallinity is decreased compared to that of pure chitosan film. For the 5/5-blend film, the reflections for chitosan are significantly weaker with a very low crystallinity of about 4.34%. It is suggested that not only the stiff chitosan chain inhibits the crystallization of PEG, but also the hydrogen bond interaction between chitosan and PEG restrains the movement of chitosan molecules and even partially destroys the original crystalline structure of chitosan, and consequently decreases chitosan crystallization upon blending.

Table 1. Diffraction angle and crystallinity of membranes

Sample	Peak I ($^\circ$)	Peak II ($^\circ$)	Peak III ($^\circ$)	X_c (%)
Chitosan (CS)	8.75	11.87	18.67	28.96
CS/PEG = 8/2	8.85	12.04	18.89	17.47
CS/PEG = 7/3	8.57	11.7	18.55	19.05
CS/PEG = 6/4	8.71	11.83	18.75	11.29
CS/PEG = 5/5	8.91	12.07	—	4.34

— No readable crystalline peak because of being covered by that of PEG

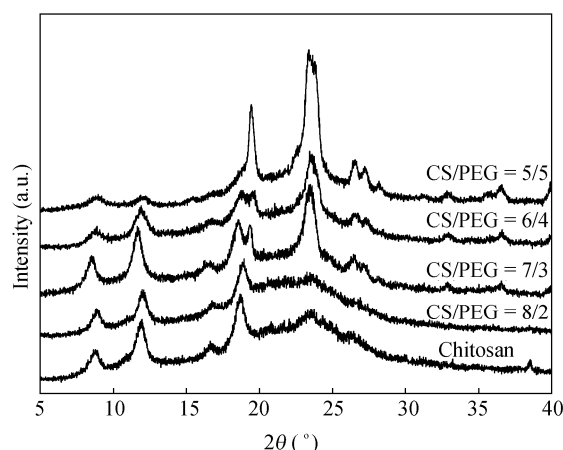
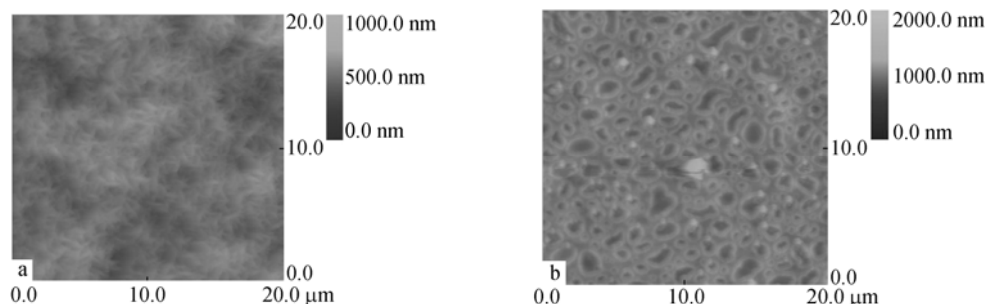


Fig. 2 X-ray diffraction pattern of membranes prepared with pure chitosan, CS and CS/PEG blends with different blending mass ratios (CS/PEG = 8/2, 7/3, 6/4 and 5/5) indicating on the side of each curve

