

Thermal Analysis and Miscibility of Chitin/Polycaprolactone Blends

ANLE YANG,¹ RENJIE WU,¹ PINFANG ZHU²

¹ State Key Laboratory of Metal Matrix Composites, Shanghai Jiao Tong University, Shanghai 200030, China

² Physical-Chemical Analysis Center, Shanghai Jiao Tong University, Shanghai 200030, China

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ABSTRACT: Chitin/polycaprolactone (PCL) blends were prepared by melt-blending of chitin and PCL with varying amounts of chitin. Thermal analysis of DSC, DMTA, and FTIR were used to characterize the blends. Results showed that increases in the amount of chitin did not cause a decrease in either the melting point or the crystallization point of PCL. The loss-modulus curve did not show a change of glass-transition temperature (T_g) from a dynamic temperature ramp test, which revealed that the pure chitin/PCL blend was not miscible at any ratio. When chitin *n*-butyrate (CB) was partly substituted for chitin in the blend, both the melting point and crystallization point of the PCL component was depressed, which implied an improvement of the miscibility of the blend. Furthermore, FTIR characterization suggested an interaction between the components. However, T_g did not change compared to that of the pure PCL in the loss-modulus curve, that is to say, that the modification of the miscibility by the introduction of CB to the blend lay only in the interfacial region, although not at the molecular level. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 3117–3123, 2001

Key words: chitin; PCL; blends; thermal analysis; miscibility

INTRODUCTION

Chitin [poly(*N*-acetyl-D-glucosamine)] is a polysaccharide that is widely distributed in nature as a component of the cell wall of various fungi as well as the shell of insects and crustaceans. Because chitin and its derivatives have excellent biocompatible and biodegradable properties, they are widely used as biomedical materials such as sutures and controlled drug-release vehicles.^{1–3} However, chitin does not dissolve in common sol-

vents nor does it have a melting point because of its strong micellar structure with strong intra- and intermolecular hydrogen bonds,⁴ so there have been various attempts to improve its solubility through acetylation,^{5–7} etherification,⁸ graft copolymerization,^{9,10} and so forth. Nevertheless, no melting behavior was obtained through these methods, so that chitin still cannot be plasticized and fabricated into different forms.

Blending is an especially important process for developing industrial applications of polymeric materials and compatibility among components has a marked influence on the physical properties of polymer blends.¹¹ Blending natural polymer with synthetic polymer seems to be an interesting way of preparing polymeric composites. Many blends of cellulose derivatives such as cellulose

Correspondence to: A. Yang (yanganle@yahoo.com).
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Table I Designation of Different Compositions

| | CP64 | CP55 | CP46 | CP37 | CPB5 | CPB15 | CPB25 |
|------------|------|------|------|------|------|-------|-------|
| Chitin (%) | 60 | 50 | 40 | 30 | 45 | 35 | 25 |
| PCL (%) | 40 | 50 | 60 | 70 | 50 | 50 | 50 |
| CB (%) | | | | | 5 | 15 | 25 |

nitrate ester/polyvinyl alcohol (PVA), poly(methyl methacrylate) (PMMA), and polyvinylpyrrolidone (PVP) have been extensively investigated.^{12–14} However, because of poor solubility, few chitin blends have been studied, except blends of chitin/PVA^{15,16} and chitosan/poly(ethylene oxide).¹⁷

Polycaprolactone (PCL) is another biocompatible polymer and has slower biodegradation *in vivo* than does poly(L-lactic acid) (PLLA).^{18,19} Moreover, PCL is known both to have a very low melting point and to be miscible with many polymers such as cellulose nitrate,²⁰ cellulose butyric ester,²¹ poly(vinyl chloride) (PVC),²² and so forth. PCL is used to react with cellulose acetic ester in the presence of catalyst to obtain plasticized cellulose.²³ In view of the similar molecular structures of chitin and cellulose, the blending of chitin and PCL should combine not only good biocompatibility and slower degradation *in vivo* of both components, but also excellent processibility of PCL. Therefore the blend is a good candidate for preparation of bioabsorbable materials used in various medical fields.

In this investigation, we prepared chitin/PCL blends (in our lab) using a Haake Rheometer mixer for melt-blending of chitin and PCL, both of which have hydrogen-bonding groups such as acetamide, hydroxyl, and ester groups that allow for inter- and intramolecular interactions. Furthermore, chitin *n*-butyrate was added to improve the miscibility between chitin and PCL. Thermal analyses of DSC, DMTA, and FTIR were conducted to study the interaction and miscibility of the blends.

