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Effects of N,O-dicarboxymethyl chitosan on phase behavior and morphological structure of chitosan/viscose rayon blends

Yunlin Guan, Xiaofei Liu, Qiang Fu , Zhi Li, Kangde Yao

Research Institute of Polymeric Materials, Tianjin University, Tianjin 300072, People's Republic of China

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Abstract

The phase behavior of chitosan/viscose rayon blends was examined by dynamic mechanic analysis (DMA) and differential scanning calorimeter (DSC), and the morphology was investigated by transmission electron microscope (TEM) and atomic force microscope (AFM). Characterization of chitosan/viscose rayon blends by DMA and DSC analysis suggests partial miscibility of chitosan with viscose rayon. The phase behavior of the blends is influenced by the presence of N,O-dicarboxymethyl chitosan. Morphology observations of the blends disclosed that chitosan microparticles are distributed over the viscose rayon phase, ranging in diameters of 0.1–2.5 μm. The addition of N,O-carboxymethyl chitosan into the blend can improve the compatibility of chitosan with viscose rayon. © 1998 Elsevier Science Ltd. All rights reserved

Keywords: Chitosan/viscose rayon blends; Phase behavior; Morphological structure

1. Introduction

The antimicrobial fiber CHITOPOLY developed by Seo *et al.* is a blend fiber composed of polynosic and chitosan—chitosan microparticles which have a mean size less than 5 μm were blended in ripening viscose by a mechanical blend method. Some research activities on its antimicrobial abilities, biological degradability, mechanical properties and applied experiments have been reported (Seo, 1990; Seo et al., 1992; Seo, 1993a, b; You, 1995) However, investigation of the phase behavior and morphology of the blend have not been covered. For the purpose of studying the phase behavior and morphology and in consideration of promising the above characteristics of CHITOPOLY, an antimicrobial ternary blend based on chitosan/viscose rayon and N,O-dicarboxymethyl chitosan as a compatibilizer has been prepared.

In a previous article (Guan et al., 1998), an antimicrobial chitosan/viscose rayon blend was prepared by a different method from that of CHITOPOLY, which blended an emulsion of chitosan with the ripening viscose. From IR spectroscopy, no reaction between chitosan and viscose rayon was found in the binary blend; however, amino groups of chitosan reacted with the carboxyl groups of N,O-dicarboxymethyl chitosan in the ternary blend. By determining the minimum growth inhibitory concentration (MIC) of bacterium on chitosan/viscose rayon blends, antimicrobial activities of the blends similar to those of CHITOPOLY fiber were obtained. This article deals with the relationship between the phase behavior and the morphological structure.

2. Experimental

2.1. Materials

Chitosan was provided by Qingdao Medicine Institute, Qingdao. Before use, it was dissolved in 10 wt% acetic acid. The solution was stirred, filtered through a sintered glass crucibe and then neutralized with alkali. The emulsion of chitosans could be prepared later. The viscosity-average molecular weight of the chitosan purified was 1.6×10^5, calculated by the Mark–Houwink equation: $[\eta] = K_m M^\alpha$, where $K_m = 1.81 \times 10^{-3}$, $\alpha = 0.93$ and the degree of N-deacetylation was 80% (Roberts & Domszy, 1982). Ripening viscose was obtained from the Tianjin Rayon Factory, Tianjin. Its degree of polymerization (DP) = 275 was determined by the equation: $[\eta] = 3.85 \times 10^{-4} M_w^{0.76}$; DP = $M_w/162$ in cadoxen at 25°C (Miyamoto et al., 1996). Acetic acid, sulphuric acid, and other reagents were analytical.

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2.2. Preparation of N,O-dicarboxymethyl chitosan

To a chitosan (20 g) suspension in 200 ml isopropanol, 50.4 ml of 10 M sodium hydroxide aqueous solution was added in six equal portions over a period of 20 min under agitation. The alkaline slurry was stirred for an additional 45 min, the solid monochloroacetic acid (24 g) was incorporated in five equal portions at 5-min intervals. The reaction mixture was heating at 60°C for 3 h. Next cold distilled water (17 ml) was added to the mixture and its pH was adjusted to 7.0 with glacial acetic acid. The reaction mixture was filtered and the solid product was washed with a 70% methanol/water mixture (300 ml) and then with anhydrous methanol. The resultant N,O-dicarboxymethyl chitosan were dried in an oven at 60°C (Hayes, 1986). The degree of carboxymethylation was 0.35, determined by the acid–base titration method (Wan et al., 1996).

