Study of Phase Behavior on Chitosan/Viscose Rayon Blend Film

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ABSTRACT: A blend of chitosan and viscose rayon was investigated. A film was made from regenerating the blend of chitosan and viscose rayon. The film was characterized by various techniques, including Fourier transform infrared spectroscopy (FTIR), wide-angle X-ray scattering (WAXS), differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), and transmission electron microscopy (TEM). The phase behavior of the blend is influenced by its composition with or without carboxymethylated chitosan (CM-Cs). Characterization of the chitosan/viscose rayon (Cs/VR) blend by DSC and DMA suggests partial compatibility of chitosan with VR and lack of compatibility in the remaining cases. Results of the TEM show that the addition of CM-Cs into the blend can improve the compatibility of Cs with VR. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci **67:** 1965–1972, 1998

Key words: phase behavior; compatibility; carboxymethylated chitosan

INTRODUCTION

Studies on the antibacterial activities of chitin and chitosan have been recently reported.[1–5] In fact, this property is usually applied through blends of polymers or naturally occurring macromolecules with chitin or chitosan. In particular, chitosan with polymers including collagens, polyvinylpyrrolidone, polyamides, cellulose, and viscose rayon were investigated for compatibilities, phase behaviors, antibacterial activities, biological degradabilities, and mechanical properties.[6–10] The present study was concerned with the investigation of the blend of chitosan with viscose rayon.

Chitin and cellulose are both extremely abundant polysaccharides widely found in nature. Chitosan is prepared by *N*-deacetylation of chitin and are generally deacetylated to about 80%. Chito-

san, the β-1-4-linked polymer of 2-amino-2-deoxy-β-*d*-glucan, is similar to cellulose in primary and secondary structures. The difference between the two polysaccharides is that chitosan has the deoxyamino group instead of the hydroxyl group at the C2 position of every pyranose ring as illustrated in Figure 1. This similarity is expected to give high compatibility between these two polymers when blended in a film. Moreover, the similarity of intra- and intermolecular hydrogen bondings in the two polymers also contributes to the compatibility. Blending cellulose and chitosan is expected to be a useful method to introduce amino groups into cellulosic materials for their functionalization.

Antibacterial chitosan/viscose rayon blends have been prepared using the chitosan microparticles which have a mean size less than 5 μm; they were blended in ripening viscose by a mechanical blend method,[10–13] but investigation of the phase behavior of the blend has not been reported.

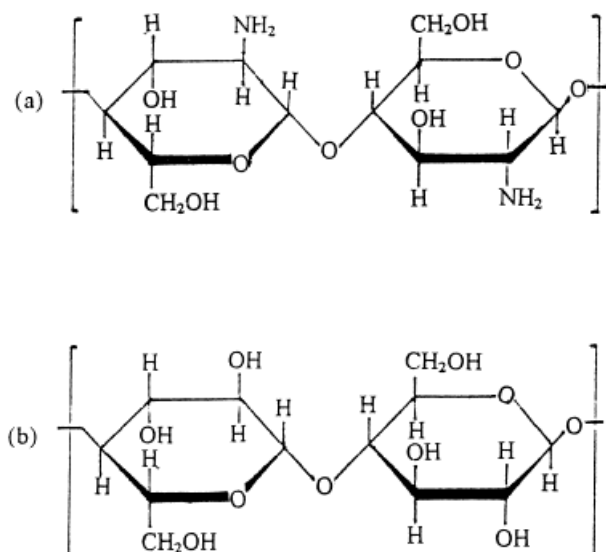In the present study, the antibacterial chitosan/viscose rayon blend film was prepared by

Figure 1 Structures of (a) Cs and (b) cellulose.

blending an emulsion of chitosan with the ripening viscose. The phase behavior of the membrane is characterized by their physical and thermal properties for the purpose of studying the compatibilizing effect of carboxymethylated chitosan.

