

THE STRUCTURE AND PROPERTIES OF CHITOSAN/POLYETHYLENE GLYCOL/SILICA TERNARY HYBRID ORGANIC-INORGANIC FILMS*

Rui Song^{a**}, Rui Xue^a, Ling-hao He^a, Ying Liu^a and Qiao-ling Xiao^b

^a Henan Provincial Key Laboratory of Surface & Interface Science, Zhengzhou University of Light Industry, Zhengzhou 450002, China

^b College of Chemistry and Chemical Engineering, Graduate University of Chinese Academy of Sciences, Beijing 100049, China

Abstract The ternary hybrid films consisting of chitosan (CS), polyethylene glycol (PEG) and nano-sized silica which was surface-modified by amino groups (RNSA) were prepared. The structures of the blend membranes were characterized by attenuation total reflection-infrared spectroscopy (ATR-IR), X-ray diffraction (XRD), optical microscopy (OM) and differential scanning calorimetry (DSC). The results showed that the addition of silica affected not only the distribution and crystallinity of PEG on the sample surface, but also the phase coarseness and the crystalline structure of chitosan in the blend system. Moreover, PEG changed the crystalline structure of chitosan. Upon annealing (at 100°C for 1 h), the blends would show the altered crystalline structure of chitosan, the reinforced phase coarseness, as well as the decreased miscibility and interaction between chitosan and PEG.

Keywords: Chitosan; Poly(ethylene glycol); Silica; Annealing.

INTRODUCTION

Chitosan is a polycation derived from chitin, a natural polysaccharide usually obtained from carapaces of the marine crustaceans such as crabs and shrimps^[1]. Chitosan has amino groups and hydroxyl groups on its backbone, which on one hand makes chitosan itself hydrophilic and on the other hand brings chitosan a polycationic property. Several studies have indicated that chitosan has some important advantages^[1–9], such as biodegradation, antibiosis, biocompatibility, non-toxicity, good film-forming characters and excellent chemical-resistant properties which allow its use in many areas such as in clinics^[2], drug delivery systems^[3], solid polyelectrolytes^[4], surfactants^[5], membranes for ultra-filtration, reverse osmosis and evaporation^[6].

Owing to its functional properties, chitosan has been widely investigated for the last two decades on industrial and biomedical applications, which is expected to be useful in the development of composite materials such as blends or hybrids with other polymers and inorganic nanoparticles. Specially, blends with other polymers such as polycaprolactone^[10], poly(vinylpyrrolidone) (PVP)^[11], DNA^[12], nylon^[13], polyethylene glycol (PEG)^[14–17], starch^[18], pullulan^[18], poly(vinyl alcohol) (PVA)^[19–22] *et al.* have shown favorable properties, which are recognized as materials supporting chitosan to obtain material with sufficient mechanical strength of prepared films and fibers. Some researches about the compatibility and interaction between the components have been reported. Among all the alternatives, poly(ethylene glycol) (PEG) is of particular interest owing to its useful properties such as low toxicity, immunogenicity, biocompatibility and biodegradability. Alexeev *et al.* found significant improvement in mechanical properties of chitosan blending with PEG^[15, 16]. Kolhe concluded

* This work was partially subsidized by Henan Innovation Project for University Prominent Research Talents (“HAIPURT”) program.

** Corresponding author: Rui Song (宋锐), E-mail: rsong@gucas.ac.cn

Received June 20, 2007; Revised August 23, 2007; Accepted September 17, 2007

that blending was a more efficient way to improve ductility of chitosan. For blend consisting of PEG and chitosan which was supposed to be the partially miscible blend, the improvement of blend in compatibility and properties is dependent on 'well-dispersion', crystallinity of PEG as well as phase coarsening and intermolecular interactions^[14]. However, the influences on crystal properties of each other have not well been understood. In addition, hybridizing with inorganic nanoparticles such as silica^[23–27] or carbon nanotube (CNT)^[28] was usually considered to be an effective method to improve the properties of materials by interaction with components. However, the influence of inorganic nanoparticles on blends had been investigated scarcely. Since the properties of films were settled by factors such as crystalline structures of ingredients, morphologies of films and molecular interactions, the investigation about the influences of inorganic nanoparticles on these properties will be highly necessary.

The objective of this investigation was to explore the effects of silica on the chitosan/PEG blend films, including dispersion and crystal properties of PEG as well as phase separation and coarsening. Besides the miscibility and interaction between chitosan and PEG, the influence of silica on the process of annealing was also investigated in order to understand the interaction involved.

