

Miscibility Study of Polymer Blends Composed of Semirigid Thermotropic Liquid Crystalline Polycarbonate, Poly(Vinyl Alcohol), and Chitosan

Moriyuki Sato, Tomohiro Koshino, Yasuko Kajitani, Isamu Inamura, Yasuo Kubo

Department of Material Science, Faculty of Science and Engineering, Shimane University, 1060 Nishikawatsu, Matsueshi, Shimane 690-8504, Japan

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ABSTRACT: Miscibility of binary and ternary polymer blends composed of thermotropic liquid crystalline polycarbonate (LCPC), poly(vinyl alcohol) (PVA), and chitosan was investigated by viscosity method, FTIR spectrum, and scanning electron microscope techniques. Effect of addition of chitosan as a compatibilizer on miscibility and morphology of binary LCPC/chitosan and PVA/chitosan and ternary LCPC/PVA/chitosan polymer blends was discussed. These measurements indicated that addition of chitosan into the blends of LCPC with PVA leads to an increase of miscibility and a formation of clear fibril structures on fractured sur-

faces, which are due to intermolecular hydrogen-bonding interaction between LCPC, PVA, and chitosan chains. It was suggested that side-chain hydroxy group of PVA and amino and hydroxy groups of chitosan play an important role in the formation of miscible phase and improvement of morphology in binary and ternary blends composed of LCPC, PVA, and chitosan. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 1616–1622, 2004

Key words: miscibility; blends; liquid crystalline polymers (LCP); poly(vinyl alcohol); chitosan

INTRODUCTION

Polymer blending is an important technique to modify polymer properties, which are governed by miscibility between component polymers at the molecular level.¹ Most polymer blends composed of different polymers are immiscible owing to unfavorable entropy values of mixing.^{2–4} In immiscible polymer blends, their physical properties are poor compared with those of parent polymers because of phase separations arising from weak interaction at the boundaries of component polymers. The miscibility and the physical properties of polymer blends can be improved by applying intermolecular interaction such as hydrogen bonding and dipole–dipole interaction between component polymers. Intermolecular hydrogen-bonding interaction by hydroxy, halogen, carbonyl, and amide groups leads to the improvement of miscibility based on favorable enthalpic interaction between polymer chains.^{4–11} Addition of compatibilizer into immiscible polymer blends also improves the miscibility and the physical properties.^{3,4}

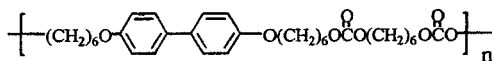
In our previous article,¹² the miscibility of polymer blends of semirigid liquid crystalline polycarbonate (LCPC) with poly(vinyl alcohol) (PVA), partially sa-

ponificated poly(vinyl acetate) (PSPVAc), and poly(vinyl acetate) (PVAc) was investigated by means of DSC and SEM techniques and it was disclosed that the LCPC forms partially miscible polymer blends with the PVA and the PSPVAc. Miscibility between the LCPC and the PVA was very low. This suggests that the side-chain hydroxy group of the PVA and the PSPVAc plays an important role in the formation of miscible polymer blends, but the intermolecular hydrogen-bonding interaction in the blends is weak.

On the other hand, chitin and chitosan are known to be biomaterials to show unique properties and are used in various fields of industry such as medical treatment, agriculture, and food stuffs.¹³ Chitin derivatives were reported to behave as a compatibilizer for immiscible polymer blends.^{14,15} Polymer blends composed of chemically modified chitin derivatives and the PVA form miscible polymer blends because of intermolecular interaction between the carbonyl group in the chitin derivative and the hydroxy group in the PVA.¹⁵ It is expected that the chitosan, having amino and hydroxy groups in the polymer backbone, acts as a compatibilizer for the LCPC/PVA binary polymer blends and gives better miscible ternary polymer blend systems of LCPC/PVA/chitosan.

The purpose of this work was to prepare binary and ternary polymer blends composed of LCPC (Scheme 1), PVA, and chitosan and to investigate the additional effect of chitosan as a compatibilizer on the miscibility

Correspondence to: M. Sato (msato@riko.shimane-u.ac.jp).