EXPERIMENTAL

Materials

Chitosan (Cs) was provided by Qingdao Medicine Institute and was dissolved in 10 wt % acetic acid. The solution was stirred overnight, filtered, and then neutralized with $2M$ sodium hydroxide; later, the emulsion of Cs could be prepared. The viscosity-average molecular weight of the Cs purified was 1.6×10^5, calculated by the Mark–Houwink equation[14]: $[\eta] = K_m M^\alpha$, where $K_m = 1.81 \times 10^{-3}$, $\alpha = 0.93$, and the N-deacetylation degree was 80%. Ripening viscose was obtained from Tianjin Rayon Factory, Tianjin. Its viscosity-average degree of polymerization (DP) = 275 was determined in cadoxen at 25°C by using the following equation[15]: $[\eta] = 3.85 \times 10^{-4} M_w^{0.76}$; DP $= M_w/162$. Acetic acid, sulfuric acid, and other reagents were analytical grade.

Preparation of Carboxymethylated Chitosan (CM-Cs)

To Cs (20 g) suspended in isopropanol (200 mL) under agitating, sodium hydroxide (50.4 mL,

$10M$) is added in six equal portions over a period of 20 min. The alkaline slurry is stirred for an additional 45 min, and the solid monochloroacetic acid (24 g) is added in five equal portions at 5-min intervals. The reaction mixture was heated at 60°C for 3 h. Next, cold distilled water (17 mL) is incorporated into the mixture and its pH 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-CM-Cs was dried in an oven at 60°C.[16] The degree of carboxymethylation determined by pH titration was 0.35.[17]

Forming of the Blend Film

The emulsion of Cs, viscose, and CM-Cs were blended. The binary blend was composed of chitosan/viscose rayon (Cs/VR), while the ternary
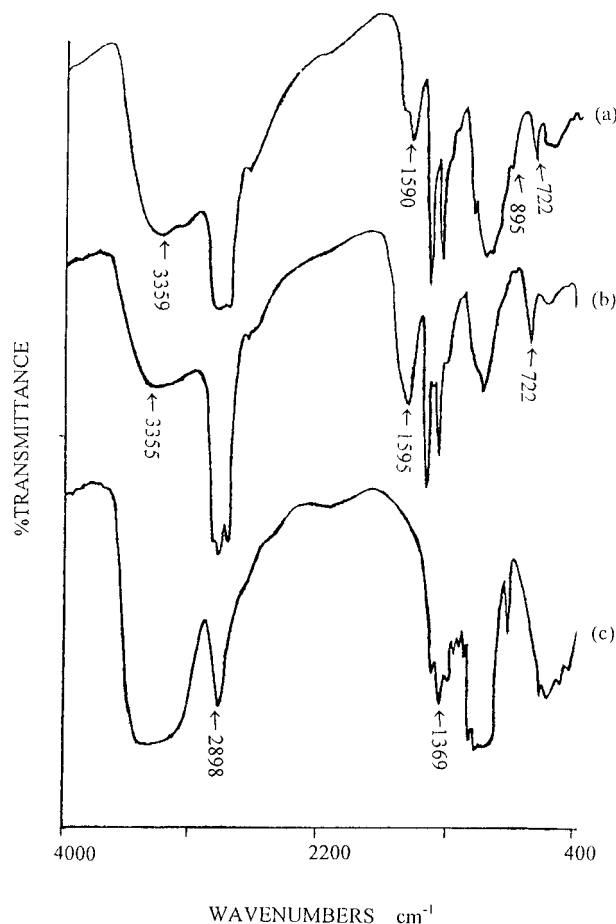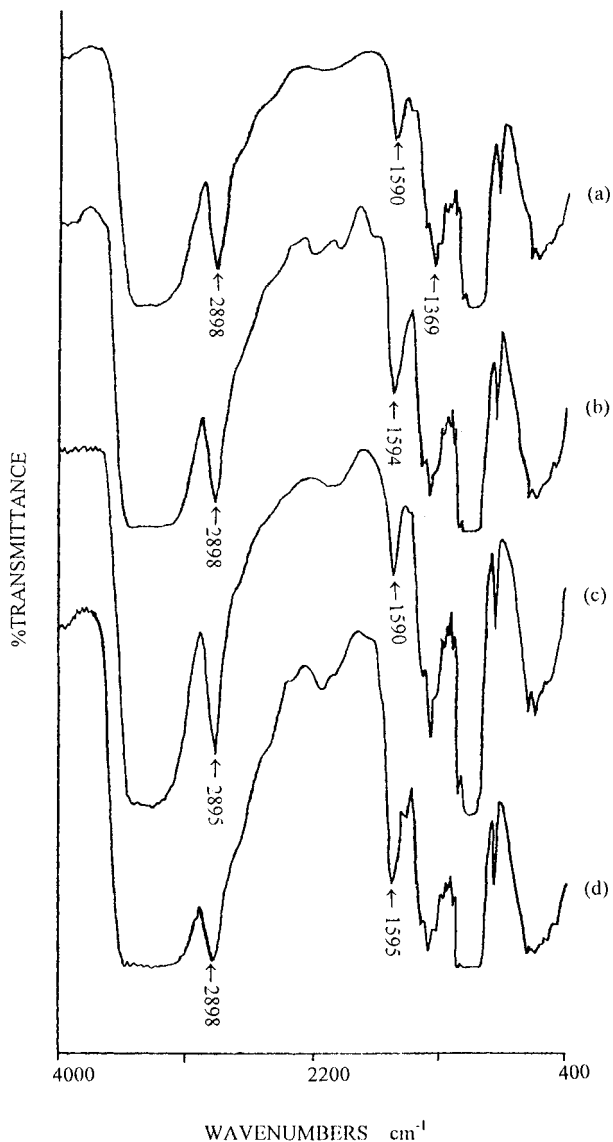