EXPERIMENTAL

Materials

β -Chitin, made available to us from Textile University (China), was dried at 80°C in a vacuum oven before use. PCL was purchased from Fluka Chemie (Buchs, Switzerland). Chitin *n*-butyric es-

ter was prepared (in our lab) by the method of Kaifu et al.⁶

Preparation of Blends

Chitin and PCL were mixed at 200°C in the Haake Rheometer mixer until torque reached balance. The blend ratios were 60/40, 50/50, 40/60, and 30/70 wt % and designated as CP64, CP55, CP46, and CP37, respectively. Chitin *n*-butyrate (CB) was partly substituted for chitin at levels of 5, 15, and 25 wt % to CP55 and designated as CPB5, CPB15, and CPB25, respectively. All of the compositions and processing conditions are shown in Table I.

Characterization

The DSC analysis was conducted in a DSC SP instrument (Rheometric Company) under a protective nitrogen gas atmosphere. The ramping heating process was performed from 0 to 160°C at a rate of 10°C/min, then kept at that temperature for 3 min, followed by the cooling process to 0°C at a rate of 10°C/min. The DMTA study was conducted in a DMTA IV machine (Rheometric Company), and the samples were mold-pressed at 120°C for the measurements. The temperature ramping sweep was from –100 to 60°C at a rate of 3°C/min. A Fourier transform infrared spectrometer (FTIR, Equinox 55) was employed to confirm the structures of different blend compositions by the KBr disk method.

RESULTS AND DISCUSSION

Effects of Chitin Amount on the Melting and Crystallization Processes of Blends

Figure 1, which gives the DSC curves of pure chitin and pure PCL, shows that chitin had a wide but weak endothermic peak at about 50–140°C, attributed to the evaporation of chitin's binding

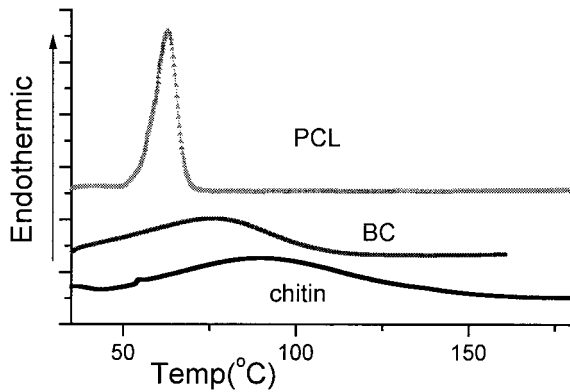


Figure 1 DSC curves of chitin, PCL, and chitin *n*-butylate.

water, whereas PCL had a strong and sharp melting peak.

Figure 2 illustrates the heating and cooling DSC curves for the blends with various amounts of chitin. For the heating process, the endothermic peak of binding water evaporation for chitin was superposed with the melting endothermic peak of PCL. However, the effect of the evaporation of binding water on the melting peak was negligible as a result of the weakness of the former peak and the comparatively very sharp peak of the latter one. Therefore, the peaks in Figure 2 were used to denote the melting point of the PCL component in the chitin/PCL blends. For the cooling process, there was no evaporation of binding water for chitin, so the peak in the DSC curve was attributed to the crystallization point of the PCL component. The data from the DSC

curves of the components and the corresponding blends are shown in Table II. It was found that the melting point changed only slightly in the heating process; however, the crystallization point in the cooling process was obviously depressed with the decrease of PCL content. Moreover, both the magnitude of the melting peak and the crystallization exothermic enthalpy were reduced with the decrease of PCL content. In the blend with the second component, chitin reduced the packing density of PCL, so the molecules were difficult to pack and crystallize—a kind of diluting effect—thus resulting in the crystallization point depression.

Effect of Chitin Amount on the Dynamic Mechanical Thermal Analysis (DMTA) of the Blends

Figures 3 and 4 illustrate the DMTA curves of the blends with changes in the amount of chitin, which showed that increasing the amount of chitin enhanced the storage modulus (E'), the loss modulus (E''), and the loss factor. In the E' curve there was a plateau from -100 to -70°C , followed by a gradual decrease of the modulus resulting from the glass transition of the PCL component in the amorphous region. Actually, such a decrease was more obvious for PCL and CP37 than for the others because of the larger amounts of PCL in the blends. The PCL component would soften when the temperature neared the melting point (60°C), and thus the storage modulus for the blends decreased steeply so that the test had to be stopped.