Scheme 1 Structure of LCPC.

and the morphology of LCPC/PVA and LCPC/PVA/chitosan blends by viscosity method, FTIR spectrum, and SEM techniques.

EXPERIMENTAL

Materials

LCPC ($M_w = 62,000$) was prepared according to our described methods.^{16,17} PVA ($M_w = 66,000$) was commercially available (purchased from Wako Pure Chemical Industries, Ltd., Osaka, Japan) and used after reprecipitation of the aqueous solution into methanol and dryness at 60°C *in vacuo*. Chitosan (Chitosan 100: 50–100 cP of viscosity) was used without reprecipitation of commercial grade product (Wako Pure Chemical Industries, Ltd.).

Preparation of LCPC/PVA and LCPC/PVA/chitosan blend films

Film specimens of LCPC/PVA [LCPC(w)/PVA(w) = 0.25/5, 0.5/5, and 0.75/5] and LCPC/PVA/chitosan blends [LCPC(w)/PVA(w)/chitosan(w) = 0.25/5/1, 0.25/5/2, 0.5/5/1, 0.5/5/2, 0.75/5/1, and 0.75/5/2] with different compositions for the FTIR measurements and the SEM photographs were prepared by solution-blending. Definite weight ratios of mixture of LCPC, PVA, and chitosan were dissolved in 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP)(v)/water(v) = 95/5 at room temperature. The solutions were allowed to evaporate at a pressure of 17–18 Torr for 48 h at room temperature. The resulting samples were stored in a desiccator before use.

Measurements

The viscometric measurements of LCPC/PVA [LCPC(w)/PVA(w) = 0.25/5, 0.5/5 and 0.75/5], LCPC/chitosan [LCPC(w)/chitosan(w) = 5/0.1, 5/0.3, 5/0.6, 5/1, 5/3 and 5/5], PVA/chitosan [PVA(w)/chitosan(w) = 5/0.1, 5/0.3, 5/0.6, 5/1, 5/3 and 5/5], and LCPC/PVA/chitosan blends [LCPC(w)/PVA(w)/chitosan(w) = 0.25/5/0.25/5/1, 0.25/5/1.5, 0.25/5/2, 0.25/5/2.5, 0.5/5/1, 0.5/5/1.5, 0.5/5/2, 0.5/5/2.5, 0.75/5/0.5, 0.75/5/1, and 0.75/5/2] were performed at concentrations of 0.05–0.5 g dl⁻¹ in HFIP(v)/water(v) = 95/5 at 30°C with an Ubbelohde-type viscometer. The FTIR spectra of polymer blends were obtained with a spectral resolution of 1 cm⁻¹ on a Jasco FTIR-350 spectrometer by the KBr disk method. The SEM photographs of fractured surfaces of polymer blends were taken on a scanning electron mi-

croscope (Hitachi S-800) after coating with gold (~40 Å) on a Hitachi E-102 ion sputter coater by using an accelerating voltage of 10 kV.

RESULTS AND DISCUSSION

Viscosity measurements

The miscibility of binary LCPC/PVA and ternary LCPC/PVA/chitosan polymer blend systems was evaluated by the viscosity measurements in HFIP(v)/water(v) = 95/5.

The viscometry is a simple and convenient method for investigating the interaction and the miscibility in solutions of polymer blends. There is a correlation between solution-state miscibility evaluated by the viscosity method and bulk solid-state miscibility of polymer blends.^{18,19} Thus, the viscometric technique predicts the miscibility in the solid state of polymer blends: interaction parameter term, Δb , obtained from the Krigbaum equation, is positive for the miscible polymer blends and negative for the immiscible polymer blends, respectively.^{18–22}

As proposed by Krigbaum and Wall,²⁰ the specific viscosity η_{spm} of a solution of polymer blends can be express as

$$\eta_{\text{spm}} = [\eta_1]C_1 + [\eta_2]C_2 + b_{11}C_1^2 + b_{22}C_2^2 + 2b_{12}C_1C_2 \quad (1)$$

where $[\eta_1]$ and $[\eta_2]$ are the intrinsic viscosities of component polymers 1 and 2, C_1 and C_2 are the concentrations of component polymers 1 and 2 in the solution of polymer blend, b_{11} and b_{22} are specific interaction coefficients of component polymers 1 and 2 in single polymer solutions, respectively, and b_{12} is the interaction coefficient for the polymer blend of component polymers 1 and 2.

