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Comparison of Interaction and Compatibility in the Blends of Poly(ε-caprolactone) with Cellulose Derivatives

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The hydrogen-bonding interaction between poly(ε-caprolactone) (PCL) and cellulose derivatives—nitrocellulose (NC), ethyl cellulose (EC) and cellulose carbamate (CC) has been studied by Fourier Transform Infrared. The FTIR results revealed that in PCL/NC blends the hydrogen-bonded carbonyl was dominant when NC content was more than 50%. Cellulose carbamate had the substituting groups with more protons, could form very strong intramolecular interaction. The hydrogen-bonding interaction between PCL and CC could not be observed in infrared spectra. In PCL/EC blends, the intermolecular interaction existed between two components although the intensity of this interaction was weaker than that of PCL/NC blends. DSC measurements showed that the addition of NC gave the most evident affection for the crystallization behaviour of PCL. The influence of EC, CC on the crystallization behaviour of PCL was lower than that of NC, gradually. So we could conclude that the substituting groups of cellulose derivatives could affect the compatibility of the blends including PCL obviously.

Key Words: Hydrogen-bonding interaction, Compatibility, Cellulose derivatives, Poly(ε-caprolactone), Blends, Intramolecular.

INTRODUCTION

Fourier transform infrared (FTIR) spectroscopy has been employed to study a large number of compatible polymer blends. The FTIR method can give useful information concerning the presence and nature of specific interactions and conformational changes that occur on blending two compatible polymers[1–7]. Coleman *et al.*[7, 8] have published a series FTIR result of the binary blend systems where one of the components was a polyester, especially poly(ε-caprolactone) (PCL). In fact, PCL has become almost a typical component in binary polymer blend studies. This is because PCL can be compatible with a wide variety of chemically distinct polymeric materials as a crystallizable component. These

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compatible blends exhibit a significant shift of the carbonyl bond with composition in FTIR spectra. The shift has been associated with a hydrogen-bonding interaction between the carbonyl groups of the polyester and the proton donator of the other polymers.

On the other hand, natural cellulose and its derivatives, with semi-rigid main chains, have been studied widely because of their properties[6, 9, 10]. The results indicated that for the most cellulose derivatives, PCL was an effective plasticizer that gave cellulose blends easier to process and more flexible than the pure cellulose esters and ethers. However, the compatibility in these binary blends, which is related to the interaction intensity and species existing between PCL and the second components, affect the action of PCL to the cellulose derivatives. In the present work, the FTIR spectra of the blends of PCL with cellulose derivatives—nitrocellulose (NC), ethyl cellulose (EC) and cellulose carbamate (CC) have been studied. The results indicate that the strength of the intermolecular interaction changed with the substituting groups. In PCL/NC blends, the strong intermolecular interaction exists. But in PCL/CC blends there is strong intramolecular interaction. The strength of the intermolecular interaction affects the compatibility of the blends. The differential scanning calorimeter (DSC) displayed that the PCL/NC blends are compatible while the PCL/CC blends are almost incompatible.

EXPERIMENTAL

Poly(ε-caprolactone) was synthesized by bulk polymerization and characterized by using a gel permeation chromatograph (GPC)/SEC (Viscotek Co.), with tetrahydrofuran as solvent at 25°C. The M_w and M_n of PCL were 27,000 and 16,600, respectively. Ethyl cellulose (EC) was a commerical product with the degree of polymerization equal to 70. Elemental analysis indicated the ethyl substitution was about 1.6. The nitrocellulose (NC) used were prepared from wood pulp and contained 12.3% of nitrogen, which corresponds to 0.7 OH groups per glucose unit. The viscosity method and Mark-Houwink equation gave the M_η of NC was 113,000. Cellulose carbamate (CC) was synthesized by using microcrystalline cellulose as raw material[11]. The substitution degree of carbamate was 0.5 obtained by elementaly analysis. The degree of polymerization of CC was about 320.