2.3. Forming of the blend film

The emulsion of chitosan, viscose and N,O-dicarboxymethyl chitosan were blended. The binary blend was composed of chitosan/viscose rayon, while the ternary blend was based on chitosan/viscose rayon by using N,O-dicarboxymethyl chitosan as a compatibilizer. The blends ranged in concentrations from 2% to 8% of the ratio by weight of chitosan to ripening viscose, while the ratio by weight of N,O-dicarboxymethyl chitosan to chitosan was 0% and 10%. The viscose blend films were regenerated at 50°C in a coagulation bath containing 10 wt% sulfuric acid, 30 wt% sodium sulfate and 1 wt% zinc sulfate. After washing with distilled water, the films were soaked in a 2 wt% sodium sulfite solution for 20 min. Finally, the films were washed with distilled water and then dried at 50°C in an oven. In this article, blend 1 (chitosan wt/viscose wt = 4/96), blend 2 (chitosan wt/viscose wt = 8/92), blend 3 (chitosan wt/viscose wt = 4/96, N,O-dicarboxymethyl chitosan wt/chitosan wt = 10/100), and blend 4 (chitosan wt/viscose wt = 8/92, N,O-dicarboxymethyl chitosan wt./chitosan wt. = 10/100) are used.

2.4. Measurements

Dynamic mechanic analysis was performed on long narrow samples (40 × 20 × 0.2 mm). A Rheovibrn DDV-EA instrument was used with a heating rate of 2°C min^{-1} and at an oscillatory frequency of 110 Hz. The samples were cooled using liquid nitrogen and the autocooling accessory.

A Dupont differential scanning calorimeter (DSC), Model 2910, was used. Each sample (510 mg) was run under nitrogen atmosphere at a scanning rate of 5°C min^{-1} at a temperature ranging from 20 to 300°C. After the first time scan, each sample was quenched and then scanned a second time.

Transmission electron microscopy (TEM) was performed to investigate the morphology of the cross-sectional area of the films with a Philips EM400ST instrument. Samples were prepared by dissecting the samples in liquid nitrogen and staining them with OsO_4.

Specimens were examined using a Park Scientific Instruments AutoProbe Scanning Force Microscope for atomic force microscope (AFM) analysis. The tips were V-shaped silicon nitride 100 μm cantilevers with a force constant of 40 nN nm^{-1} and a scanning frequency of 4 Hz.

3. Results and discussion

3.1. Phase behavior of the blends

Dynamic mechanic analyses (DMA) for the blends are presented in Fig. 1. Two transitions of chitosan were observed at −55 and 105°C (Guan et al., 1998). The viscose rayon exhibits four glass transition or second order transitions temperatures at −50, 27, 205 and 250°C. Temperature ranges covering these transitions overlap completely with those of Manabe's report (Manabe et al., 1986). For the blends, a small peak ca. 120°C is found in addition to the four transitions which correspond to those of viscose rayon. Moreover, the absorption ca. −50°C in curves (b), (c), (d) and (e) is much stronger than that of viscose. These might be due to the α,β absorption of chitosan at the vicinal temperature and phase separation may be regarded as occurring in the blends.