The coefficient b_{11} is related to the constant k in the Huggins eq. (2), when component polymer 1 is in the solution alone. This also applies to b_{22} ,

$$\eta_{\text{sp}}/C = [\eta] + k[\eta]^2C \quad (2)$$

The relationship between b_{11} and k can be written as

$$b_{11} = k_1[\eta_1]^2 \quad (3)$$

where k_1 is the Huggins constant for component polymer 1 in solution. The theoretical interaction coefficient between the two polymers, b_{12}^* , can be expressed as

$$b_{12}^* = (b_{11}b_{22})^{1/2} \quad (4)$$

As described by Krigbaum and Wall,²⁰ information on the intermolecular interaction in binary polymer blends (polymer 1 and polymer 2) can be obtained

TABLE I
 Δb Values of Binary Polymer Blends Composed of
 LCPC, PVA, and Chitosan

No.	LCPC(w)/PVA(w)/chitosan(w)	Δb (dl ² g ⁻²)
1	0.25/5/0	0.04
2	0.50/5/0	0.04
3	0.75/5/0	0.04
4	0/5/0.1	0.83
5	0/5/0.3	2.10
6	0/5/1.0	6.03
7	0/5/5.0	15.4
8	5/0/0.1	-6.02
9	5/0/0.3	-7.76
10	5/0/1.0	-8.58
11	5/0/5.0	-11.0

from a comparison of experimental interaction coefficient b_{12} and the theoretical b_{12}^* values. Hence, the miscibility of binary polymer blends can be simply characterized by the interaction parameter term Δb :

$$\Delta b = b_{12} - b_{12}^* \quad (5)$$

As described above,¹⁸⁻²² positive values of Δb refer to attractive intermolecular interaction and miscibility in binary polymer blend systems, while negative values are found for solutions of immiscible polymer blends.

In this work, we have used the above eqs. (1)-(5) and determined the interaction parameter term Δb to evaluate the miscibility of binary LCPC/PVA and ternary LCPC/PVA/chitosan polymer blend systems. For the ternary LCPC/PVA/chitosan polymer blends, the LCPC/PVA system and the chitosan can be treated as component 1 and component 2 in eq. (1), respectively. b_{12}^* is calculated by using eq. (4). b_{11} and b_{22} can be assumed to be experimentally determined values by using eq. (3) for the LCPC/PVA blend and the chitosan. Δb values are calculated from eq. (5). The Δb values for the binary LCPC/PVA, LCPC/chitosan, and PVA/chitosan blends are listed in Table I. Figure 1 shows the effect of chitosan concentration on the Δb value in the binary LCPC/chitosan and PVA/chitosan blends. In Figure 2, a relationship between the additional concentration of chitosan and the Δb value in the ternary polymer blend systems (LCPC/PVA/chitosan) are presented. From Table I, the Δb values for binary LCPC/PVA blends are positive, but are very low and close to zero. This suggests that the LCPC/PVA blends form a miscible phase, but the attractive intermolecular interaction between the LCPC and the PVA is very weak. These facts support our previously reported results that the LCPC forms partially miscible binary polymer blends with the PVA and the miscibility between them is very low. In addition, the Δb values in the binary LCPC/chitosan blends are negative over the entire additional concentrations of