Morphology Characterizations

AFM is used to examine the surface structure of the samples, and the corresponding images are presented in Fig. 3. It is well known that chitosan molecules are quite rigid, the condition of sample preparation normally has marked effect on crystallization. For this reason, chitosan film could present branch crystals, spherulites and so on^[24]. Since both chitosan and PEG are crystalline polymers, they may interact with each other in a certain manner so that the original crystalline structures of each component have been disturbed or partially damaged to a different extent, leading to various crystalline structures of the blend films. Pure chitosan film appeared as slender acicular structure dispersed homogeneously (Fig. 3a). With the addition of PEG, the surface structure changed markedly. When the PEG contents become lower, such as the case of the film with blend ratio of 7:3, besides the chitosan crystal structure, PEG spherulites could be also resolved. When the content of PEG was up to certain extent (such as 5:5 in this case), PEG became a key influencing factor due to the crystal nature of PEG and to the effect of chitosan on PEG. Consequently, the blend film showed fine spherical particles structure. The samples even possessed irregular hole structure with the incorporation of PEG (Figs. 3b, 3d). To corroborate the above AFM observations, SEM was used to further observe the surface morphology of the blend films, and the results are showed in Fig. 4. The surface of chitosan appeared more smooth and uniform, the result is coincident with the literature^[13] and with the above AFM results (SEM image was not given). With the addition of PEG, the surface of blend films displayed some irregular holes. This result is in well agreement with that obtained by AFM analysis. The aperture is approximately 2 μm in the 8/2 and 5/5 blend films, and smaller aperture in samples of 7/3 and 6/4 (see Figs. 4a–4d). We speculated that the reason behind this observation would be that when PEG was added to chitosan matrix, the two phases of chitosan and PEG displayed a trend of self-gathering during solution volatilization due to the limited compatibility. As a result of migration, many holes were generated on the surface of blend films.



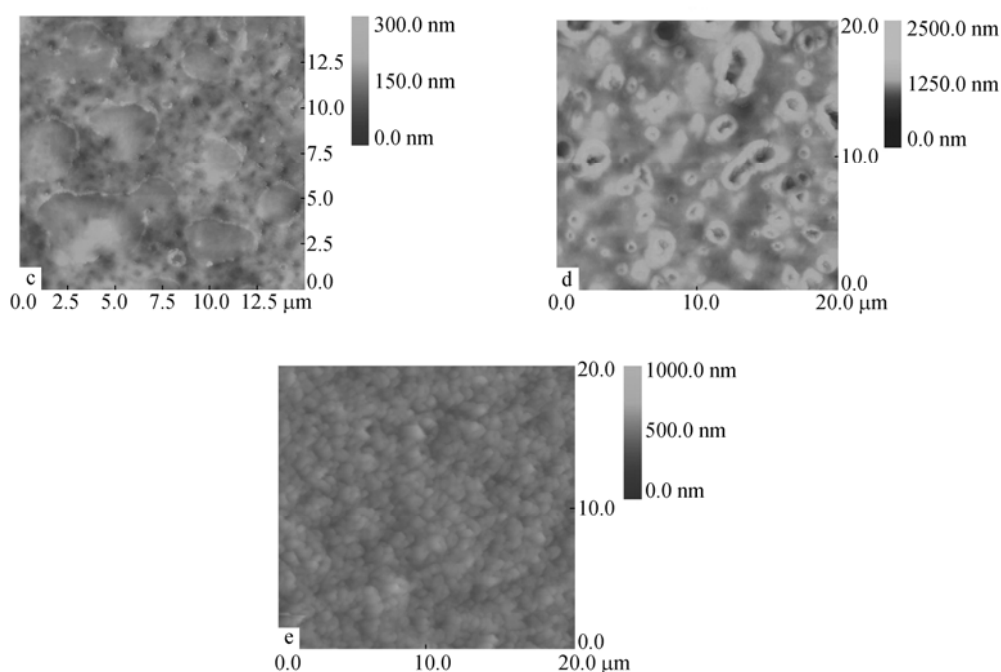


Fig. 3 AFM results that showed the effect of blending on surface morphology of membranes
Topographic images obtained in tapping mode using commercial silicon microcantilever probes at a scan rate of 1 Hz;
a) Chitosan; b) CS/PEG (8/2/); c) CS/PEG (7/3); d) CS/PEG (6/4); e) CS/PEG (5/5)