Figure 2 IR spectra of (a) Cs, (b) CM-Cs, and (c) VR.

Figure 3 IR spectra of (a) blend 1, (b) blend 2, (c) blend 3, and (d) blend 4.

blend was based on Cs/VR using CM-Cs as a compatibilizer. For the blends, the viscose ranged in concentrations from 4 to 8% (Cs wt/VR wt) of Cs and from 0 to 10% (CM-Cs wt/Cs wt) of CM-Cs. 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. Film thickness ranged from 0.02 to 0.10 mm. The thinner films were used for the Fourier

transform infrared spectroscopy (FTIR) experiments, while the thicker ones were applied in the dynamic mechanical analysis (DMA) study.

Measurements

Infrared (IR) spectra of all the samples were obtained with a Nicolet 170SX. After being dried completely at 50°C, the sample could be used for IR analysis. The paraffin paste was used in analyzing Cs powders.

Wide-angle X-ray-scattering (WAXS) experiments were performed for the Cs using a Rigaku Model 2038 diffractometer. The X-ray source was Ni-filtered CuKα radiation (25 kV, 10 mA). The dried membranes of uniform thickness were mounted on aluminum frames and scanned from 5 to 40° 2θ at a speed of 4° 2θ/min and a chart speed of 2 cm/min.

Dynamic mechanical analysis (DMA) was performed on long narrow samples (40 × 20 × 0.2
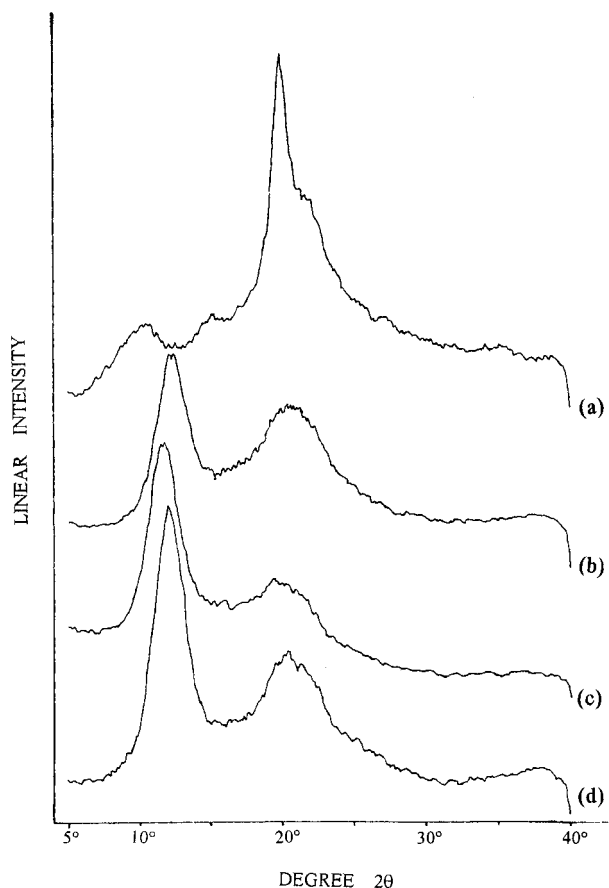
Figure 4 WAXS diffractograms of (a) Cs, (b) VR, (c) blend 1, and (d) blend 2.
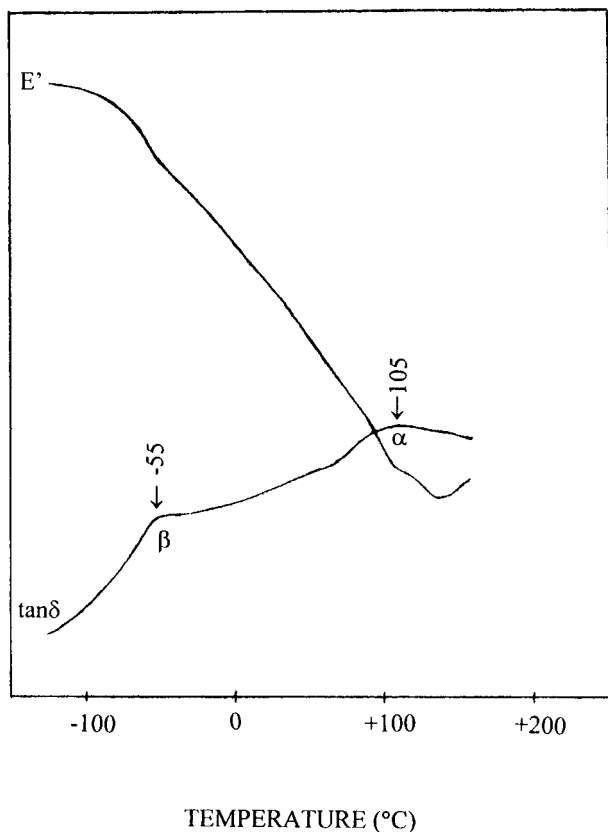
Figure 5 Temperature dependence of tan δ and E' for Cs.