Casting films from tetrahydrofuran solutions prepared PCL/NC, PCL/EC blends. Thin films of the blends prepared for the FTIR were cast from 1% (w/v) tetrahydrofuran solutions on to potassium bromide windows at room temperature. After the majority of the solvent had evaporated, the films transferred to a vacuum desiccator to remove residual solvent and stored under vacuum. All the films used in this study, were sufficiently thin to be within an absorbance range where the Beer-Lambert law is obeyed. Because CC cannot dissolve in many organic solvents, mixing the CC powder and melting PCL in nitrogen atmosphere prepared the blends of PCL/CC. Infrared spectra were obtained on a Bruker FTIR spectrometer. A minimum of 32 scans at a resolution of 2 cm^{-1} was averaged.

About 10 mg of each sample of the PCL blends with different cellulose derivatives encapsulated into an aluminum pan was used for measurements of DSC thermograms on a Perkin-Elmer Pyric-1 DSC. In the DSC apparatus, the samples were first heated at a rate of 20 to 370 K min^{-1} and maintained at this temperature for 3 min. After that the samples were cooled to 210 K at a rate of 10 K min^{-1}. The the samples were heated again from 210 to 370 K at a rate of 10 K min^{-1}. The crystallization temperature (T_c) and the melting temperature (T_m) can be obtained. The crystallinity of PCL in the blends was obtained according to the equation

$$C_r\,(\%) = \left(\frac{\Delta H_f}{X\Delta H_f^{\circ}}\right) \times 100\%$$

where ΔH_f is the apparent enthalpy of fusion per gram of the blends obtained by DSC, X is the weight fraction of PCL in the blends and ΔH_f° is the thermodynamic enthalpy of fusion per gram of completely crystalline PCL, $\Delta H_f^{\circ} = 135.5$ J/g[12].

RESULTS AND DISCUSSION

Fig. 1 gives the FTIR spectra of pure PCL recorded at melting state and solid state, respectively. It is obvious that the carbonyl stretching vibrations of PCL in the preferred (crystallized) and amorphous conformations occur at 1724 and 1736 cm^{-1} respectively, also reported by Coleman[8]. The end-groups of PCL are hydroxyl groups. It can be observed that there is the hydroxyl stretching frequency in the range from 3400 to 3600 cm^{-1}, although the absorbance is weak.