Jiang et al. (1996) measured the thermal decomposition

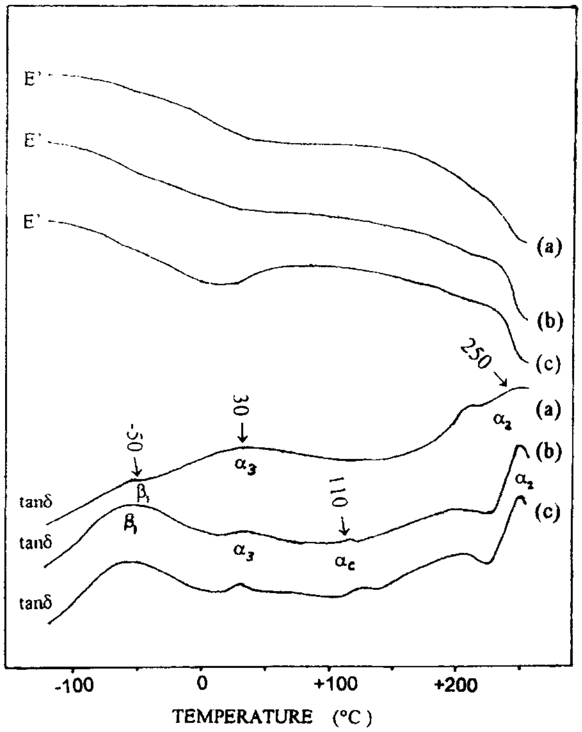


Fig. 1. Temperature dependence of tan δ and E' for viscose rayon (a), blend 1 (b) and blend 2 (c).

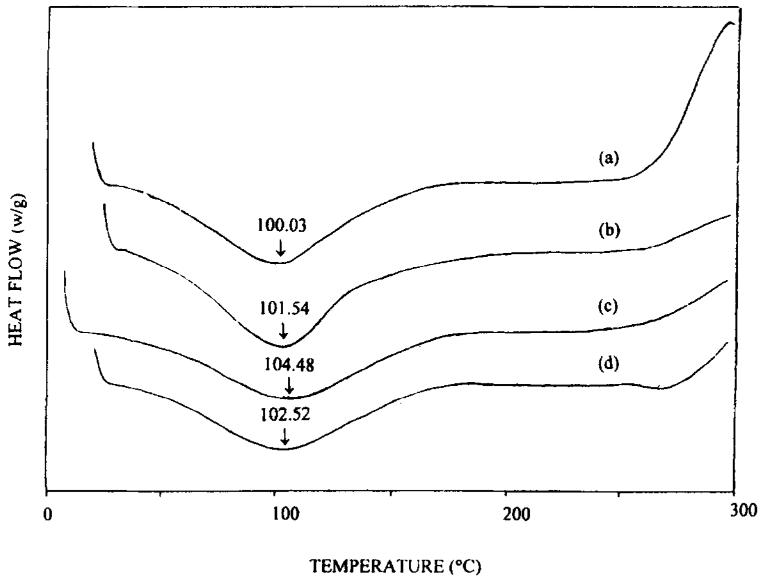


Fig. 2. Spectra of the first scan of chitosan (a), viscose rayon (b), blend 1 (c) and blend 2 (d).

temperature of chitosan film higher than 250°C, and they considered that chitosan did not show a glass transition before the decomposition temperature. Since there are similar rigid chain structures between chitosan and viscose rayon, viscose rayon also should not show a glass transition before decomposition.

The thermal transitions of chitosan, viscose rayon and their blends were determined by DSC analyses before they decomposed. Compared with their second time scan (cf. Fig. 3), the transition temperatures in the first time scan (cf. Fig. 2) all approached 100°C. It may be considered that there was free water in the samples before they were heated.

For chitosan, the transition was observed at ca. 89.7°C (cf. Fig. 3a). Fig. 3(b) shows a similar transition for viscose rayon at 111.5°C. A single transition for blend 1 and blend 2 was observed ca. 111.4°C and 92.1°C, respectively (cf. Fig. 3c and d). Moreover, the temperature of this transition for the binary blend was higher than that of the ternary one. This implied that the compatibility of the latter was better than that of the former. In other words, the blend has a good compatibility between chitosan and viscose rayon with the aid of CM-chitosan. This hypothesis can be proved by the results of TEM analyses as well.

3.2. Morphology

The morphology of the blends is shown in Fig. 4. In these micrographs, the dark areas (OsO_4 stained) are the chitosan

