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# Crystallizability of Poly($\varepsilon$-caprolactone) Blends with Poly(vinylphenol) under Different Conditions*

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**Abstract** The intermolecular interaction between poly(vinylphenol) (PVPh) and polycaprolactone (PCL) and the crystallization behavior of PCL in PCL/PVPh blends with different compositions and under different conditions were investigated by Fourier transform infrared spectra (FTIR) and differential scanning calorimetry (DSC). It has been shown that the PCL in the blends with different blend ratios all exists in crystalline state after solution casting, even though the crystallinity decreases with increasing PVPh content. For the melt crystallized samples, PCL in its 80/20 PCL/PVPh sample can still crystallize. The crystallinity is, however, lower than that of the solution cast sample. For blends containing 50% or 20% PCL, the as-cast samples are semicrystalline and can change to compatible amorphous state after heat treatment process. FTIR analysis shows the existence of hydrogen bonding between PCL and PVPh and the fraction of hydrogen bonds increases remarkably after heat treatment process.

**Keywords:** Poly(vinylphenol); Polycaprolactone; Polymer blends; Crystallinity; Hydrogen bonding.

## INTRODUCTION

Blending one polymer with another has been widely employed to improve the properties of polymer materials. The synergistic effect between the components with complementary properties usually results in the blends exhibiting quite new performances. It should be pointed out that the complementarities of components provide only an essential element of an effective modification of the material properties. Actually, the multiscale structures of the blend, especially the phase structure, play a crucial role in determining the final properties of the blends. This is even protruding for blends of crystalline polymers, either for crystalline/amorphous or crystalline/crystalline systems, since crystallization shows pronounced influence on the phase structure, which in turn affects the intrinsic multiscale structures of the crystalline component[1–3]. As an example, blending poly(vinylidene fluoride) (PVDF) with atactic poly(methyl methacrylate) encourages the crystallization of PVDF in its $\beta$-form with extensive piezo- and pyroelectric properties. Therefore, polymer blends with at least one crystalline component have been extensively studied[4–9].

General speaking, the phase structure of the crystalline/amorphous polymer blends depends strongly on the miscibility of the system and the crystallization behavior of the crystalline component. The miscibility lies on the inter-molecular interactions between the components, such as, hydrogen bonding (H-bonding)[10–12]. It was recognized that incorporating inter-molecular hydrogen bonds into an immiscible polymer blend can promote the

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compatibility of the system[10], which changes the phase separation behavior and the microstructure of the blends. On the other hand, the crystallization behavior relies on the processing conditions as well as the phase structure[13]. As an example, it was reported that polycaprolactone (PCL) in a solution cast 20/80 PCL/SAN (styrene-*co*-acrylonitrile) blend is crystallizable, whereas in its melt blending counterpart stays in amorphous state. This has been attributed to the different solvent evaporation rate or retention time during film formation. Furthermore, the crystallization behavior of the crystalline component will also be influenced by the incorporated H-bonding. For example, through blending PCL with three different polymers, it has been confirmed that hydrogen bonding strength has a greater effect on the crystallization rate of PCL than does the influence of glass transition temperature of the blends[11]. The same result has been reported by Talibuddin and coworkers in their studies on the crystallization of PEO in its blend with ethylene-methacrylic acid or styrene-*p*-hydroxystyrene copolymers. They found that the amorphous components can segregate over a great distance regardless of their glass transition temperatures. This leads to the conclusion that strong hydrogen bonding interaction can reduce the crystal growth rate and promote the diluent segregation[12]. In addition, it should be pointed out that the formation of hydrogen bonding is processing dependent. Coleman *et al.*[14] has reported that the solution cast phenoxy film exhibits a higher degree intermolecular hydrogen bonding than the film cooled from 150 °C. This result is ascribed to solvent plasticization. Considering that crystallization and intermolecular interaction coexist in most crystalline/amorphous polymer blends, structural dependence of the polymer blend on the preparation conditions should be related with the complicated coeffects of both crystal growth and intermolecular interaction. Taking this into account, a model polymer blend will be helpful to reveal the influence of preparation condition on the crystallization characteristics and the final microstructures of the polymer blends.