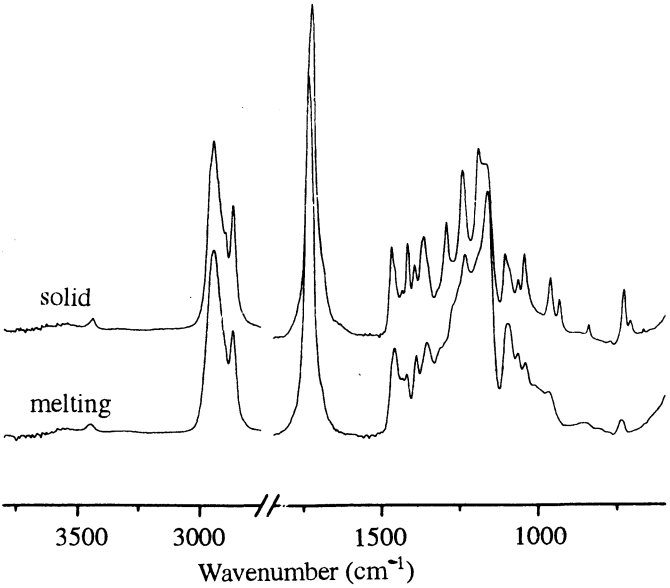

Fig. 1. The infrared spectra of pure PCL at two different states

Fig 2 shows the spectra of PCL/NC blends recorded at room temperature. This figure is split into two frequency ranges, 3700–3100 and 1800–1550 cm^{-1}. The spectrum in the region of 3700–3100 cm^{-1} of pure NC may be considered to be composed of two components: a broad band centred at 3310 cm^{-1} attributed to hydrogen bonded hydroxyl groups (self-associated) and a relatively narrow and strong band at 3570 cm^{-1} attributed to free hydroxyl groups. With the addition of PCL, significant frequency shifts and band broadening in the 3700–3100 cm^{-1} region are observed. The main band shifts to the lower frequency and closes to the hydroxyl stretching frequency of pure PCL at 3440 cm^{-1}. At the same time, the relative intensity of the hydrogen bonded hydroxyl band of NC decreases with increasing the content of PCL and this band disappears when the content of PCL is over 40%. Increasing the concentration in carbonyl groups favours the interaction of carbonyl and hydroxyl groups, leading to shifts of the hydroxyl groups from higher frequency to lower. These results indicate that the intermolecular hydrogen-bonding interaction between NC and PCL exists in the blends. This intermolecular interaction indicates that the equilibrium between the

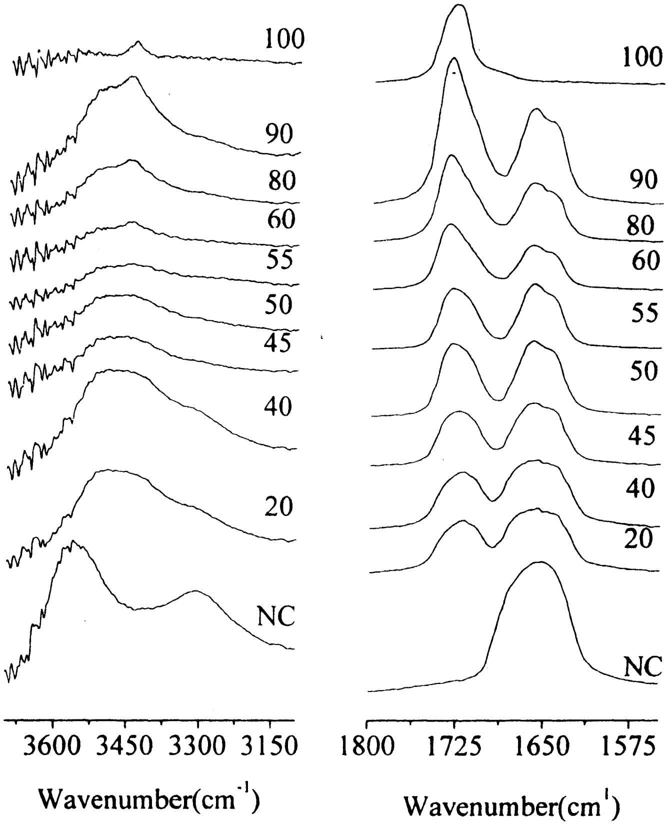

Fig. 2. FTIR spectra for PCL/NC blends in the two regions. Numbers correspond to the PCL percentage in the blends.

self-associated hydroxyl groups and the free hydroxyl groups is destructed. And the band centred at 3310 cm^{-1} also disappears gradually.

It is well known that the carbonyl stretching frequency of PCL is sensitive to the intermolecular interactions. The change of the carbonyl group band confirms further the existence of the hydrogen-bonding interaction (Fig. 2). The spectrum of pure PCL exhibits two bands: one peak at 1724 cm^{-1} as a main band and another at 1736 cm^{-1} as a shoulder. As the concentration of PCL decreases in the blend, a third band also as a shoulder centred at 1716 cm^{-1} and its relative intensity increases with the NC content. The shoulder peak at 1716 cm^{-1} has been proved to associate with the hydrogen boned carbonyl groups[6, 8]. In other words, this band indicates an intermolecular interaction involving the PCL carbonyl group and the NC hydroxyl group (*i.e.*, C═O---H—O—). Meanwhile, the peak maxima of the carbonyl group band moves from 1724 cm^{-1} for pure PCL spectrum to 1735 cm^{-1} in the spectrum of PCL/NC. Nevertheless, the apex shifts to lower frequency when the concentration of PCL in the blends decreases further. At last, the apex stays at 1720 cm^{-1} when the content of NC is more than 70% in the blends. DSC results in the next section of the present work will show that PCL cannot crystallize when the concentration of NC is more than 50% in the blends. So we may extrapolate that the hydrogen-bonded carbonyl is dominant when the concentration of PCL is less than 50% in the blends.