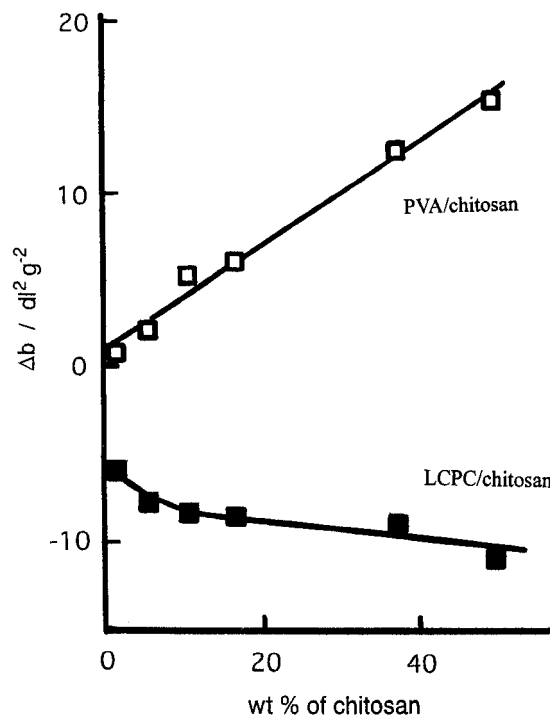


Figure 1 Relationship between concentration of chitosan and Δb value in binary LCPC/chitosan and PVA/chitosan blends.

chitosan, but are positive in the binary PVA/chitosan blends, as shown in Table I and Figure 1. It means that the former is immiscible, but the latter is miscible.

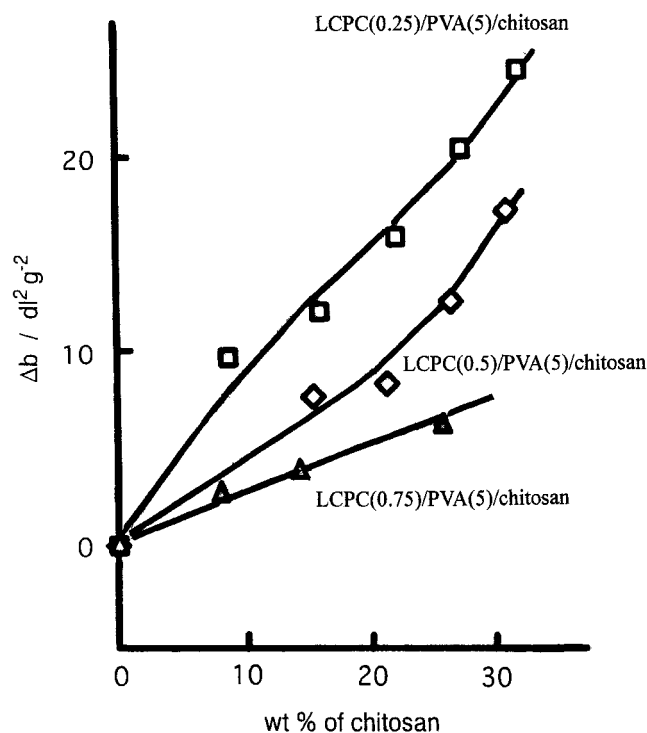


Figure 2 Relationship between concentration of chitosan and Δb value in ternary LCPC/PVA/chitosan blends.