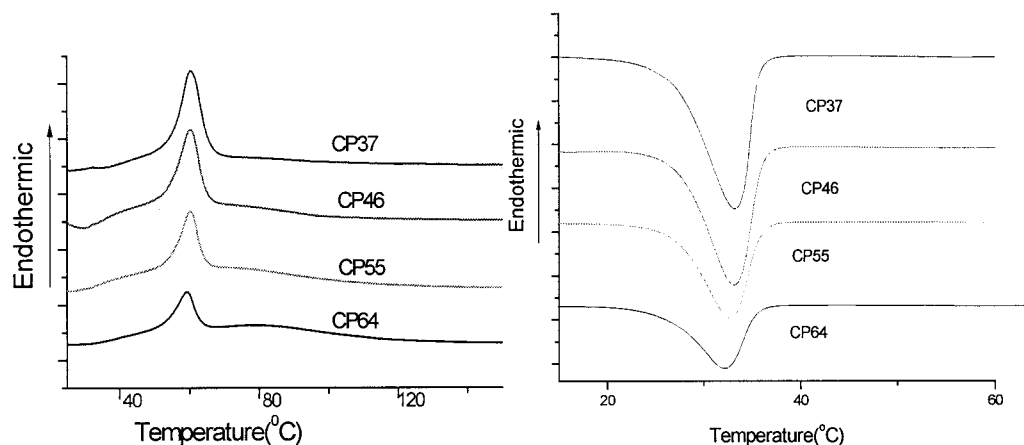


Figure 2 Effects of blend ratio on the DSC ramping analysis of blends: (a) heating process; (b) cooling process.

Table II T_m , ΔH_m , T_c , ΔH_c of Chitin (CH), CB, PCL, and the Corresponding Blends

| | CH | CB | PCL | CP64 | CP55 | CP46 | CP37 | CPB5 | CPB15 | CPB25 |
|--------------------|----------------|----|------|------|------|----------------|------|------|-------|-------|
| T_m (°C) | — ^a | — | 63.0 | 59.8 | 60.4 | 60.4 | 60.5 | 59.4 | 59.4 | 59.1 |
| ΔH_m (J/g) | — | — | 54.2 | — | — | — ^b | — | — | — | — |
| T_c (°C) | — | — | 33.6 | 32.5 | 33.2 | 33.2 | 33.3 | 31.2 | 30.8 | 27.5 |
| ΔH_c (J/g) | — | — | 43.0 | 11.8 | 16.3 | 20.1 | 26.5 | 16.4 | 14.9 | 14.6 |

T_m , melting point of PCL; ΔH_m , melt enthalpy of PCL; T_c , crystallization point of PCL; ΔH_c , crystallization enthalpy.

^a Chitin and CB have no melting point.

^b Because the melting endothermic peak for PCL is superposed with the endothermic peak of water vapor evaporation for chitin, the endothermic enthalpy of PCL cannot be evaluated.

Because the appearance of the E'' peak in the transition region was accompanied by the enormous decrease of E' , the $\text{tg}\delta$ ($= E''/E'$) curve did not show the regular loss peak. Consequently for a semicrystalline polymer such as PCL, unlike rubbers where one can use the peak of $\text{tg}\delta$ to determine the glass-transition temperature, one can only use the peak of E'' to characterize T_g in a DMTA test. The E'' versus temperature curve showed that the loss peaks for all the compositions were almost at the same temperature, despite being of different magnitudes, which accounted for the ineffectiveness of the chitin component to change the glass transition of PCL. Therefore, it meant the chitin/PCL blend was not miscible at the molecular level.

Effect of CB Addition on the DSC Analysis of Blends

The DSC data for blends with partial substitution of chitin *n*-butyrate for chitin at levels of 5, 15, and 25 wt % are shown in Table II, which confirms that both the melting points and the crys-

tallization points were all depressed; the latter depression was obvious with the increase of the substitution content of chitin *n*-butyrate.