mm). A Rheovibrn DDV-EA instrument was used with a heating rate of 2°C min 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 (5–10 mg) was run under a nitrogen atmosphere at a scanning rate of 5°C min at a temperature ranging from 20 to 300°C. After the first time scan, each sample was quenched and then scanned the 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.

RESULTS AND DISCUSSION

IR Spectra Analyses

The IR spectrum of Cs [cf. Fig. 2(a)] shows ca. 895 and 1155 cm^{-1} peaks that display the saccha-

rine structure and a weaker amino characteristic peak at ca. 1590 cm^{-1}.[18,19] Although there were peaks of paraffin paste at 2853, 1461, and 1377 cm^{-1}, the absorption at 3359 cm^{-1} for the hydroxyl group was still very strong.[20]

For the VR film, the hydroxyl group peak was demonstrated in Figure 2(b). The frequencies of the absorption bands observed ranged from ca. 3400 to 3230 cm^{-1}.[21]

For CM-Cs, the carboxyl groups reacted with the hydroxyl groups and the amino groups. So, the strength of its hydroxyl group peak was weakened, and the position of its amino peak was moved from ca. 1590 to 1595 cm^{-1} [cf. Fig. 2(c)].

Figure 3(a), obtained from blend 1 in which the concentration of Cs was 4/100 (Cs/VR), does not show a qualitative difference between the spectra of VR and Cs in the hydroxyl group peak which ranged from ca. 3400 to 3230 cm^{-1} and the amino peak at ca. 1590 cm^{-1}. This may prove that there was no reaction between Cs and VR.