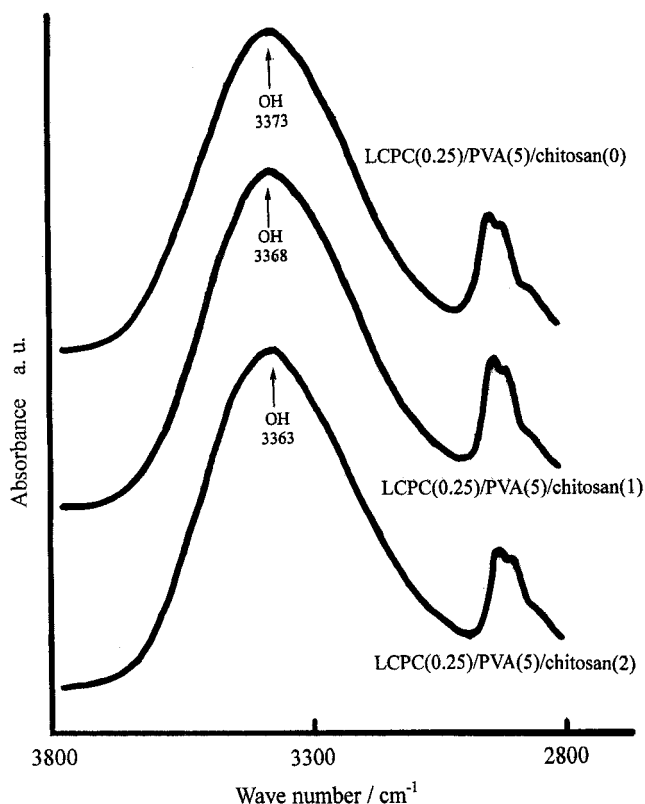


Figure 3 Scale-expanded FTIR spectra of LCPC(0.25)/PVA(5)/chitosan blends in the range of 2800–3800 cm^{-1} .

Therefore, the chitosan is expected to behave as a compatibilizer for the binary LCPC/PVA blends. The chitosan was added into the low-miscible LCPC/PVA blend systems as the ternary component and the additional effect of chitosan as a compatibilizer on the miscibility and the morphology was evaluated in three ternary LCPC/PVA/chitosan polymer blend systems. As shown in Figure 2, the Δb values drastically increase with an increase of chitosan concentration in all the ternary polymer blends. The values tend to increase with a decrease in the additional concentration of LCPC. In the two ternary LCPC(0.25)/PVA(5)/chitosan and LCPC(0.5)/PVA(5)/chitosan blend systems, the Δb 's are higher than those for the miscible PVA/chitosan blends. The values in the LCPC(0.75)/PVA(5)/chitosan blends are lower than those for the PVA/chitosan blend systems, but are positive in all the chitosan concentrations. These facts show that the LCPC and the chitosan govern the miscibility in the ternary blends. The chitosan especially acts as a good compatibilizer for the low-miscible LCPC/PVA blends and dramatically improves the miscibility between the LCPC and the PVA.

From these results, it is suggested that, in the binary PVA/chitosan blends and the ternary blend systems of the LCPC/PVA/chitosan, attractive interaction acts between the component polymers and the blend systems show the miscibility due to the additional effect of chi-

tosan as the binary or ternary component, but the binary blends of LCPC and chitosan are immiscible by repulsive interaction. Intermolecular hydrogen-bonding interactions due to the side-chain hydroxy group of PVA and the amino and hydroxy groups of chitosan probably play an important role in enhancement of the miscibility in these kinds of polymer blends.

FTIR analyses

The FTIR spectrometry is a powerful technique to detect the specific interaction between component polymers in the blend systems. Absorption bands based on hydroxy and carbonyl stretching in the FTIR spectrum is sensitive to the hydrogen-bonding formation.^{8,23} As described above, the intermolecular hydrogen-bonding interaction between the LCPC, the side-chain hydroxy group of PVA, and the amino and hydroxy groups of chitosan is the most likely candidate of the specific interaction in the LCPC/PVA/chitosan blends.

The FTIR spectra of binary LCPC/PVA and ternary LCPC/PVA/chitosan blends were measured and the specific interaction between the LCPC, the PVA, and the chitosan chains was evaluated. In Figures 3 and 4, scale-expanded FTIR spectra for the binary and the ternary LCPC(0.25)/PVA(5)/chitosan(0–2.0) and