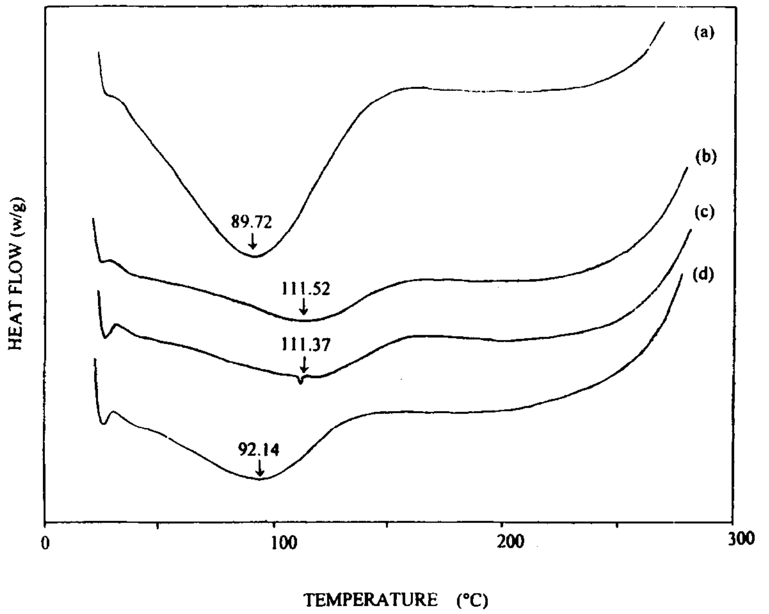
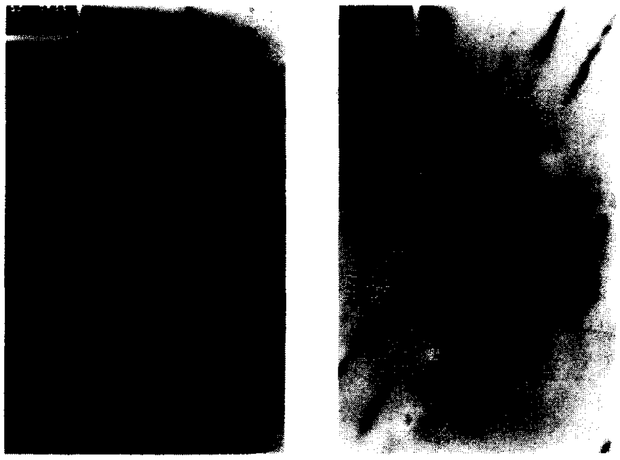
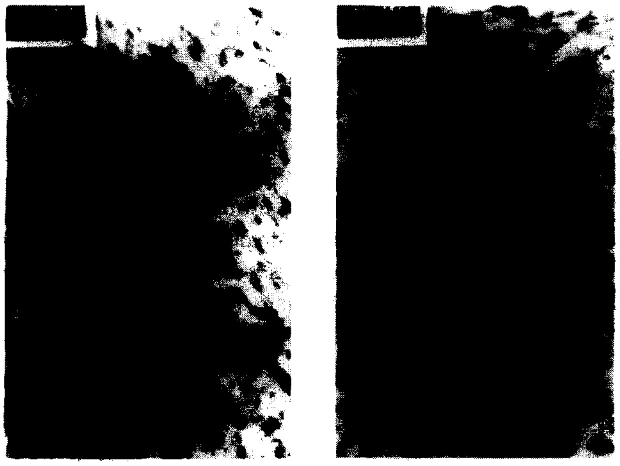


Fig. 3. DSC spectra of the second scan of chitosan (a), viscose rayon (b), blend 1 (c) and blend 2 (d).



(a) the blend 1 (b) the blend 2



(c) the blend 3 (d) the blend 4

Fig. 4. TEM photographs of chitosan/viscose rayon blends (magnification 11000 ×): (a) blend 1; (b) blend 2; (c) blend 3; (d) blend 4.

phase and the bright areas are the viscose rayon phase. As seen from the figures, blend 1 and blend 2 have a similar structure. Chitosan microparticles are distributed over the viscose rayon phase, their diameters vary from 0.1 μm to 2.5 μm (Fig. 4a and b). With increasing the chitosan content, a distinct rough microspheric phase separation appears within blends 3 and 4. However, the degree of phase separation of blend 3 is larger than that of blend 4. Moreover, in blend 4, the diameters of the chitosan microparticles are between 0.1 μm and 0.5 μm, which is much smaller than those in blend 3. And the microparticles of blend 4 are dispersed more uniformly than those of blend 3 (Fig. 4c and d).