Poly(vinylphenol) (PVPh) is an amorphous polymer, which can form hydrogen bonding with many polymers having ester groups, such as, PCL. Owing to the strong intermolecular hydrogen bonding between hydroxyl group of PVPh and carbonyl groups of PCL, it has been demonstrated that the PVPh/PCL blends are miscible in the amorphous state at ambient temperatures[15–18]. Therefore, the blends of PVPh and PCL were chosen as a sample system to study the influence of intermolecular interactions on the crystallization behavior of PCL under different preparation conditions.

## EXPERIMENTAL

The PCL ($M_w$ ~14000, $M_n$ ~10000) and PVPh ($M_w$ ~11000) were purchased from Sigma-Aldrich Com. Blending of PCL with PVPh was carried out by solution casting. Both components were dissolved in tetrahydrofuran (THF) at room temperature yielding a 3 wt% solution. The prepared sample was first evaporated at room temperature for 1 day and further dried in vacuum oven for 12 h to ensure total elimination of the solvent.

Differential scanning calorimetry (DSC) measurements were performed on a TA Instruments Q2000 in nitrogen atmosphere. The as-prepared blend samples were first heated from 20 °C to 150 °C with a rate of 10 K·min$^{-1}$ to check the crystallization status of the PCL in solution cast PCL/PVPh films. Subsequently, the samples were cooled to 20 °C again and reheated from 20 °C to 150 °C with a rate of 10 K min$^{-1}$ to show the crystallization status of the PCL in melt-crystallized PCL/PVPh films. The enthalpies of fusion ($\Delta H_f$) were determined from the DSC curves, and the $\Delta H_f$ obtained from the first and second scans is designated as $\Delta H_{f1}$ and $\Delta H_{f2}$, respectively. The crystallinity of PCL in the blends was calculated by the following equation:

$$X_c = \frac{\Delta H_f}{W_{PCL} \times \Delta H_f^0} \times 100\% \tag{1}$$

where $\Delta H_f$ = 136 J·g$^{-1}$ is the heat of fusion of 100% crystalline PCL[19], and $w_{PCL}$ is the weight fraction of PCL in the blends. The degree of crystallinity measured from the first and second heating scans are designated as $X_{c1}$ and $X_{c2}$, respectively.

Fourier transform infrared spectra (FTIR) of the blends were measured with a Spectrum 100 FTIR spectrometer (Perkin-Elmer) equipped with a DTGs detector. All IR spectra were run in a transmission mode, and 32 scans were collected with a spectral resolution of 4 $cm^{-1}$. The films used in IR studies were prepared by solution casting. Thickness of the thus prepared films is ~15 μm, which is sufficiently thin to obey the Beer-Lambert law. The as-prepared films (designated as RT1) were first measured by FTIR at room temperature, then heated to and kept at 150 °C for 5 min in a Linkman temperature cell, and finally cooled to room temperature again. The IR spectra of the samples obtained at 150 °C and after cooled down to room temperature are designated as 150 °C and RT2, respectively.

## RESULTS AND DISCUSSION

The first and second DSC heating scans of the PCL/PVPh blends are shown in Fig. 1. Fairly narrow endothermal peaks of PCL in the blends can be found during the first scans. The peak temperatures shift slightly to lower values with PVPh content, reflecting that the crystallization of PCL in the blends has been slightly affected by PVPh. The crystallinities of PCL in the blends with different ratios are summarized in Table 1. From Table 1, it can be clearly seen that the crystallinity of PCL ($X_{c1}$) in the blends decreases with increasing PVPh content. These results illustrate the influence of PVPh on the solution crystallization of PCL. In the second scans, the DSC curves are quite different from those shown in the first scans. For the 80/20 PCL/PVPh blend, a broad endothermic peak is observed. It presents actually double melting peaks, which are often observed in miscible crystalline/amorphous polymer blends[20]. For the 50/50 and 20/80 PCL/PVPh blends, no endothermic peaks can be detected at all. This may imply that the crystallization of PCL in the blends is inhibited during melt-crystallization or at least cannot be detected by DSC.