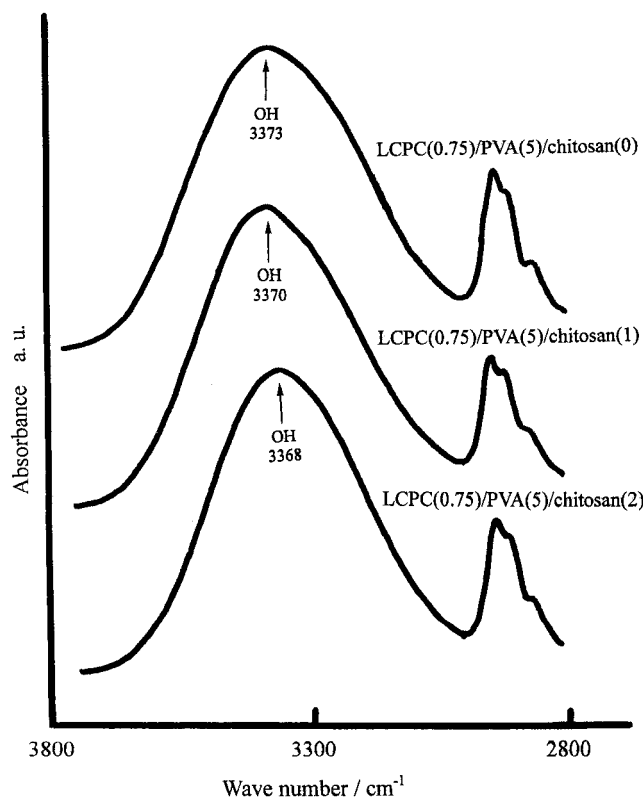


Figure 4 Scale-expanded FTIR spectra of LCPC(0.75)/PVA(5)/chitosan blends in the range of 2800–3800 cm^{-1} .

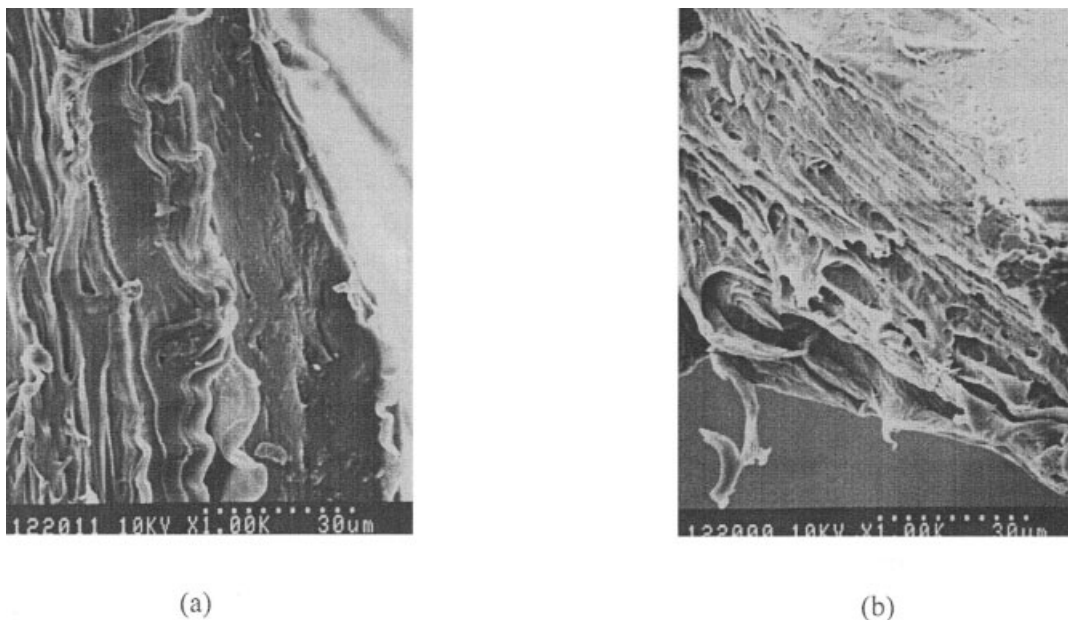


Figure 5 SEM photographs of fractured surfaces of (a) LCPC(0.25)/PVA(5) and (b) LCPC(0.25)/PVA(5)/chitosan(2) blends.