EXPERIMENTAL

Materials

Chitosan with a degree of deacetylation of 93% was received from Shanghai Reagent Company, China. PEG ($M_w = 10000$) was received from Tianjin Chemical Reagent Company, China. Silica with surface modified by amino groups and with diameter of *ca.* 20 nm (RNSA hereinafter), was supplied by Prof. Z.J. Zhang in Henan University, China.

Preparation of Hybrid Membranes

Chitosan was dissolved in 2 vol% aqueous acetic acid solution at a concentration of 2 wt%. Appropriate amount of PEG and RNSA were added to the solution, and the mixture was thoroughly stirred until there was no air bubble in the solution. Films were obtained by casting solution on a glass dish and allowing the solvent to evaporate at 40°C. To check the annealing effect, all samples were treated at 100°C under vacuum for 1 h, and then cooled down to room temperature in the vacuum.

Characterizations

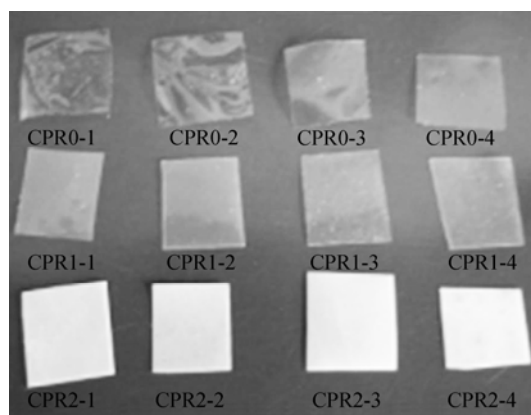
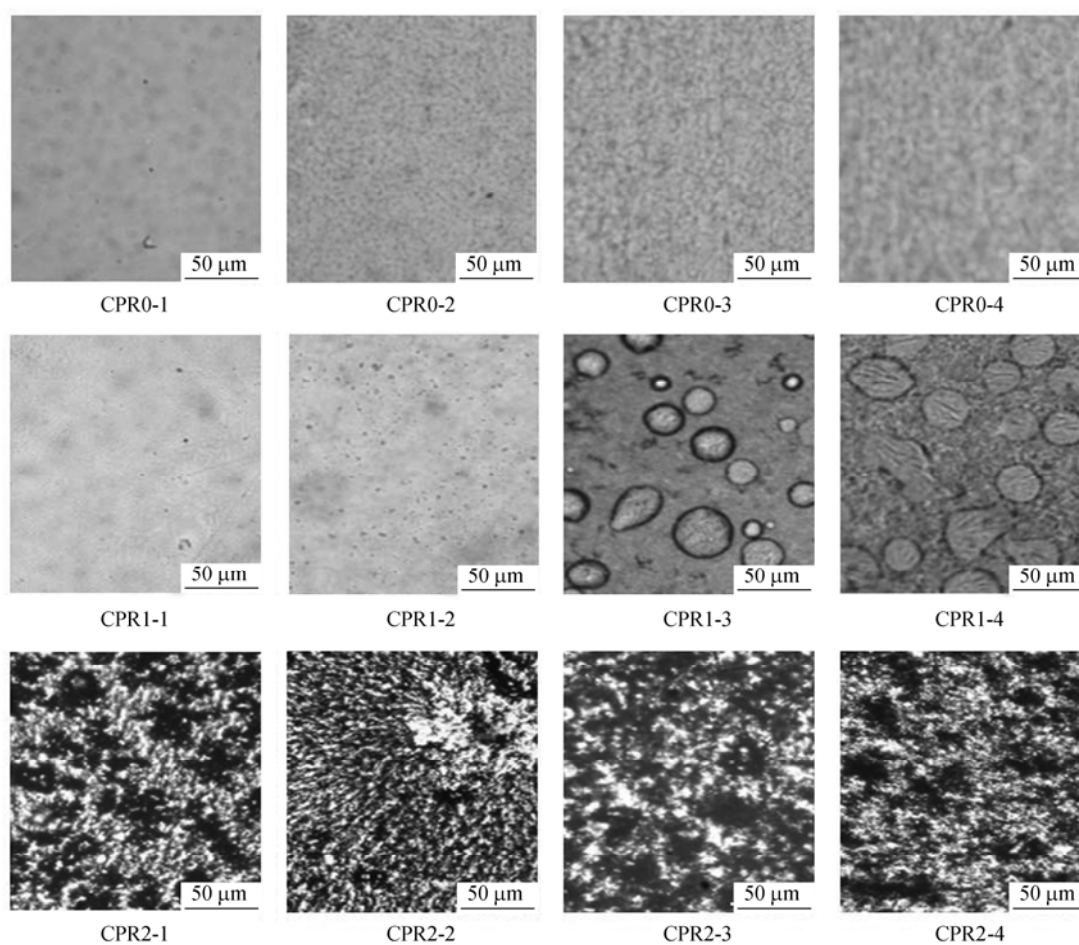
Attenuation total reflection-infrared spectra (ATR-IR Bruker-TENSOR 27) were used to probe surface character of films. For all the measurements, the spectra were obtained with 32 scans at a resolution of 2 cm⁻¹ interval. An optical microscope (OM, Nikon, E600POL) was used to acquire the morphology and phase coarsening of the samples. TA Instruments Q100 was used to perform differential scanning calorimetry (DSC) analysis. About 5 mg of samples were sealed in aluminum pans. After samples were cooled to 0°C and maintained at the temperature for about 1 min, DSC curves of all samples were collected during heating from 0°C to 100°C at a speed of 10 K/min. Prior to DSC runs, the temperature and heat transition of the instrument were calibrated with indium and zinc standards. A continuous nitrogen flow (20 mL/min) was maintained during the DSC scan. An X-ray diffractometer (XRD, Bruker, D8) was used to inspect the diffractograms of the blend membranes at 25°C. The X-ray source was Ni-filtered CuK α radiation (30 kV and 30 mA). The dry membranes were mounted on aluminum frames and scanned at a speed of 0.5 (°)/min from 5° to 40° (2 θ).