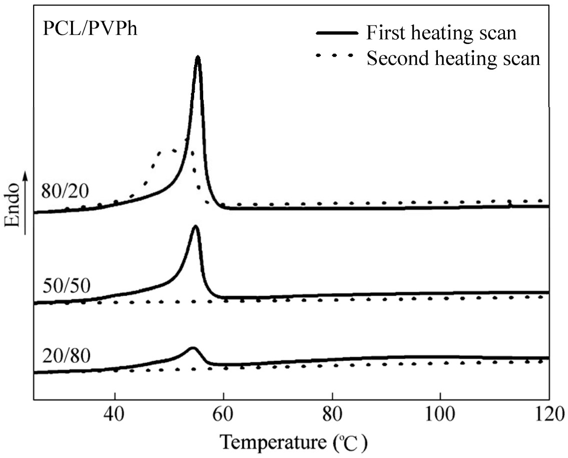

**Fig. 1** First and second heating scans of DSC thermograms of PCL/PVPh blends of different compositions

**Table 1.** Degree of crystallinity of PCL/PVPh blends of different compositions

| PCL/PVPh (wt%) | $\Delta H_{f1}$ ($J\cdot g^{-1}$) | $\Delta H_{f2}$ ($J\cdot g^{-1}$) | $X_{c1}$ (%) | $X_{c2}$ (%) |
|---|---|---|---|---|
| 80/20 | 78.1 | 65.0 | 71.8 | 59.7 |
| 50/50 | 45.8 | 0 | 67.4 | 0 |
| 20/80 | 16.4 | 0 | 60.2 | 0 |

FTIR is a powerful technique for analyzing the polymer chain conformation, orientation and crystallization. Characteristic infrared bands of PCL in the crystalline phase have been studied widely in the literatures and are summarized here in Table 2. The crystallization of PCL can be followed by utilizing two $CH_2$ rocking peaks which appear at 731 $cm^{-1}$ and 710 $cm^{-1}$, respectively. These peaks are originated from a factor group splitting due to the intermolecular interaction of the $CH_2$ sequences packed in an orthorhombic unit cell just as in the case of PE crystals[21]. When PCL is melted, the peak at 710 cm$^{-1}$ completely disappears and the 731 cm$^{-1}$ peak is reduced to about one-third its original height. Figure 2 shows the FTIR spectra in the region from 760 cm$^{-1}$ to 680 cm$^{-1}$ of PCL/PVPh blends from different processing conditions. It can be seen that when the PCL composition is 80%, both bands at 731 cm$^{-1}$ and 710 cm$^{-1}$ can be detected in the solution-cast sample. When the sample was melted, the band at 710 cm$^{-1}$ disappeared and the peak 731 cm$^{-1}$ was reduced to a large extent. The bands at 731 cm$^{-1}$ and 710 cm$^{-1}$ can also be observed clearly in the melt-cooled sample, but the absorbance intensity of the band at 731 cm$^{-1}$ of the melt-cooled sample was lower than that of the solution-cast one, which suggests a lower degree of crystallinity of PCL in the melt crystallized sample. The bands at 731 cm$^{-1}$ and 710 cm$^{-1}$ can also be detected in the solution cast sample containing 50% PCL, while the band at 710 cm$^{-1}$ does not appear. This should also be caused by the reduced crystallinity of PCL with increasing PVPh content. After the melt-recrystallization, the band at 731 cm$^{-1}$ reduced remarkably and is only a little different from that in the molten state of sample. This reveals the difference between the molten and the melt-crystallized samples, which may indicate the crystallization of a very small amount PCL in the blend even though no endothermic peak can be detected by DSC. For the PCL/PVPh blend containing 20% PCL, even though the peak at 731 cm$^{-1}$ can be observed in the original solution cast sample, the absence of the 710 cm$^{-1}$ band may indicate the rather lower crystallinity of PCL in the 20/80 PCL/PVPh blend than the blends containing higher amount of PCL. Moreover, after melt-recrystallization, only tiny difference between melt and melt-cooled samples can be observed. This indicates that the PCL in the melt-recrystallized 20/80 PCL/PVPh blend is still in the amorphous state.

**Table 2.** Characteristic infrared bands of PCL

| Wavenumber (cm$^{-1}$) | Assignments | |
|---|---|---|
| 2944 | $'\nu_{as}$ ($CH_2$) | amorphous |
| 2865 | $\nu_s$ ($CH_2$) | crystalline |
| 1727 | $\nu$(C=O) | crystalline |
| 1295 | $\nu$(C—O C—C) | crystalline |
| 1245 | $\nu_{as}$ (COC) | crystalline |
| 1192 | $\nu$(OC—O) | crystalline |
| 731 | $\gamma_{in}$ ($CH_2$) | crystalline |
| 710 | $\gamma_{out}$ ($CH_2$) | crystalline |