LCPC(0.75)/PVA(5)/chitosan(0–2.0) blends in the range of $2800\text{--}3800\text{ cm}^{-1}$ are shown, respectively. The OH stretching absorption bands at 3373 cm^{-1} observed in the binary LCPC/PVA blends were shifted into lower wave numbers by $5\text{--}10\text{ cm}^{-1}$ with the addition of chitosan as the ternary component in the blends of LCPC and PVA. The shift to the lower wave numbers tends to increase with the decrease of LCPC additional concentration to the PVA (lower wave number in the LCPC-poor blends). This is indicative of

the intermolecular hydrogen-bonding interaction in the ternary LCPC/PVA/chitosan polymer blends and the better miscibility in the LCPC-poor ternary polymer blends.

SEM observations

In our previous article,¹² we reported that the PVA-rich LCPC/PVA binary blends show better morphology than those of the PVA-poor blends. The SEM

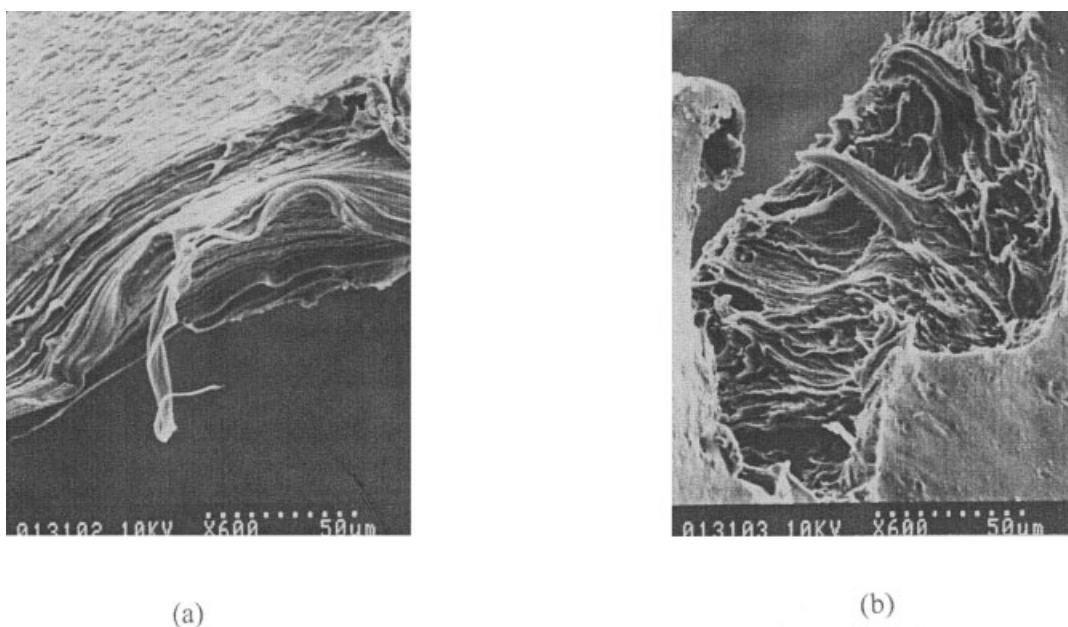


Figure 6 SEM photographs of fractured surfaces of (a) LCPC(0.5)/PVA(5) and (b) LCPC(0.5)/PVA(5)/chitosan(2) blends.