Intermolecular interaction in the PCL/EC and PCL/CC blends

Our previous work[13] showed that a special interaction exists between the carbonyl groups of PCL and the hydroxyl groups of EC in the PCL/EC blends. As shown in Fig. 3, with the addition of PCL, the hydroxyl band of EC shifts to the lower frequency significantly and the band broadening is observed. The maximum absorption of the carbonyl groups appears in the range 1731–1726 cm^{-1} with

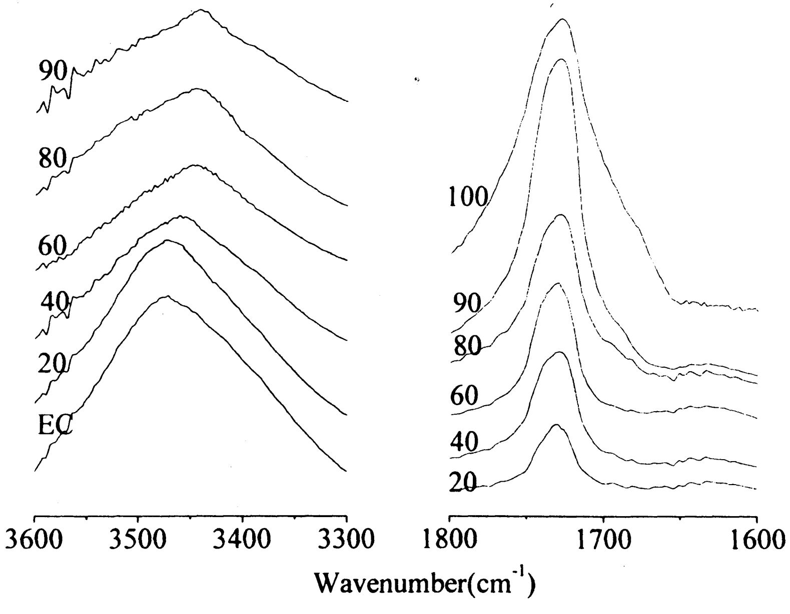

Fig. 3. FTIR spectra for PCL/EC blends in the two regions. Numbers correspond to the PCL percentage in the blends.

shoulders at 1738 cm^{-1}. When the content of EC in PCL/EC blends is more than 80%, the frequency difference between the carbonyl bands of the amorphous PCL and those of PCL in the blends is 5 cm^{-1}. Although the corresponding shift to the lower frequency of the carbonyl group bands cannot be observed directly in the IR spectra, it is evident that the hydrogen-bonding interaction between the O—H groups the C═O groups exists indeed on the basis of the change of O—H bands and C═O bands.

In the cellulose carbamates, the hydroxyl groups are substituted by the amido groups, which also are the proton donors. We can reasonably infer that the intramolecular interaction of CC (self-association of CC) is strong. Fig. 4 gives the FTIR spectra of PCL/CC blends with different PCL content. In CC spectrum, there is a strong absorption in the 3700–3100 cm^{-1} region, especially the curve exhibits a very broad and strong band centred at about 3300 cm^{-1} indicative of extensively hydrogen-bonded hydroxyl groups. It is obvious that a strong interamolecular interaction exists in CC. With increasing of PCL component in the blends, the intensity of the band at 3300 cm^{-1} decreases gradually and the