The IR spectrum of blend 2 in which the concentrations of Cs and CM-Cs were 4/100 (Cs/VR) and 10/100 (CM-Cs/Cs), respectively [cf. Fig.
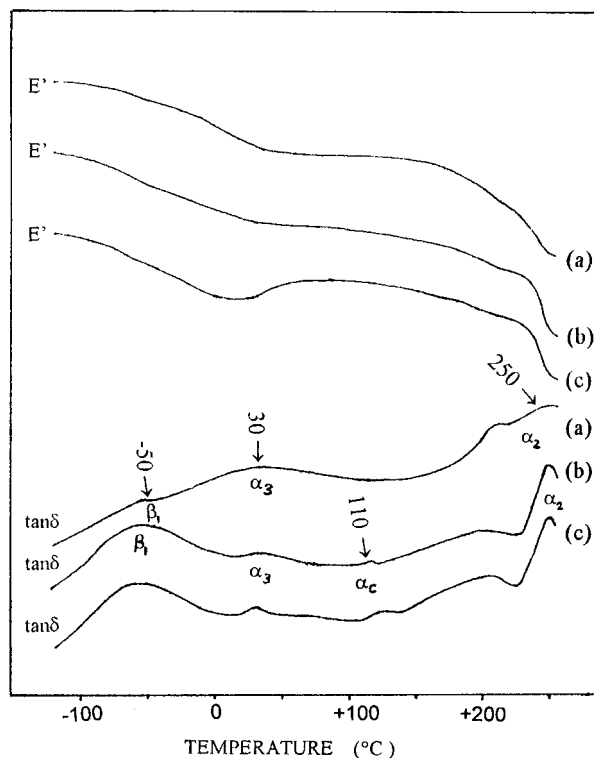
Figure 6 Temperature dependence of tan δ and E' for (a) VR, (b) blend 1, and (c) blend 2.
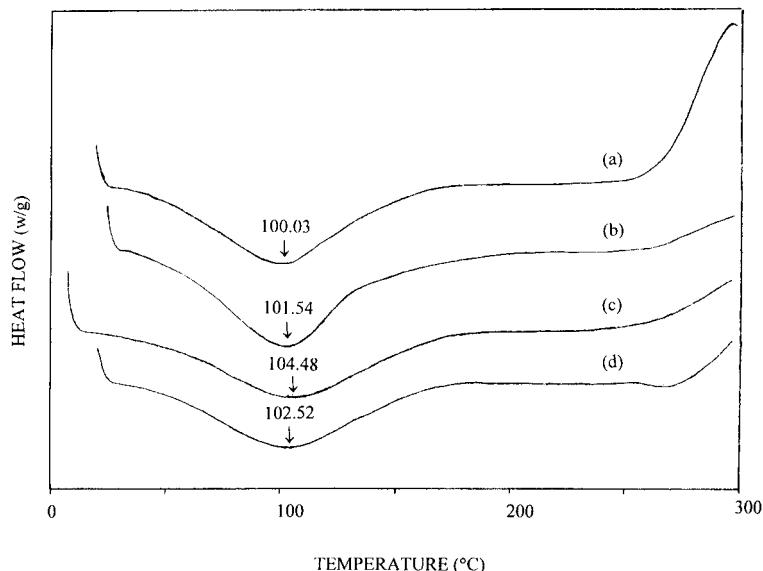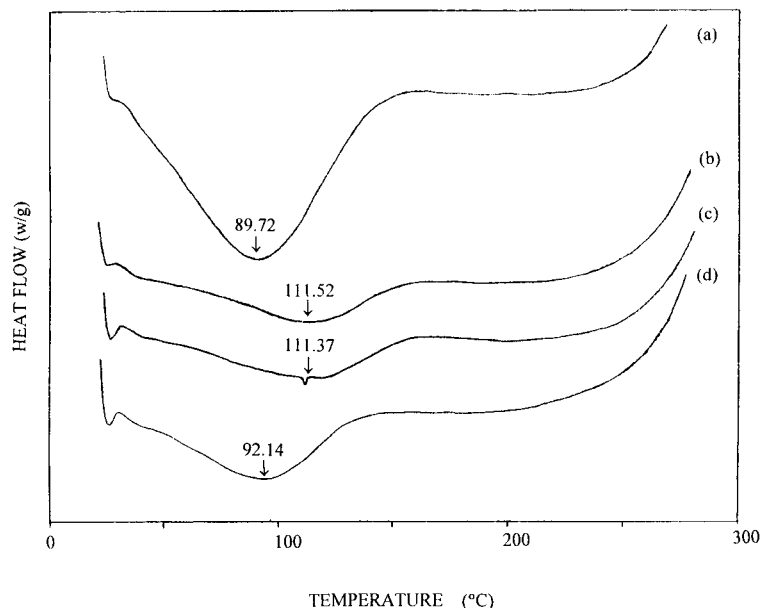
Figure 7 DSC spectra of the first time scan of (a) Cs, (b) VR, (c) blend 1, and (d) blend 2.

3(b)], shows the almost identical spectrum of blend 1 except that the amino peak shifted from ca. 1590 to 1594 cm^{-1}. This may be due to the reaction between the carboxyl groups of CM-Cs and the amino groups, resulting in NH$_3^+$— causing the NH$_2$— peak to move.