RESULTS AND DISCUSSIONS

Table 1 shows the different compositions investigated, here all the compositions are expressed as weight ratios, and the corresponding appearances of all samples are shown in Fig. 1. Pure chitosan film was transparent, and blending with RNSA and PEG would decrease the transparence of films since RNSA as opaque inorganic particles could weaken the transparence of films. PEG as an organic polymer also could impact the transparence of films by interaction with chitosan, *i.e.*, initial incorporation of PEG decreased the transparence a little; upon double the PEG loading, the films became non-transparent. The variation presented in the appearance

Table 1. Compositions of the prepared hybrid films

CPR0	CS/PEG/RNSA	CPR1	CS/PEG/RNSA	CPR2	CS/PEG/RNSA
CPR0-1	1/0/0	CPR1-1	1/0.2/0	CPR2-1	1/0.4/0
CPR0-2	1/0/0.05	CPR1-2	1/0.2/0.05	CPR2-2	1/0.4/0.05
CPR0-3	1/0/0.1	CPR1-3	1/0.2/0.1	CPR2-3	1/0.4/0.1
CPR0-4	1/0/0.2	CPR1-4	1/0.2/0.2	CPR2-4	1/0.4/0.2

**Fig. 1** The appearance of all samples**Fig. 2** Optical microscope results of the hybrid films

could be viewed as the competition between two processes. (1) Chitosan could interact with PEG through hydrogen bonding. (2) Phase separation due to the limited compatibility between chitosan and PEG could be observed for a wide range of compositions.

Optical Microscope (OM) Observations

The optical microscope (OM) observations are shown in Fig. 2. For all samples, no trace of RNSA particles was found, which implied the homogeneous distribution and no aggregation of RNSA in the films.

Homogeneous phase morphology was generally observed in group CPR0 and samples CPR1-1, CPR1-2; however, coarsening of morphology was seen in samples CPR1-3, CPR1-4 (Fig. 2). That means phase coarsening was reinforced by adding adequate RNSA in the samples. According to the point of Kolhe, coarsening of morphology implied that the occurrence of phase separation^[14]. So in this case RNSA particles would promote this process.

More complex structures were observed in group CPR2 (Fig. 2): compared with pure chitosan films (CPR0-1) which showed no obvious crystal morphology, blend membrane with PEG indicated a branch-like crystal in morphology, and this morphology had been mentioned previously about chitosan crystal^[29]. The appearance of branch-like crystal suggested that the addition of PEG could destroy the original crystalline structure of chitosan. This point will be discussed further in the following XRD results. In addition, RNSA displayed no obvious impact on phase coarsening in group CPR2 that was correlated to the special structure of films in the above discussion.