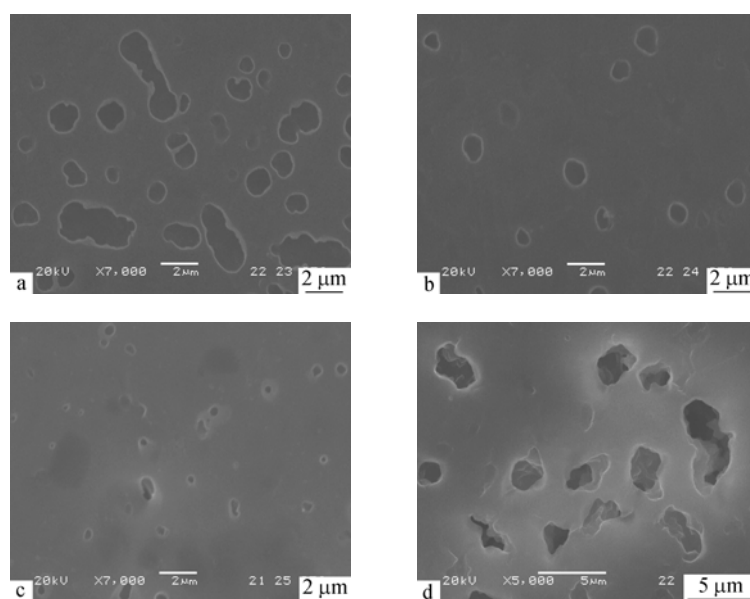


Fig. 4 SEM images that showed the effect of blending on surface morphology of membranes
a) CS/PEG (8/2/); b) CS/PEG (7/3/); c) CS/PEG (6/4/); d) CS/PEG (5/5/)

Thermal Behaviors

To get more insight on the thermal behavior of the blend samples, DSC measurements were performed and the results are shown in Fig. 5. For well resolution the curves were exhibited in two separate temperature ranges: one was 35–75°C, and the other was 80–160°C. The peak at around 60°C for blend films can be assigned to the

melting point of PEG (Fig. 5a). The melt peak of PEG became more obvious and moved to high temperatures with the increasing content of PEG (8/2 is read at 53.7°C, 7/3 is read at 55.2°C, 6/4 is read at 55.7°C, 5/5 is read at 57.1°C, pure PEG is read at 63.2°C). It is generally accepted that the T_m corresponding to one component of the blend films would decrease owing to the increasing of lattice defects resulted from the partial miscibility of the noncrystalline phase^[14]. There are two peaks at around 100°C with a narrow temperature interval in the curves of pure chitosan and blend films (Fig. 5b). The peaks for pure chitosan are read at around 107°C and 125°C. With more content of PEG, one of the peaks for blend films is shifted to the lower temperature region, and the another one is shifted to the higher temperature region. It is reported that the two peaks are probably attributed to solvent because the films contain acetic acid, residual water, bound moisture, and so on^[14, 17].