Figure 3(c), obtained from blend 3 where the concentration of Cs was 8/100 (Cs/VR), displays no difference from the spectrum of blend 1. Figure 3(d), obtained from blend 4 where the concentrations of Cs and CM-Cs, were 8/100 (Cs/VR) and 10/100 (CM-Cs/Cs), respectively, the spectrum displays an identical change to that of blend 2.

Figure 8 DSC spectra of the second time scan of (a) Cs, (b) VR, (c) blend 1, and (d) blend 2.

(a)   (b)
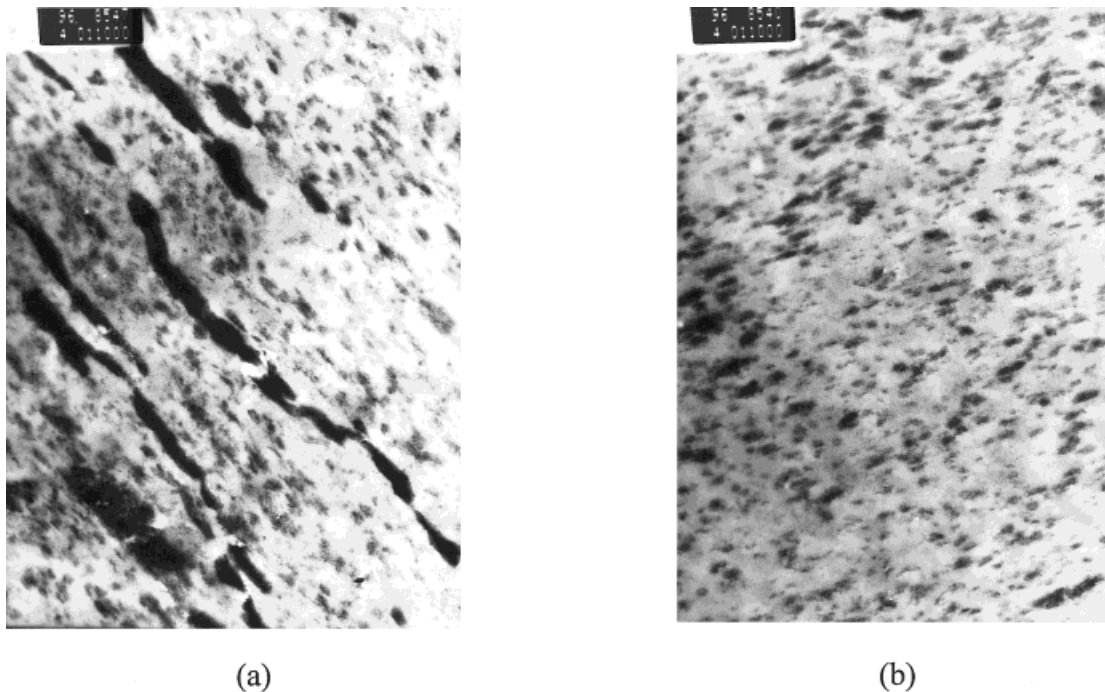
Figure 9   TEM photographs of (a) blend 1 and (b) blend 2 (magnification 11,000×).

Wide-angle X-ray Analyses

The diffractogram of Cs membrane consists of three major crystalline peaks at 10.2°, 15.0°, and 19.5° [cf. Fig. 4(a)][7] Figure 4(b) is a diffraction pattern from the VR film; the dominant peaks are at 101(102.6°), 101(20.3°), and 002(21.6°).[22,23] Figure 4(c), obtained from blend 1, shows nearly no difference from the diffractogram of viscose. This may prove that the small amount of Cs existing does not influence the crystallinity of viscose. Figure 4(d), obtained from blend 2, indicates no change in the diffraction angle from the diffractogram for blend 1.