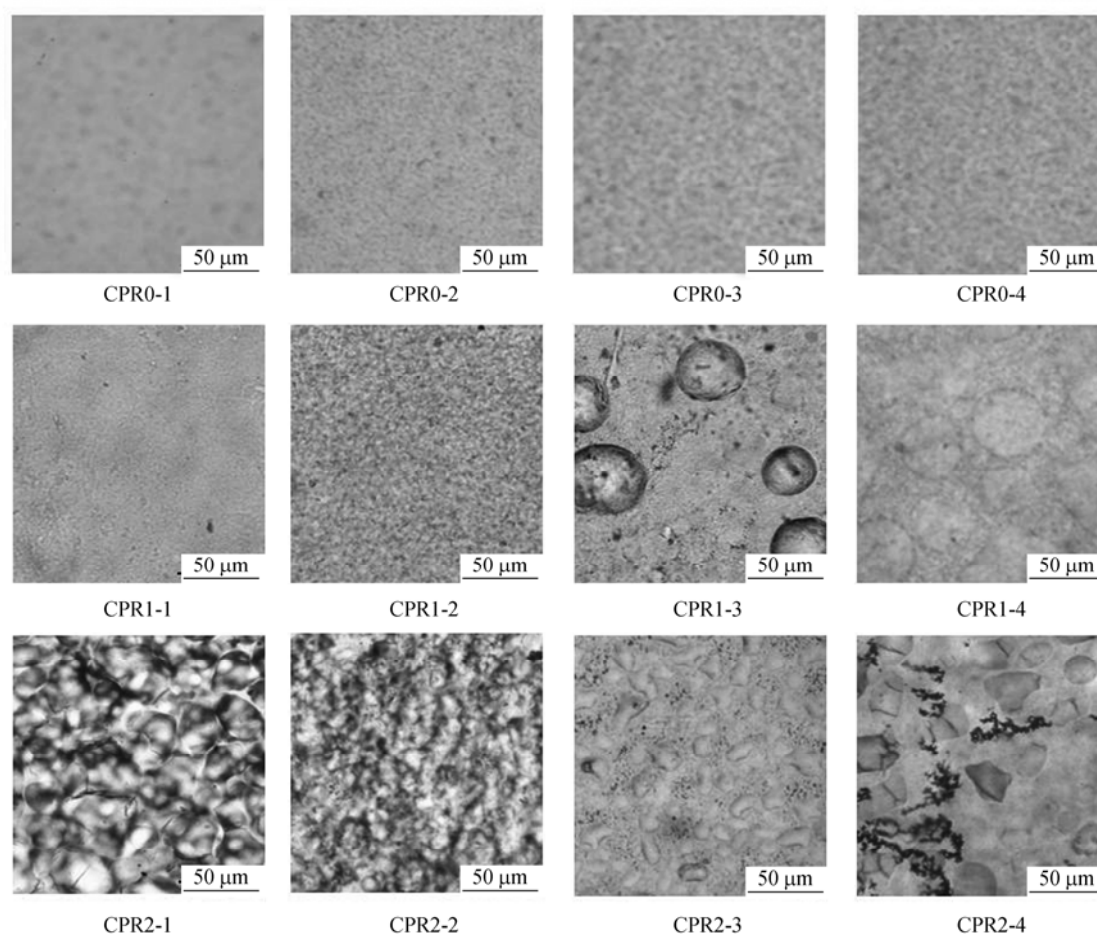


Fig. 3 Optical microscope results of the hybrid films after annealing

To check the annealing effect, all the samples were annealed at 100°C for 1 h (Fig. 3). In contrast to CPR0, CPR1-1 and CPR1-2 — no significant change in morphology was detected — the phase coarsening of samples CPR2, CPR1-3 and CPR1-4 was enhanced due to the annealing process. Therefore, phase separation was induced by annealing process, and this observation was coincident with the report by Kolhe^[14].

ATR-IR Characterization

It seemed that the addition of RNSA showed no effect on pure chitosan (Fig. 4), but had a profound effect on chitosan/PEG blends as probed with the ATR-IR technique which can give the near-surface infrared absorption of samples (Figs. 5, 6). In Fig. 5, the characteristic absorption of PEG became stronger with increasing of RNSA. The absorption band of chitosan at 1251 cm^{-1} was covered by double peaks of PEG at 1241 cm^{-1} and 1280 cm^{-1} . Moreover, the absorption peaks at 1466, 1371, 1360, 1113, 962 and 842 cm^{-1} attributed to the absorption of PEG appeared and became more obvious with the adding of RNSA. The enhanced characteristic absorption of PEG suggested a tendency that RNSA would promote PEG's accumulation on the surface of samples. However, there seems no difference upon adding RNSA for group CPR2 (Fig. 6), as could be also corroborated from the above OM results (Fig. 2).