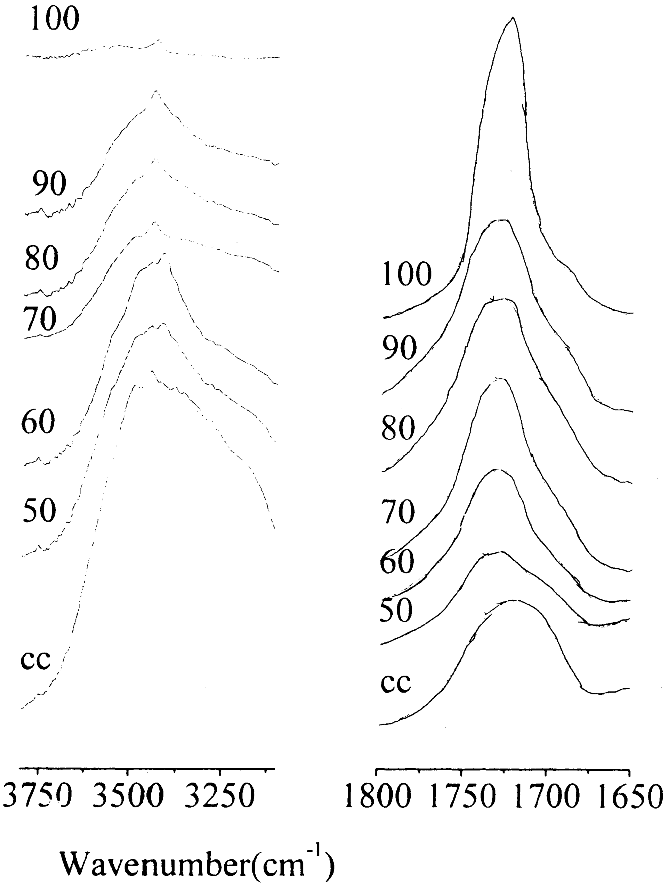

Fig. 4. FTIR spectra for PCL/CC blends in the two regions. Numbers correspond to the PCL percentage in the blends

apex of the hydroxyl band approaches to the hydroxyl band of pure PCL. Namely, the frequency difference (Δν) between the hydrogen-bonded hydroxyl groups and the free hydroxyl groups in CC decreases. Purcell and Drago[14] have shown that the Δν between the free hydroxyl absorption and those of the hydrogen-bonded species yields a measure of the average strength of the intermolecular interaction. We would anticipate that the interaction between the hydroxyl group of cellulose carbamate and the carbonyl group of PCL is much weaker than the intramolecular interaction in CC.

The change of the carbonyl band of PCL in PCL/CC blends is more complex than that of PCL in PCL/NC and PCL/EC blends. From the curve of CC, a carbonyl band attributed to CC at 1710 cm^{-1} can be observed. In fact, the carbonyl absorption in the blends of PCL/CC is composed of two components: one associated with PCL and the other with CC. In order to analyze clearly the change of carbonyl band of PCL, the differential spectrum and the curve fitting methods are used. By subtracting the spectra of the blends from the spectrum of CC using appropriate weighting factors based on the elimination of the band at 1618 cm^{-1} we obtain "pure" PCL spectra. Curve fitting for the "pure" PCL spectra reveals that three bands are necessary to satisfactorily match the spectra of the blends in the carbonyl region. The results are shown in Table-1. Curve fitting results show a slight increase in the intensity of the absorption band corresponding to the non-interacting carbonyl group of PCL and a decrease in the intensity of the absorption band related to the crystalline carbonyl groups of PCL when PCL composition decreases in blends. Only a weak band centred at about 1716 cm^{-1} is observed where we would anticipate the hydrogen-bonded carbonyl groups to absorb. It indicates that the intensity of the interaction between PCL and CC is very weak.