The atomic force microscope topographic picture(4 μm × 4 μm) and the corresponding three-dimensional one for viscose rayon are displayed in Fig. 5. The surface of the viscose rayon sample has a roughness of less than 40 nm and a homogeneous surface is seen in the three-dimensional picture. In blend 1, a phase separation is observed (Fig. 6). Some irregular clumps are distributed in the surface of the blend film. This result agrees with that of TEM. In contrast to Fig. 5, a noticeable roughness develops. The vertical height of the dispersed phase is 60–80 nm. The characteristics of the photographs for blend 3 (Fig. 7) are almost identical with those for blend 1, and the only difference is that the height of the dispersed phase is 200–300 nm. When chitosan content is enhanced to 8%, the pictures for the blend 4 are much clearer (Fig. 8). Chitosan microparticles are dispersed in the rayon matrix, ranging in diameter from 200 m to 800 nm. Fig. 8(a) indicates a height of 150–200 nm for the dispersed phase. From the three-dimensional picture, one can see that hill-like chitosan moieties of various height are distributed on the flat surface of the rayon matrix.

From the TEM and the AFM analyses, it is assumed that, in the above chitosan/viscose rayon blends, chitosan microparticles are scattered uniformly in the rayon matrix, and by mixing a small amount of N,O(dicarboxymethyl chitosan in the blend, the compatibility between chitosan and viscose rayon becomes better.

4. Conclusions

A ternary blend of chitosan/N,O-dicarboxymethyl chitosan/viscose rayon is synthesized. In this blend,

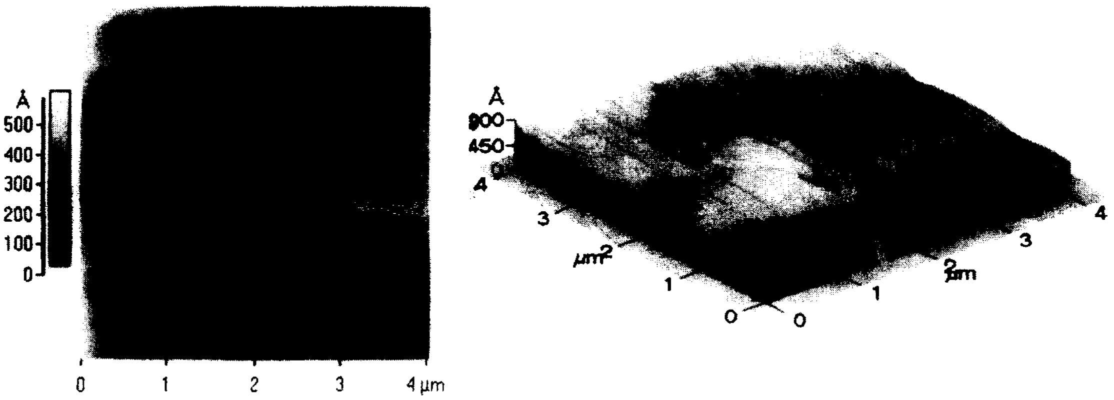
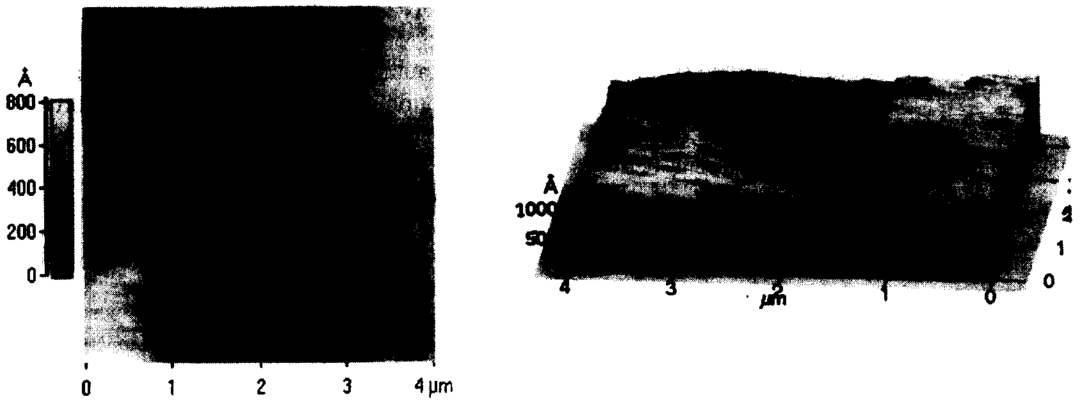
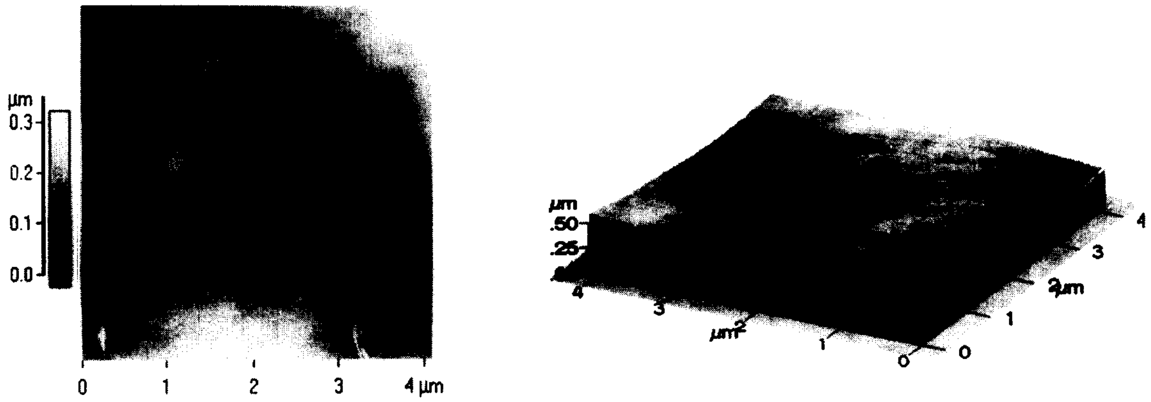