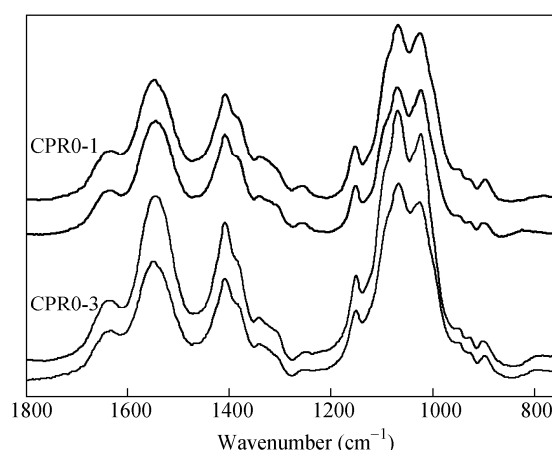


Fig. 4 ATR-Infrared spectra for surface of films for CPR0 samples
In each pair, top: annealed; bottom: non-annealed

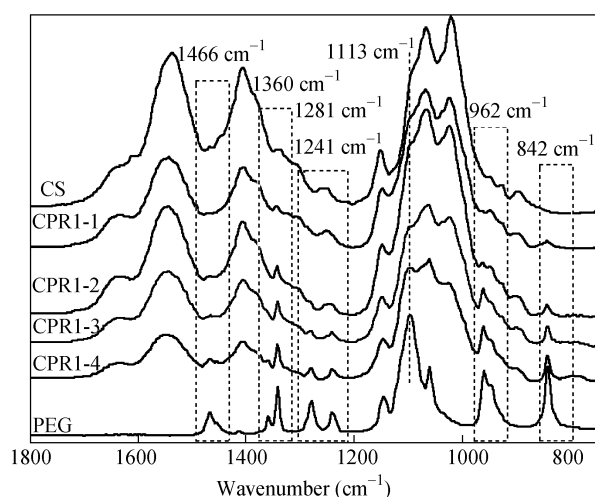


Fig. 5 ATR-Infrared spectra for surface of films for CPR1 samples

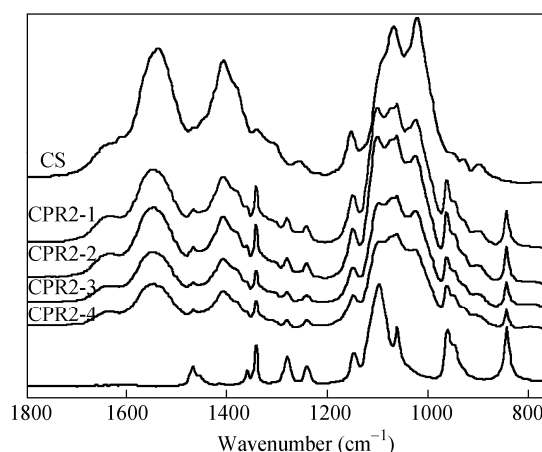


Fig. 6 ATR-Infrared spectra for surface of films for CPR2 samples

Upon annealing, RNA still failed to affect the infrared absorption of pure chitosan film (Fig. 5), while other samples displayed the increased absorption peaks assigned to PEG, suggesting an accumulation of PEG component on sample surface (Figs. 7, 8). On one hand, this observation was related to the annealing temperature (100°C) that was well above the melting temperature of PEG. At this temperature, PEG melted and migrated, and then it would recrystallize during the subsequent cooling step. Therefore, for samples that contained more PEG, the influence of annealing on films would become more intense. On the other hand, the structure change of chitosan, upon annealing, also played an important part in the accumulation of PEG on film surfaces. This aspect will be discussed further in the analysis of XRD measurements.

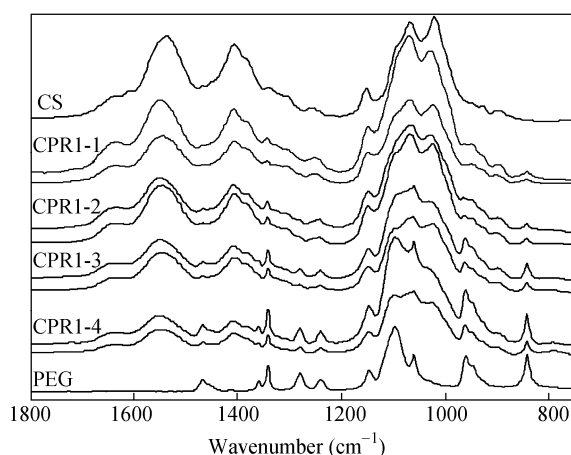


Fig. 7 ATR-Infrared spectra for surface of CPR1 samples before and after annealing
In each pair, top: annealed; bottom: non-annealed

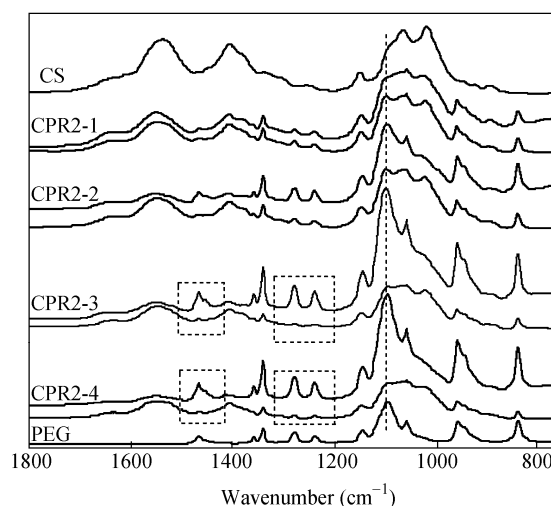


Fig. 8 ATR-Infrared spectra for surface of CPR2 samples after and before annealing
In each pair, top: annealed; bottom: non-annealed