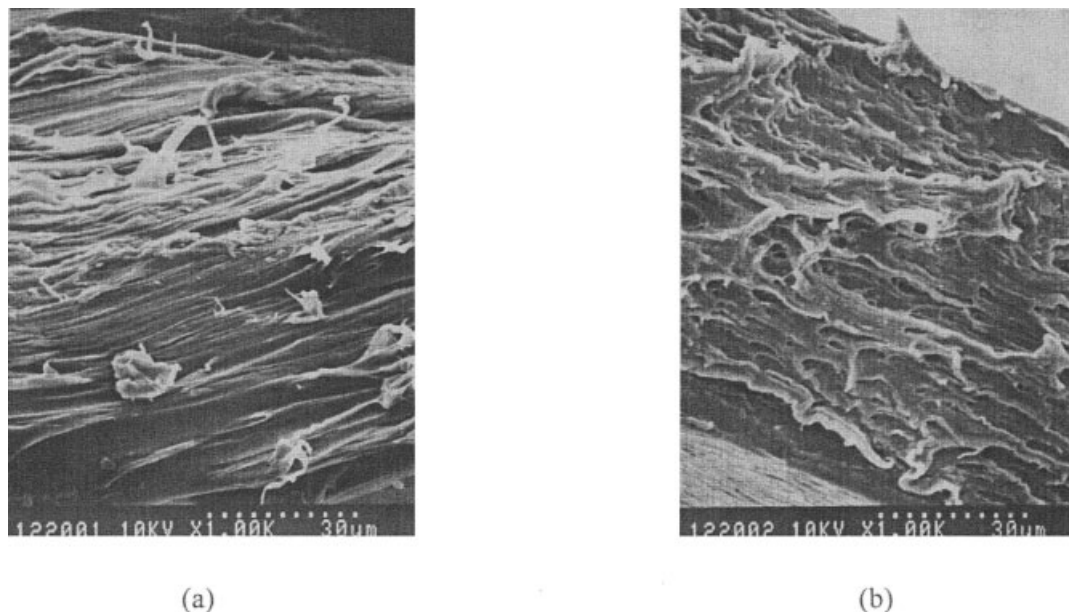


Figure 7 SEM photographs of fractured surfaces of (a) LCPC(0.75)/PVA(5) and (b) LCPC(0.75)/PVA(5)/chitosan(2) blends.

photographs for fractured surfaces of binary and ternary blend samples were taken to confirm the miscibility and the morphology of blends of LCPC, PVA, and chitosan and to disclose the correlation to the viscosity measurements and the FTIR analyses.

In Figures 5-7, the SEM photographs of fractured surfaces of the binary LCPC/PVA and the ternary LCPC/PVA/chitosan blend systems are presented. They indicate that the ternary LCPC/PVA/chitosan blends form clear fibril structures based on the miscibility by the interaction between the LCPC, the PVA, and the chitosan. In the binary LCPC/PVA blends, both the miscible and the immiscible parts are found to coexist owing to the partial miscibility between the LCPC and the PVA, but clear phase-separated domain and fibril structures are not observed. In addition, the photographs show that the miscibility and the morphology of these blends become poor with the increase of LCPC (LCPC-rich) concentration. These observations support the above-mentioned results concerning the viscosity measurements and the FTIR analyses, which describe that the LCPC-poor and the chitosan-rich ternary LCPC/PVA/chitosan polymer blends show better miscibility and the chitosan acts as a compatibilizer for the binary LCPC/PVA blends.

CONCLUSION

The viscosity measurements suggested that the binary PVA/chitosan and all the ternary LCPC/PVA/chitosan blend systems have positive Δb values because of the attractive intermolecular interaction, which refer to the miscibility in the blend systems. The binary blend systems composed of the LCPC with the chi-

tosan showed negative Δb values and were immiscible by the repulsive interaction.

The FTIR analyses and the SEM observations supported these data. In the ternary LCPC/PVA/chitosan blends, the FTIR absorption bands of the OH group observed in the binary blends of the LCPC and the PVA were shifted to lower wave numbers by 5–10 cm^{-1} by increasing the additional concentration of chitosan. This is indicative of the specific interaction and the miscibility between the LCPC, the PVA, and the chitosan. In the SEM photographs of fractured surfaces of the ternary blends composed of the LCPC, the PVA, and the chitosan, clear fibril structures showing the better miscibility than the binary LCPC/PVA blends were seen. From these results, it is suggested that the chitosan acts as a compatibilizer to the binary LCPC/PVA blends and improves the miscibility. The side-chain hydroxy group of the PVA and the amino and hydroxy groups of chitosan play a role in the formation of miscible phase due to the intermolecular hydrogen-bonding interaction in the ternary blends of the LCPC, the PVA, and the chitosan.

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