As suggested by Nishi and Wang,¹⁴ the melting point depression for compatible blends is predicted by the equation

$$\frac{1}{T_m} - \frac{1}{T_m^0} = -\frac{RV_2}{\Delta H_2 V_1} \chi_{12}(1 - \phi_2)^2$$

where T_m^0 is the melting temperature of the pure crystalline polymer; ϕ_2 is the volume fraction of the crystalline polymer component; T_m is the value for a blend containing ϕ_2 volume fraction of the crystalline polymer component; V_2 is the molar volume fraction of the second amorphous component; V_1 is the molar volume of the repeating unit of the second component; ΔH_2 is the enthalpy of fusion per mole of repeating unit of 100% crystallized polymer; and χ_{12} is the interaction parameter. Values of R , ΔH_2 , V_1 , and V_2 are all greater than 0, so depression of the melting point reflects the negative value of χ_{12} ; moreover, the

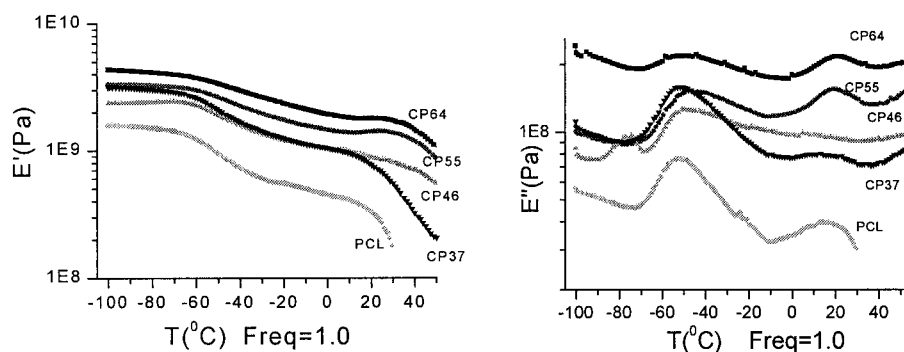


Figure 3 (a) E' and (b) E'' curves in the ramping test of blends with varying amounts of chitin.

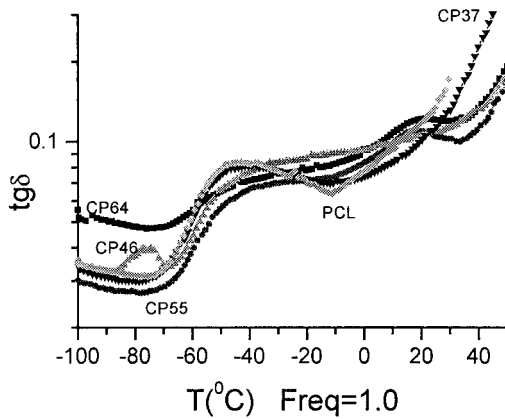


Figure 4 $\text{tg}\delta$ ($= E''/E'$) curves of blends with change in amount of chitin.

increased depression of the melting point reflects the smaller value of χ_{12} . From the preceding relation and analysis, for polymer blends in which one of the components crystallized, a depression in the melting point reflects a specific interaction between the two components.

Like chitin, chitin *n*-butyrate has no melting point and its addition could be considered as a second amorphous component with a powder form in the blend. This effect on the properties of PCL lies only in the interfacial region and thus is limited.

Because the density of chitin *n*-butyrate is similar to that of chitin, the effect of partial substitution of chitin *n*-butyrate for chitin on the volume fraction of the chitin component in the blend is very small and can be disregarded. Thus, the fact that the melting point of PCL was clearly depressed with the increase of chitin *n*-butyrate

content reflected the increase of compatibility of the blends.

The packing of side butyric groups between chitin molecules extended the intermolecular distance and reduced the intra- and intermolecular hydrogen bonds, resulting in the decrease in solubility parameter, which enhanced the solubility of chitin *n*-butyrate in such common solvents as acetone, acetic acid, and DMSO. Moreover, CB was well dispersed and partly soluble in the caprolactone monomer, which might be ascribed to its having the same ester group as did PCL, and implied the specific interaction of chitin *n*-butyrate with PCL. Thus, there was an enhancement of the interaction of the chitin/PCL blend upon the addition of chitin *n*-butyrate, with a concomitant improvement of compatibility.

The crystallization peak was depressed more obviously than was the melting point, which is ascribed not only to the aforementioned dilution effect but also to the retardation of crystallization of PCL by CB in the cooling process.

Effect of CB Addition on the DMTA Analysis of the Blends

The E' and E'' versus temperature curves of the blends with the addition of different levels of CB are shown in Figure 5, which confirms that both the transition region and the magnitude of E' of CPB5 are similar to those of CP55, and that the transition for CPB25 is broader and steeper. However, the glass-transition temperature of the PCL component, with the change of CB content, was almost the same as that of CPB25, whereas the melting point of PCL was depressed with the