X-ray Diffraction Analysis

So far, at least seven polymorphs have been proposed for chitosan^[12, 30–32], including “tendon-chitosan”, “annealed”, “I-2”, “L-2”, “form I”, “form II”, and “noncrystalline”. Ogawa *et al.* have proposed three forms: noncrystalline, hydrated crystalline and anhydrous crystalline^[30]. The X-ray diffraction spectra of hybrid films are shown in Fig. 9. The peaks around $2\theta = 11.7^\circ$, 14.2° , 17° , 18.6° and 23° should be assigned to chitosan: the peak around $2\theta = 11.7^\circ$ corresponding to the hydrated crystalline structure^[30]; while the peaks around $2\theta = 14.2^\circ$ and 23° corresponded to the anhydrous crystalline structure and the amorphous structure, respectively^[30]. Meanwhile, the reflections for PEG were at $2\theta = 19.5^\circ$, 24° , 26.7° and 33.3° . As shown in Fig. 9(a), RNA exhibited no influence on the crystalline structures of chitosan and PEG. The diffraction of PEG tended to cover the reflection of chitosan with increasing PEG, and the addition of PEG impacted the crystal of chitosan: pure chitosan and chitosan hybridizing with RNA tend to crystallize in the form of hydrated crystalline ($2\theta = 11.7^\circ$) and amorphous structure ($2\theta = 23^\circ$). Once blending with less amount of PEG, the main crystalline structures were in hydrated crystalline ($2\theta = 11.7^\circ$) and anhydrous structure ($2\theta = 14.2^\circ$). With more content of PEG, the hydrated crystalline ($2\theta = 11.7^\circ$) would prevail in chitosan structure. As indicated, the gradual disappearance of amorphous — indicative diffraction ($2\theta = 23^\circ$) for samples CPR1 and CPR2 suggested PEG would promote the crystallization of chitosan.

The variation in the crystalline state of chitosan could be ascribed to the double effects of PEG: (1) based on the above-discussed role of PEG in the blend, it could weaken the interaction between chitosan and water and thus allow chitosan to crystallize in the form of the anhydrous structure (see the XRD result of CPR1); (2) on the other side, PEG is a water-soluble molecule, more PEG would absorb more water into membrane and thus make the hydrated crystalline structure be formed as revealed in the XRD result of CPR2. This evolution in the crystal structure could correspond to the crystal morphology in OM observation (Fig. 2).