TABLE-1
CURVING FITTING RESULTS FOR PCL'S CARBONYL GROUPS IN PCL/CC BLENDS OBTAINED AT 25°C AFTER SUBSTRACTED

Samples	The absorbency area ratio of peaks at the range from 1675 to 1775 cm^{-1}		
	A_1 (at 1716 cm^{-1})	A_2 (at 1724 cm^{-1})	A_3 (at 1736 cm^{-1})
PCL/CC (100/0)	0.08	0.57	0.35
PCL/CC (90/10)	0.07	0.53	0.40
PCL/CC (80/20)	0.10	0.44	0.46
PCL/CC (70/30)	0.09	0.43	0.48
PCL/CC (60/40)	0.11	0.38	0.51
PCL/CC (50/50)	0.11	0.36	0.53

A_1 represented for the ratio of the absorbence area of hydrogen-bonded carbonyl to the total absorbence area of carbonyl group, A_2 and A_3 for the crystalline and amorphous of PCL respectively.

FTIR results for PCL blended with cellulose derivatives indicate clearly that the interaction relies on the substituting group and the proton numbers per glucose unit. In PCL/NC blends, the ratio of the number of hydroxyl groups to the number of carbonyl groups is rather small because nitrocellulose only has 0.7 OH groups in one glucose unit. The probability of finding a free hydroxyl group is small although the intensity of the intramolecular interaction of NC is bigger than that of the interaction between PCL and NC by FTIR spectra. On the other hand, the substituting groups of CC can provide more protons per glucose unit. The intramolecular interaction of CC is too strong to form the hydrogen-bonding interaction with PCL easily. In PCL/EC blends, because the proton numbers in one glucose unit of EC are between those of NC and CC, the intensity of hydrogen-bonding interaction should be between those of PCL/NC blends and PCL/CC blends according to the FTIR results.

DSC measurements of the blends of PCL with cellulose derivatives

The intermolecular interaction between PCL and cellulose derivatives can affect the crysallization behaviour of PCL and the compatibility of the blends. We studied the crystallization behaviour of PCL by DSC measurements. In PCL/NC blends, the crystallization temperature (T_c), the melting point (T_m) and the crystallinity (C_r) of PCL decrease significantly with increasing NC content (Table-2). When NC is more than 50% the crysallization process cannot be observed in the DSC thermograms. This means that the crystallization of PCL in the blends is difficult. The addition of NC can obviously decrease the crystallization ability of PCL. However, the three parameters (T_c, T_m, C_r) in the blends of PCL with EC change tardily with decreasing PCL content. In other words, the addition of EC can affect the crystallization ability of PCL, but the influence is weak. It has been acceptable that the weakening of the crystallization ability in the blends is a typical feature of the compatible polymer system and should be related to the change of compatibility in the blend. The better the compatibility between components, the greater the weakening of the crystallization ability of crystallizable components in the blends. In fact, the PCL/NC blend system has been affirmed to be a thermodynamic miscibility blend[6]. As pointed out in previous work[13], PCL is partially compatible with EC. Comparison with PCL/EC blends, CC affects the crystallization behaviour of PCL slightly and PCL/CC blends have lower compatibility. That the T_c of the PCL in PCL/CC is higher than that in PCL/EC is a powerful proof.

Associating the results of FTIR with DSC measurements, we can conclude that with increasing OH groups in one glucose unit (or the proton numbers per glucose unit), the probability of forming self-associated hydrogen-bonding interaction in cellulose derivatives increases obviously. And the probability of the existence of hydrogen-bonding interaction between PCL and the second components decreases, which leads to the weakening of the compatibility in the blends. Of course, the change of the interaction between two components is one of the factors that affect the compatibility of the blends.

TABLE-2
DSC RESULTS FOR THE BLENDS OF PCL WITH CELLULOSE DERIVATIVES

Blend systems	PCL content (wt. %)	Crystallinity of PCL, C_r (%)	Crystallinity temperature, T_c (°C)	Melting temperature, T_m (°C)
PCL/NC	100	64	30	57
	90	46	19	56
	80	35	15	50
	70	17	4	43
PCL/EC	90	59	20	56
	80	60	16	54
	60	56	15	54
	40	48	15	52
	20	37	12	49
PCL/CC	90	57	32	55
	80	57	32	55
	70	56	32	55
	60	55	32	56
	50	42	32	56
	20	35	26	50

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