Thermal Behavior of Chitosan, Viscose Film, and the Blends

Figure 5 shows the DMA spectra of the neutral Cs film. Two transitions of Cs were observed at ca. −55 and 105°C. The results are similar to those of Cs films previously dried at 100°C.[8]

Figure 6(a) indicates the temperature dependence of isochronal dynamic viscoelasticity (E' and tan δ) for the viscose film. Three peaks were observed in the tan δ versus temperature curves of ca. 250, 30, and −50°C. They were named tenta-

tively as the α_2, α_3, and β_1 absorption from the higher-temperature side. The α_2 absorption can be separated into $\alpha_{2,1}$ (250°C) and $\alpha_{2,2}$ (205°C). Temperature ranges covering the α_2 absorption and the α_3 absorption overlap completely with those of the absorption reported by Manabe et al.[24] They considered that the α_2 absorption is due to the micro-Brownian movement of cellulose chains in the amorphous region, in which intra- and intermolecular hydrogen bondings are completely ($\alpha_{2,2}$) or partially ($\alpha_{2,1}$) destroyed. They also regarded that the α_3 absorption corresponds to the cooperative motion of cellulose chains and water molecules in the amorphous region, in which intra- and intermolecular hydrogen bondings are almost completely destroyed.[24] The β_1 absorption as a small shoulder has not been reported in the literature. Figure 6(b), obtained from blend 1, indicates three peaks in the tan δ versus temperature curves at temperatures which are almost identical to the α_2 (1), α_3 (1), and β_1 (1) absorption from the higher-temperature side. However, the peak of the $\alpha_{2,1}$ (1) absorption in this curve is much narrower than that in the curve of VR. It might be considered that this change relates to the crystallinity and the destroyed ex-

tent of hydrogen bondings of the blend. In addition to the α_3 absorption of ca. 30°C, there is a small peak at ca. 110°C. Moreover, the β_1 absorption in the curve is much stronger than that of the viscose film. It might be considered that the α, β absorption of Cs occurred at the vicinal temperature of VR in the blend and be regarded that phase separation occurs in the blend. Figure 6(c), obtained from blend 2, does not show a qualitative difference from the curve of blend 1.

Jiang et al. measured the thermal decomposition temperature of Cs film higher than 250°C, and they considered that Cs did not show a glass transition before the decomposition temperature.[25] Since there are similar rigid chain structures between Cs and VR, VR also should not show a glass transition before decomposition.

The thermal transitions of Cs, VR, and their blends were determined by DSC analyses before being decomposed. The transition temperatures in the first time scan (cf. Fig. 7) all approached 100°C, compared with their second time scan, where they did not (cf. Fig. 8). This may be considered that there was free water in samples before heating them.

For Cs, the transition was observed at ca. 89.7°C [cf. Fig. 8(a)]. Figure 8(b) shows a similar transition for VR at 111.5°C. A single transition for blends 1 and 2 was observed ca. 111.4 and 92.1°C, respectively [cf. Fig. 8(c,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 Cs and VR with the aid of CM-Cs. This hypothesis can be proved by the result of the TEM analyses as well.

Transmission Electron Microscope Analyses

The morphology of the blends is shown in Figure 9. In these micrographs, the dark areas (OsO$_4$-stained) are the Cs phase and the bright ones are the VR phase. A distinct rough microspheric phase separation appears within the blends (Cs/VR = 8/100). However, the degree of phase separation of blend 3 [cf. Fig. 9(a)] is larger than that of blend 4 [cf. Fig. 9(b)]. Moreover, in blend 4, the Cs microparticles' diameters are between 0.1 and 0.5 μm, which are much smaller than those in blend 3. Also, the microparticles of the latter are dispersed more uniformly than are those of

the former. From the TEM analyses, it is assumed that, for the above Cs/VR blends, Cs microparticles are scattered uniformly in the rayon matrix, and with mixing a small amount CM-Cs into the blend, the compatibility between Cs and VR becomes better.

CONCLUSIONS

A ternary blend of chitosan/carboxymethylated chitosan/viscose rayon (Cs/CM-Cs/VR) was synthesized. In the blend, which is discussed in the above paragraph, there is partial miscibility of Cs with VR and lack of miscibility in the remaining cases. Cs microparticles are distributed over the VR phase, with diameters ranging from 0.1 to 2.5 μm.

From the analyses of the blends, an identical conclusion can be drawn: There is nearly no influence on the phase behavior of VR when adding a small amount of Cs. In comparing the analyses of the binary blend with those of the ternary blend, the phase behavior was shown to be influenced by the blend's composition with or without CM-Cs. Moreover, the transition temperatures of the ternary blends (Cs/VR = 4/100 and 8/100) are lower than those of the corresponding binary blends, and the diameters of Cs microparticles in the ternary blend (Cs/VR = 8/100) are smaller than those in the relevant binary blend. In other words, the above ternary blend exhibits better compatibility than that of the binary one.

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