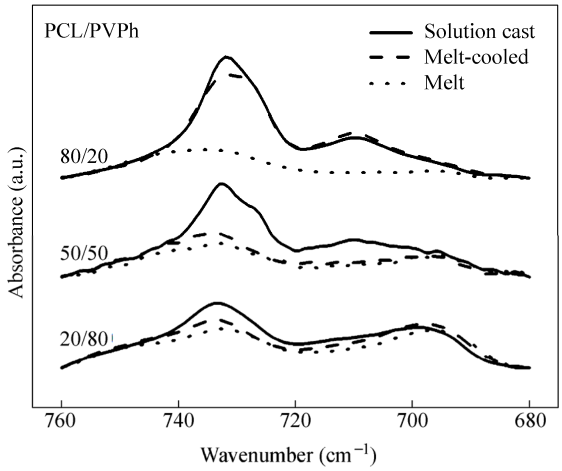

**Fig. 2** FTIR spectra in the region from 760 cm$^{-1}$ to 680 cm$^{-1}$ for three PCL/PVPh blends
The samples were cast from THF and recorded at room temperature first (solid line), after heated at 150 °C for 5 min (dotted line), and then cooled to room temperature again (dashed line).

Bands located at 1295, 1245, and 1192 cm$^{-1}$ are the conformational sensitive bands, which are also related with the crystallization of PCL. Therefore, these bands are also frequently used to follow the crystallinity development of PCL[22–25]. Figure 3 shows the infrared spectra of PCL/PVPh blends with different blend rations in the region of 1123–1314 cm$^{-1}$. For the 80/20 PCL/PVPh blend, there are apparently three strong absorbance bands at 1295, 1244 and 1192 cm$^{-1}$ for the as-cast film (see Fig. 3a), indicating the high degree of crystallinity of the solution cast film. When the film was heated to 150 °C for 5 min, these absorbance bands disappeared as shown by the dashed line in Fig. 3(a). These three absorbance bands appeared again after the film was cooled from 150 °C to room temperature with relatively lower intensity than that of the as-cast film. This indicates the existence of crystalline entities of PCL with decreased crystallinity. This result is in accordance with that obtained from the crystalline sensitive bands of PCL.