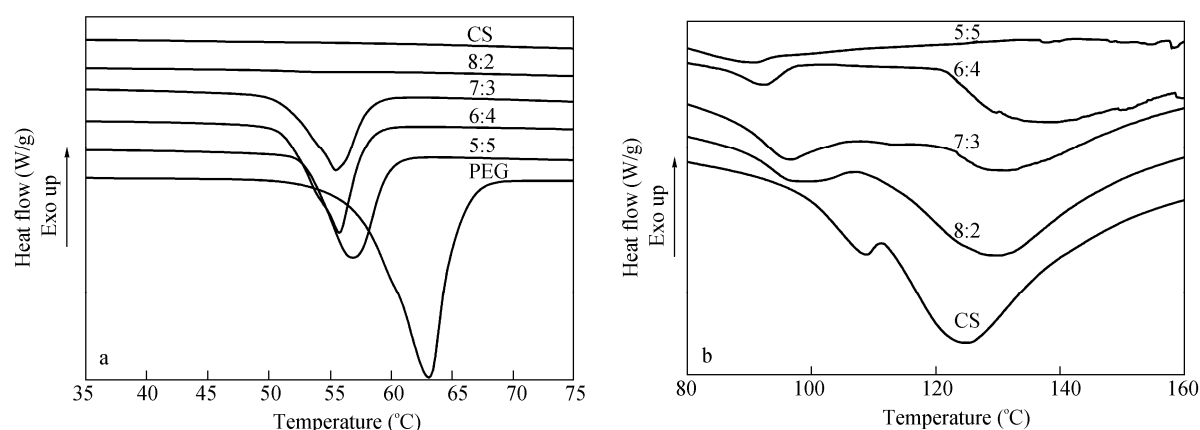


Fig. 5 DSC traces obtained by heating samples from 0°C to 180°C at a heating rate of 10 K/min under a nitrogen atmosphere
a) 35°C–75°C; b) 80°C–160°C

To eliminate the effects from solvent, numerous studies on the thermal properties of chitosan used a quench technique *via* DSC scanning^[25, 26]. Pure chitosan and blend samples, therefore, were heated from 0°C at a rate of 10 K/min up to 180°C and then cooled to room temperature at the same rate under nitrogen atmosphere in the first heating run, and then, the samples were reheated again at the same rate until 250°C. A thus-obtained DSC curve for chitosan in the second heating run is presented in Fig. 6. Several reports measured the glass transition temperature T_g of chitosan by DSC secondary scanning; but no consistent results were obtained^[25, 27–29]. In fact, the glass transition temperature of chitosan is still a subject of controversy. The main reason may be that, being a natural polymer, some properties like crystallinity, molecular weight and deacetylation degree, can present wide variations according to the source and/or method of extraction and will influence the T_g . In our case, there is no obviously readable T_g for chitosan in DSC curve. The only peak is at near 200°C and no significant changes are observed after blending. Boyal *et al.* suggested that a possible kind of transition, named the liquid-liquid transition, in a polymer which is being exposed to a thermal environment at a temperature higher than its T_g , corresponds to the motion of very long chain segments or even the whole chain from imaginary liquid to the real liquid^[30]. In addition, the decomposition temperatures of the pure chitosan and blend films were detected by DSC. In this case, all the samples were heated from 0°C at a rate of 10 K/min up to 350°C, and the results are displayed in Fig. 7. The main event of these calorimetric curves is an exothermic peak at *ca.* 270°C, owing to the degradation of the main chain. The peak of pure chitosan is read at *ca.* 274°C. With the adding of PEG, this exothermic peak would shift to the high temperature region (8/2 is read at 275°C, 7/3 is read at 292°C). However, with more content of PEG, this peak will shift to lower temperature due to the low compatibility at the high content of PEG. Thus, PEG in appropriate content will increase the thermal stability of the chitosan film.

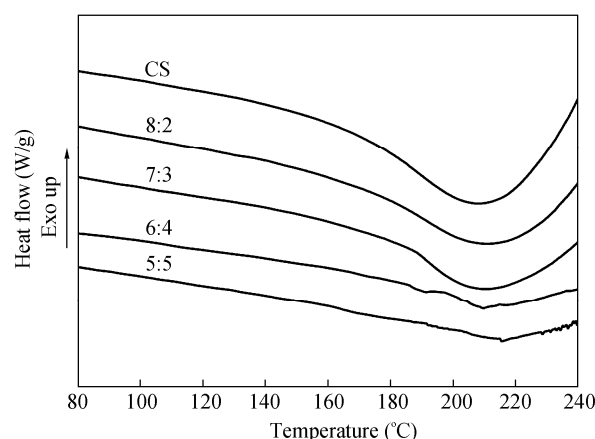


Fig. 6 DSC thermograms of pure chitosan and blend membranes obtained from the second heating. Membranes were heated from 0°C at a rate of 10 K/min up to 180°C and cooled to room temperature, and then, reheated again at the same rate until 250°C