Fig. 5. AFM image for viscose rayon: (a) topographic image; (b) three-dimensional image.



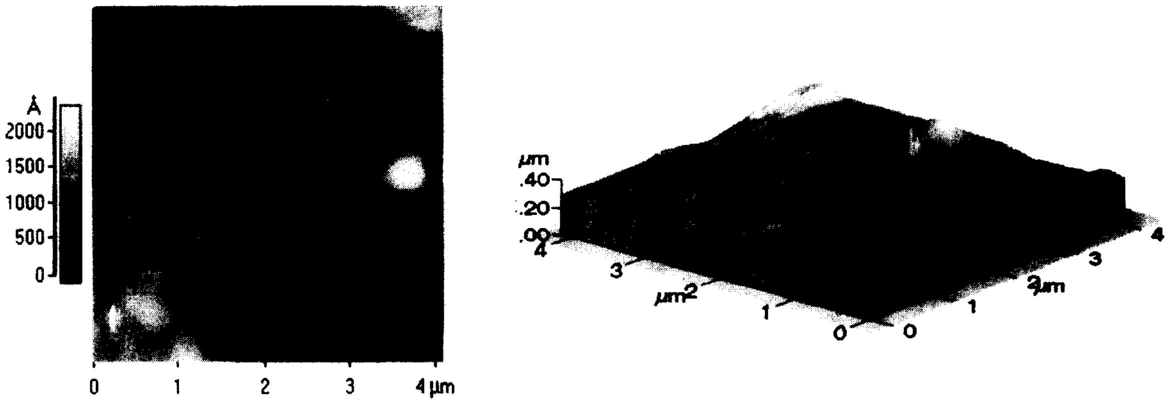
(a) Topographic image **(b) Three dimensional image**

Fig. 6. AFM image for blend 1: (a) topographic image; (b) three-dimensional image.



(a) Topographic image **(b) Three dimensional image**

Fig. 7. AFM image for blend 3: (a) topographic image; (b) three-dimensional image.



(a) Topographic image **(b) Three dimensional image**

Fig. 8. AFM image for the blend: (a) topographic image; (b) three-dimensional image.

there are partial miscibility of chitosan with viscose rayon, and chitosan microparticles are distributed over the viscose rayon phase, ranging in diameters of 0.1–2.5 μm.

From the analyses of the blend, an identical conclusion can be drawn. The phase behavior is different between viscose rayon and chitosan/viscose rayon blend, while the morphology structure of viscose rayon is changed by adding a small amount chitosan. Comparing with the analyses of the binary blend with that of the ternary blend shows that the phase and the morphological behavior are both influenced by the presence of N,O-dicarboxymethyl chitosan. Moreover, the transition temperatures of ternary blends 3 and 4 are lower than that of the corresponding binary blends 1 and 2, and the diameters of chitosan microparticles in ternary blend 4 are smaller than that in the relevant binary blend 2. In other words, the above ternary blends exhibit better compatibility than the binary ones.

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