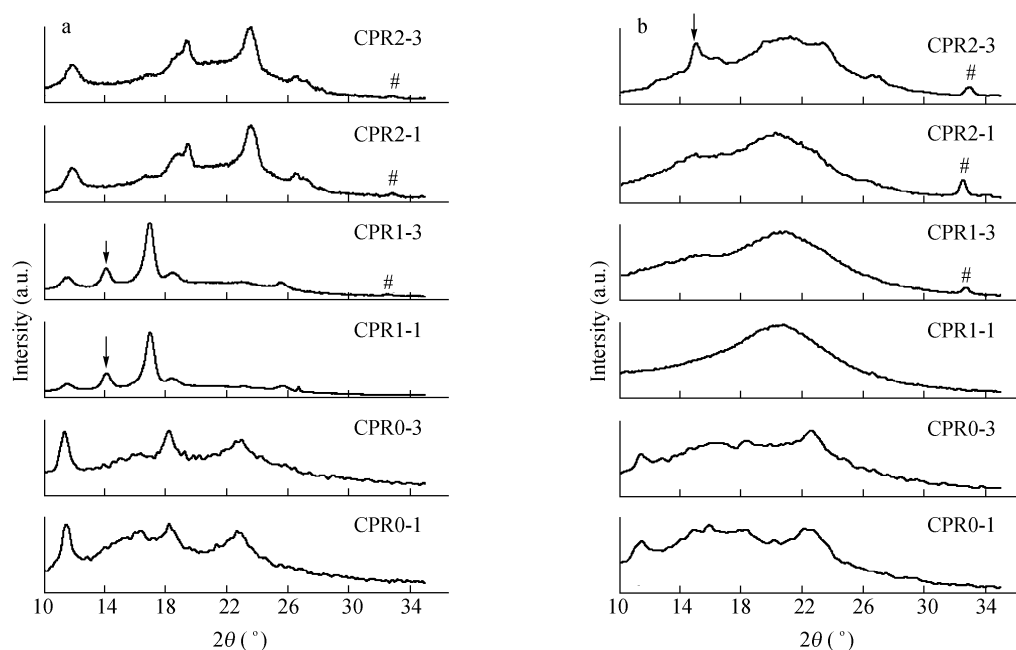


Fig. 9 X-ray spectra for samples (a) annealed and (b) without annealing

After annealing process, both the hydrated crystalline ($2\theta = 11.7^\circ$) and anhydrous crystalline ($2\theta = 14.2^\circ$) were weakened and the amorphous structure ($2\theta = 23^\circ$) was reinforced for pure chitosan and chitosan after blending with RNA (Fig. 9b). As for the chitosan blending with PEG, the sharp peaks were replaced by the diffusing peaks around 23° (2θ), which represented the amorphous structure of chitosan. This observation suggested that the structure of chitosan blending with PEG would readily be changed upon annealing. Besides, as increasing the amount of RNA and PEG, some obvious peaks of PEG at 33.3° (2θ) and even sharp peak of chitosan at 15.5° (2θ) appeared, implying the improved crystalline properties. More importantly, the peak at $2\theta = 15.5^\circ$ on CPR2-3 had some shift comparing with the anhydrous crystalline structure of chitosan at 14.2° (2θ) before annealing. According to the Bragg equation, the distance between the plans in each direction became smaller due to the increased 2θ value, so it was noted that the structure of chitosan after annealing became tighter, and this aspect was consistent with the report of other literatures^[30–32]. The process of structure change of chitosan during dehydration is schematically shown in Fig. 10. In crystal structure of hydrated chitosan, water molecules entered into the formation of hydrogen bond. After dehydration, molecular chains of chitosan began to shift and shrink the structure of chitosan due to abrupture of hydrogen bond^[33]. Then the ATR-IR results became understandable: the shrinkage of chitosan structure would make the melting PEG migrate and then

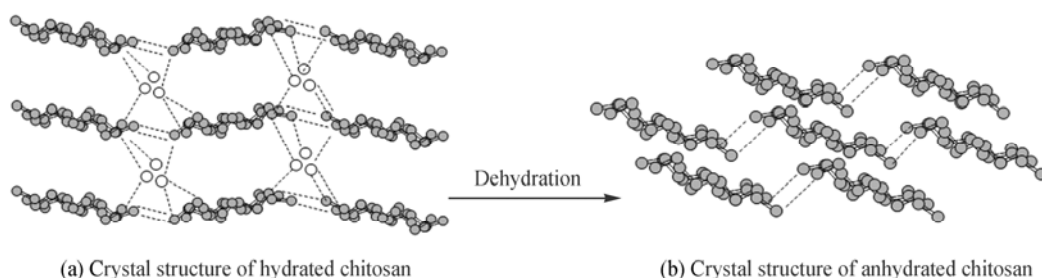


Fig. 10 Plausible solid-state transformation from the hydrated form (a) to the anhydrous form (b) of tendon chitosan (Shaded polymer chains denote up-pointing molecules. Hydrogen bonds before and after transformations are also shown.)

re-crystallize on the film surface. In addition, the enhanced phase coarsening upon annealing as indicated in the OM photographs (Fig. 3) could be explained by the altered structure of chitosan as well as migrated and re-crystallized PEG.

One more point should be emphasized was that the crystallinity of PEG had been increased by increasing the content of RNSA in samples CPR1 since the peak of PEG at 33.3° (2θ) became more obvious. The change of crystallinity for PEG in other samples was not easy to be observed by XRD measurements due to severe overlapping of the diffraction peaks in the diffraction pattern.

Thermal Behavior Analysis

The depression of melting point (T_m) of a crystalline polymer blended with other polymers provides information about their miscibility and interaction^[34]. Both chitosan and PEG are crystalline polymers; pure PEG melts at *ca.* 60°C, while chitosan undergoes thermal degradation at *ca.* 270°C prior to melting. Thus, the melting point of PEG was monitored to understand the miscibility and the interaction between the two polymers. This view was supported by the Nishi-Wang equation^[35] that was used to obtain the interaction parameter (χ_{12}):

$$\frac{1}{T_m} - \frac{1}{T_{m2}^{\circ}} = \frac{-R}{\Delta H_{2u}} \frac{V_{2u}}{V_{1u}} \chi_{12} (1 - \psi_2)^2$$

where subscripts 2 and 1 refer to PEG and chitosan, respectively, T_m° and T_{m2}° are the equilibrium melting temperature (K) of PEG in blend and that of pure PEG, respectively; R is the universal gas constant, ΔH_{2u} is the heat of fusion permole of 100% crystalline PEG, V_{2u} and V_{1u} are molar volumes of the repeating units of the polymers and ψ_2 represents volume fractions of PEG in the blend. According to this equation, the interaction parameter (χ_{12}) which represents miscibility and interaction is dependent on the depression of melting point (T_m) of a crystalline polymer after blending with other fixed content polymer. The more negative χ_{12} derived from the more decreased melting point, suggests better miscibility and stronger interaction between both of polymers. The result from DSC showed a decrease in the melting temperature (T_m) of PEG for all samples compared with the pure PEG, suggesting that chitosan and PEG are miscible (Table 2).