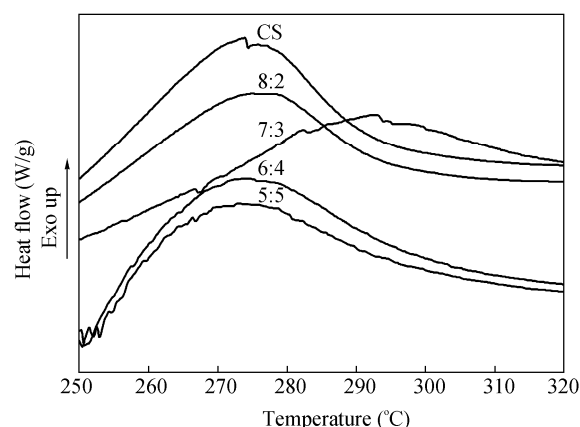


Fig. 7 DSC thermograms of pure chitosan and blend membranes from 0°C at a rate of 10 K/min up to 350°C

It is known that chitosan is a semicrystalline polymer due to its strong intramolecular hydrogen bonds on the backbone, and it also has a rigid amorphous phase because of its heterocyclic units. As a result, upon heating within a certain range of temperature below its decomposition temperature, the variations in heat capacity corresponding to the change in specific volume near T_g is probably too small to be detected by the DSC technique. To further investigate the thermal behaviors of the films, the more sensitive, DMA technique is therefore employed.

Dynamic Mechanical Properties

In principle, both loss modulus (E'') and mechanical damping tangent ($\tan\delta$) in the DMA measurements can be used to measure the characteristic temperatures matched with various relaxation processes, even though a very small quantitative difference may be frequently found between the temperature values determined by E'' or $\tan\delta$ ^[31–33]. Since the peaks recorded in the plots of $\tan\delta$ seem to be more clearly and easily located, $\tan\delta$ will be primarily used in the present case. Figure 8 displays $\tan\delta$ as a function of temperature for the pure chitosan and blend films. Three peaks registered at around 103, 158, and 269°C are observed for pure chitosan. Although

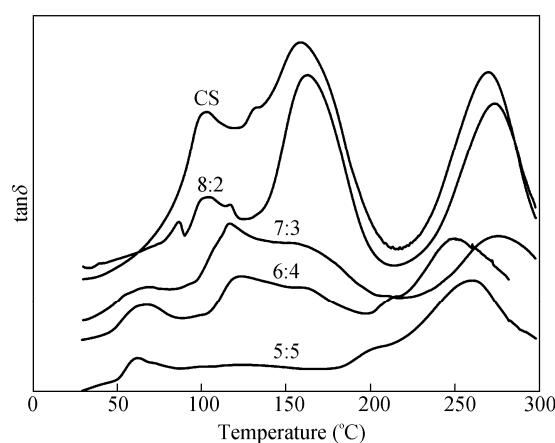


Fig. 8 Dynamic mechanical properties (damping tangent ($\tan\delta$) as a function of temperature) of chitosan/PEG blend membranes by DMA. Membranes were heated from 30°C to 300°C at a rate of 3 K/min and an oscillating frequency of 1 Hz.

there is no agreement point on the T_g of chitosan, the results are concentrated on a range from 130°C to 203°C. The peak recorded at around 158°C should be ascribed to the α -relaxation of chitosan, corresponding to its T_g in our study. Another $\tan\delta$ at 103°C (β -relaxation) may be caused by partial acetamide groups attached to the C-2 position in the chitosan backbone. The third observed event at around 269°C should correspond to an exothermic peak possibly linked to the decomposition procedure.