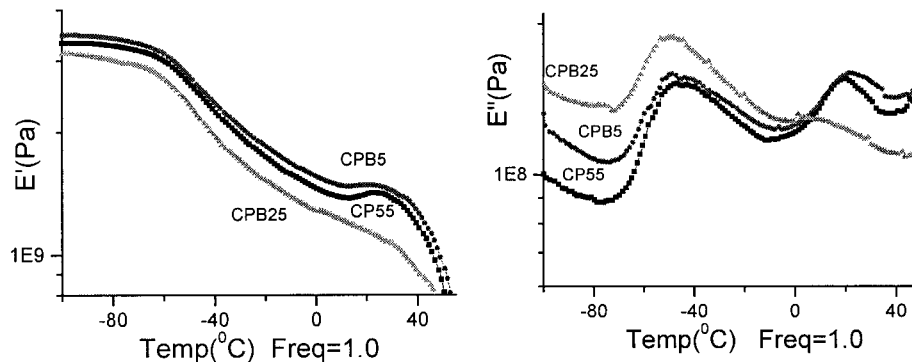


Figure 5 (a) E' and (b) E'' curves of blends with the addition of varying amounts of CB.

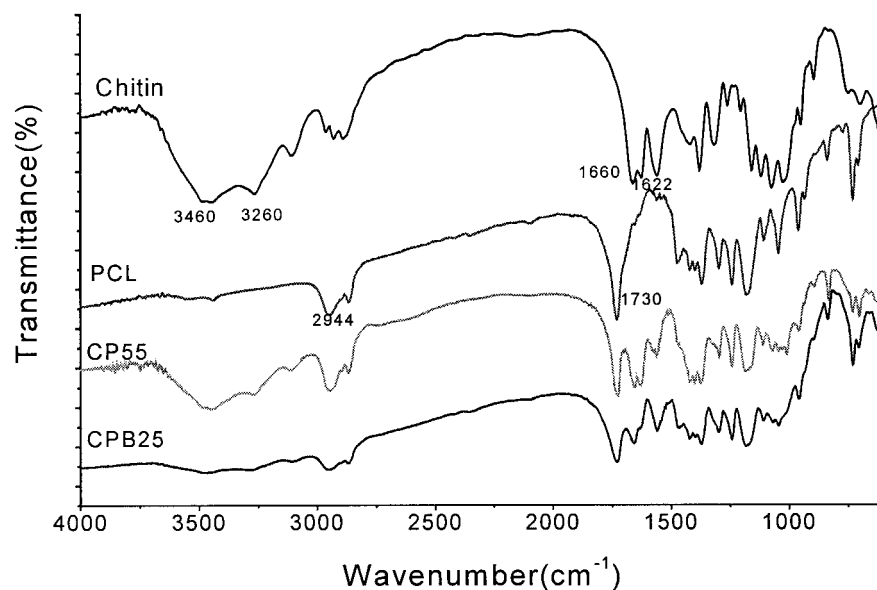


Figure 6 FTIR characterization of blends with chitin *n*-butyrate.

substitution of CB for chitin in the DSC analysis and the T_g of PCL was not changed. Therefore, the addition of chitin *n*-butyrate to the blends improved the miscibility of the two components. However, this miscibility was not at the molecular level because of the infusibility of the CB particle; rather, the miscibility was only in the interfacial region, by reason of the introduction of flexible polar butyryl groups, which not only split the hydrogen bonds but also intensified the interaction between PCL and chitin.

FTIR Characterization of Chitin/PCL Blends with Chitin *n*-Butyrate

There were dual peaks at 1660 and 1622 cm^{-1} for the acetamide group, typical for β -chitin, and a peak at 1730 cm^{-1} for the ester group, typical for PCL, as shown in Figure 6. It is clear that the spectrum for CP55 is simple superposition and keeps all the peak information for both chitin and PCL. However, for CPB25, the ester group of PCL at 1730 cm^{-1} , the acetamide group at 1622 cm^{-1} , and the hydroxyl group at 3460 and 3260 cm^{-1} were all obviously reduced. This implies that the effect of β -chitin on the blend was greatly reduced with the addition of chitin *n*-butyrate and, furthermore, the interaction between chitin *n*-butyrate and PCL resulted in the weaker absorption peak of the ester group of the PCL component.

CONCLUSIONS

The results of thermal analyses and FTIR characterization of chitin/PCL blends show that pure chitin was immiscible with PCL. Moreover, partial substitution of CB for chitin resulted in depression of the melting point and the crystallization point of the PCL component, although there was no change for the glass-transition temperature from the DMTA test. Therefore, it might be concluded that the miscibility was improved to a very limited level by the addition of CB powder. Enhancement of the interfacial compatibility between the components might result from the interaction between the ester groups of PCL and the flexible butyryl group of CB.

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