Table 2. Melting properties of PEG in all samples*

	CPR1-1	CPR1-2	CPR1-3	CPR1-4	CPR2-1	CPR2-2	CPR2-3	CPR2-4
T_m (°C)	–	47.41 51.84	52.19 53.32	52.24 53.45	52.79 55.48	52.79 55.27	52.17 55.54	52.92 55.42
ΔH (J/g)	–	–	24.35 21.75	23.97 23.25	38.20 44.24	40.20 43.84	43.31 44.72	41.18 45.68

* In each group of data, up: non-annealed; down: annealed

For CPR1 samples, the melting peak of PEG displayed a transition from weak to strong with addition of RNSA, suggesting the increasing of melting enthalpy (which correlates with crystallinity) (Fig. 11a). However, after CPR1-3, the data of endotherm melting enthalpies (ΔH) noted in Table 2, will not increase again. This observation would be ascribed to the fact that RNSA could act as the nucleating agent in the crystallization of PEG: a little content of RNSA would not induce PEG to crystallize until its loading beyond some value; once the crystallization is initiated, the crystallinity will be almost completed due to the strong crystalline tendency of PEG. Therefore, the crystallinity will reach a plateau after initial increasing. This view could be also used to understand the invariant ΔH pre- or post-adding RNSA/or annealing process (see Table 2, sample CPR1-3, CPR1-4 and CPR2).

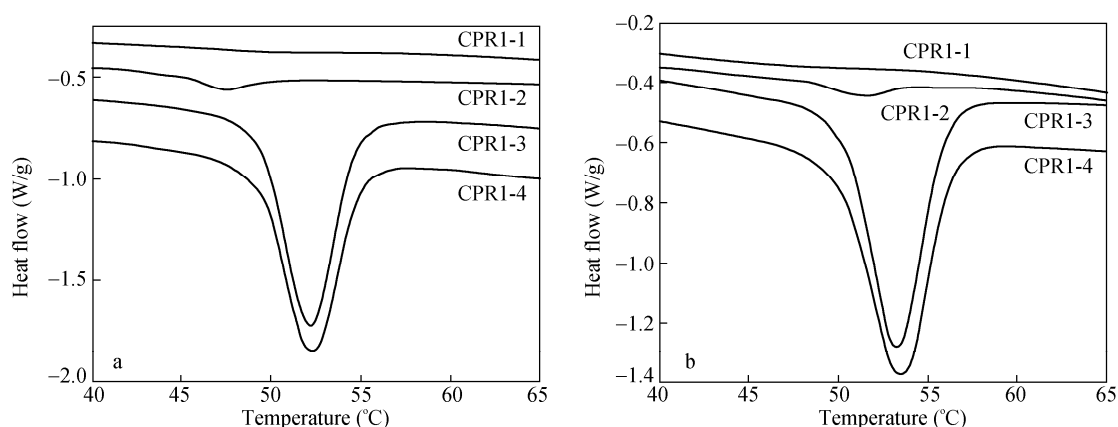


Fig. 11 The melting curves of PEG in the CPR1 samples with (a) non-annealed and (b) annealed

The invariant T_m indicated RNA had no effect on miscibility and interaction of blends. However, after annealing, the increased T_m s compared with non-annealed samples were found in all samples, suggesting a decrease in miscibility and interaction between chitosan and PEG led by annealing (Fig. 11b, Table 2)

CONCLUSIONS

The interaction of components in the chitosan/PEG/silica ternary hybrid films had been investigated. There is a strong molecular interaction between chitosan and PEG, so that the original crystal structures of chitosan and PEG have been changed. The addition of RNA would serve as a nucleating agent for PEG and compel PEG to accumulate on the surface of films. Annealing would decrease the miscibility and interaction between chitosan and PEG, enhance the phase coarsening, as well as change the crystalline structure of chitosan blended with RNA and PEG.

ACKNOWLEDGMENT We are grateful to Prof. Z.J. Zhang of the Henan University for supplying the silica nanoparticles used in this research.

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