Four relaxation peaks for the 8/2 blend film registered at about 86, 104, 162 and 273°C are observed. In comparison with the results of pure chitosan, the peaks at 104, 162, and 273°C should correspond to those of the chitosan component with a slight shift. According to our complementary results by DSC analysis, PEG will melt at around 63°C. Therefore, the peak at around 86°C should be ascribed to a sort of possible solid-solid transition between PEG and chitosan^[34]. The reason for this observation could be that the intermolecular interactions coming from the hydrogen bonds between the two components restrained and hindered the translation of the melting PEG in the blend. As a consequence, the composition displayed solid behavior at higher temperature. A similar behavior was also observed in the case of the 7/3, 6/4, and 5/5 blend films. However, differences in the peak area and position could be found. With increasing the content of PEG, the peak temperature recorded at around 86°C moved to a lower temperature region. The possible reason is that, with the increasing content of PEG, the solid-solid transition temperature is closer to the melting temperature of PEG. In addition, the peak temperatures at around 160°C for the blend films that corresponding to the T_g of chitosan became significantly weaker and is markedly wider. In fact, the interactions between chitosan and PEG restrained and hindered the movement of chitosan molecules and destroyed orderliness of molecular chains, so that chitosan crystallinity was suppressed. At the same time, with increasing of PEG and the decreasing of chitosan, the latter was “diluted” by the former, which would increase the movement mode and space of chitosan molecules. With addition of PEG, the variation of the decomposition temperature is in good agreement with the above DSC result, namely, the decomposition temperature is the highest when the blend ratio was up to 7:3. Moreover, as well revealed in Fig. 8, the peak temperature for the 5/5 blend film at around 104°C became significantly weaker because the movement intensity of the amide groups decreases with the decreasing content of chitosan.

The strain dependence of the stress for the blend films is illustrated in Fig. 9. As indicated, the slopes of these curves decrease with increasing PEG content, suggesting the reduced stiffness and the improved ductility for the samples. In fact, due to its rigid structure originated from the strong intramolecular bond force, when the chitosan is effectively blended with PEG, the original crystalline structure of chitosan and PEG could have been seriously destroyed, and as a consequence, the blend films obtain a partially miscible structure with more amorphous domains due to the interactions between chitosan and PEG.

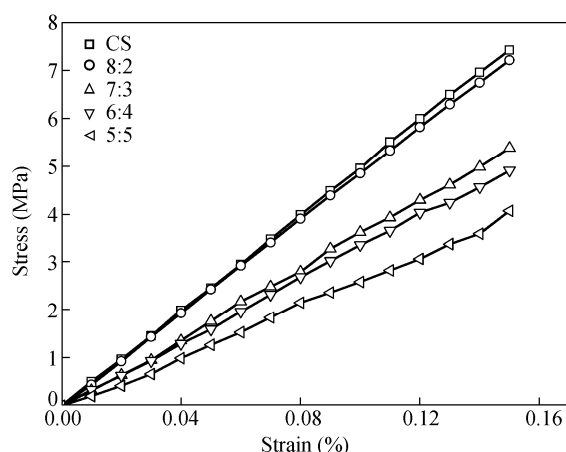


Fig. 9 Strain dependence of stress performed at room temperature on dry films at oscillating frequency of 1 Hz
Blending mass ratios (CS/PEG): 10/0; 8/2; 7/3; 6/4 and 5/5

CONCLUSIONS

Biodegradable blend films composed of chitosan and PEG with various composition ratios were prepared. Molecular interactions and surface morphology were characterized using FTIR spectroscopy, X-ray diffraction, atomic force microscopy (AFM) and scanning electron microscopy (SEM), respectively. Thermal behaviors were analyzed by differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA). Our results suggest the following: (i) No chemical reaction occurred between chitosan and PEG, although there exist interactions that probably come from hydrogen bonds. (ii) With the increasing content of PEG, the crystal structures of the blend films change from slender acicular structure to fine spherical particles structure; the surface microstructure of blend films would change from the smooth and featureless one to the surface morphology filled with holes with varying size. (iii) With increasing the content of PEG, the differences in the peak area and position of the blend films become significantly weaker, while the peak at the glass transition temperature becomes markedly wider. (iv) Comparing with the high brittleness and hardness of pure chitosan, the ductility of the blend films is tremendously improved due to the reduced crystallinity of chitosan.

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