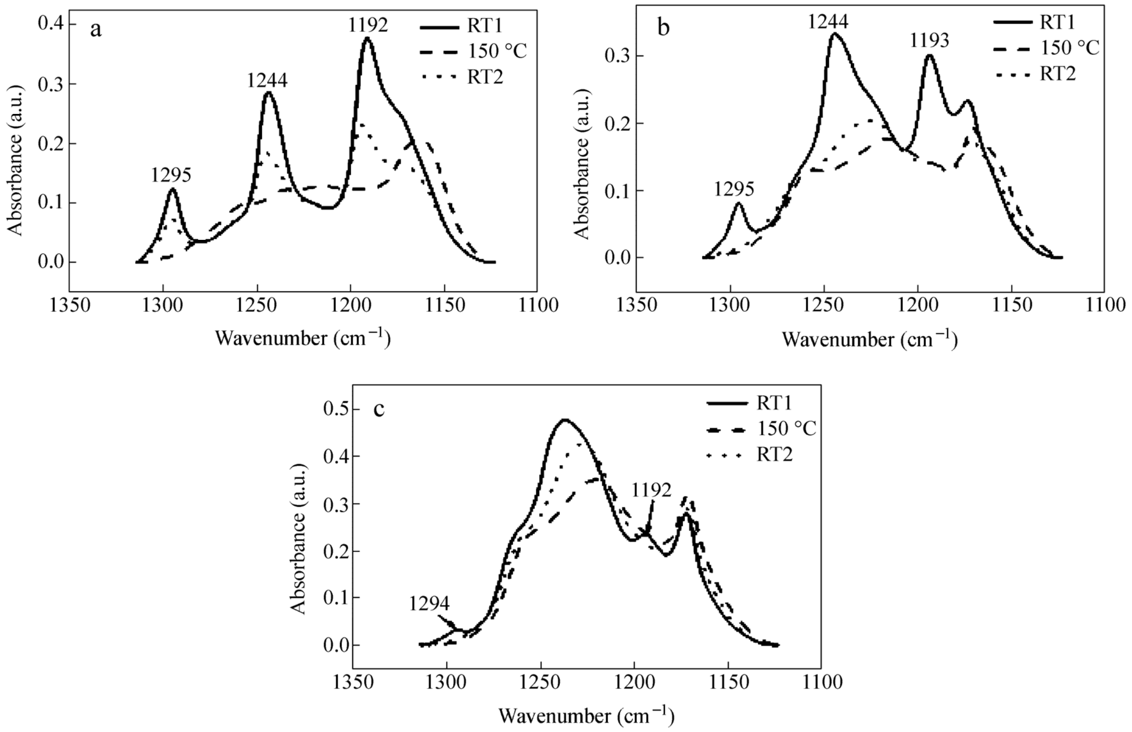

**Fig. 3** FTIR spectra in the region from 1314 cm$^{-1}$ to 1123 cm$^{-1}$ of PCL/PVPh films of different blend compositions: (a) 80/20, (b) 50/50 and (c) 20/80
The samples were first cast from THF and recorded at room temperature (solid line), then heated at 150 °C for 5 min (dashed line) and cooled to RT again(dotted line).

With increasing PVPh content, the IR spectra change greatly. For the 50/50 blend, as shown in Fig. 3(b), the bands at 1295, 1244, and 1193 cm$^{-1}$ can be observed obviously for the solution cast sample, and disappear completely after heating the sample to 150 °C. When the sample was cooled to room temperature again, the IR spectra also do not show these three bands any more. The original band at 1244 cm$^{-1}$ is now shifted to low frequency and appears as a broad band. Moreover, a band at 1172 cm$^{-1}$ due to an O—H in-plane bending mode of the phenol group of PVPh can be clearly seen. From the above results, it can be concluded that when the fraction of PVPh reached 50%, the PCL in the solution cast film is in the semicrystalline state whereas it turns to amorphous state when cooled from the melt. There are literatures which report that the crystallization of the crystalline component in a crystalline/amorphous binary blends could be inhibited when the fraction of the amorphous component is more than 50%[20, 26]. With further increase of the PVPh content, as shown in Fig. 3(c), the 1294 cm$^{-1}$ and 1193 cm$^{-1}$ bands can be identified in the as-cast film. However, the intensities of these bands decrease remarkably. This implies a limited degree of crystallinity of PCL in the blend and demonstrates the influence of PVPh on the crystallization of PCL. At the same time, the further intensity increase of the 1172 cm$^{-1}$

band illustrates the increase of PVPh content. It should be pointed out that after the thermal treatment, all of the bands at 1295, 1245, and 1192 cm$^{-1}$ disappeared. This result confirms that the crystallization of PCL in the 20/80 PCL/PVPh blend from melt is totally suppressed.

The above experimental results clearly indicate the influence of PVPh on the crystallization behavior of PCL. It has been proved that PCL/PVPh blends are miscible in the molten state in the whole composition range due to specific intermolecular interactions[17]. So, it is important to pay attention to the change of the intermolecular interactions before and after heat treatment. The hydrogen bonding interaction can be detected easily by FTIR. For PCL, its crystallization results in the shift of the stretching frequency of C=O groups from 1735 cm$^{-1}$ to low frequency at about 1725 cm$^{-1}$. When the hydrogen bonding interaction occurs between the carbonyl group of PCL and hydroxyl group of PVPh, further frequency shift of the carbonyl stretching frequency takes place, *e.g.*, a band at 1708 cm$^{-1}$ will be found. This band shift was also observed in other blends having hydrogen bonding interactions between carbonyl and hydroxyl groups[27, 28]. The infrared spectra of carbonyl stretching of PCL in the blends are shown in Fig. 4. In the blends containing 80% (wt%) PCL, the as-cast film shows a rather strong absorbance band at 1725 cm$^{-1}$ (Fig. 4a), which is attributed to the carbonyl stretching vibration in the crystalline phase. In addition, two shoulder bands could be distinguished at about 1735 cm$^{-1}$ and 1708 cm$^{-1}$, respectively. While the 1735 cm$^{-1}$ band is related to the free carbonyls in amorphous region, the 1708 cm$^{-1}$ band is assigned to the PCL carbonyl group hydrogen bonded to the PVPh phenolic hydroxyl group. When the film was heated to 150 °C for 5 min, the crystals of PCL are molten, the carbonyl stretching band at 1725 cm$^{-1}$ disappears. Now the band at 1735 cm$^{-1}$ corresponding to the free carbonyls in amorphous region can be clearly identified. The 1708 cm$^{-1}$ band appears as a shoulder of the 1735 cm$^{-1}$ band. After cooling the sample to room temperature again (RT2), three absorbance bands can be observed once more just like the as-cast film.

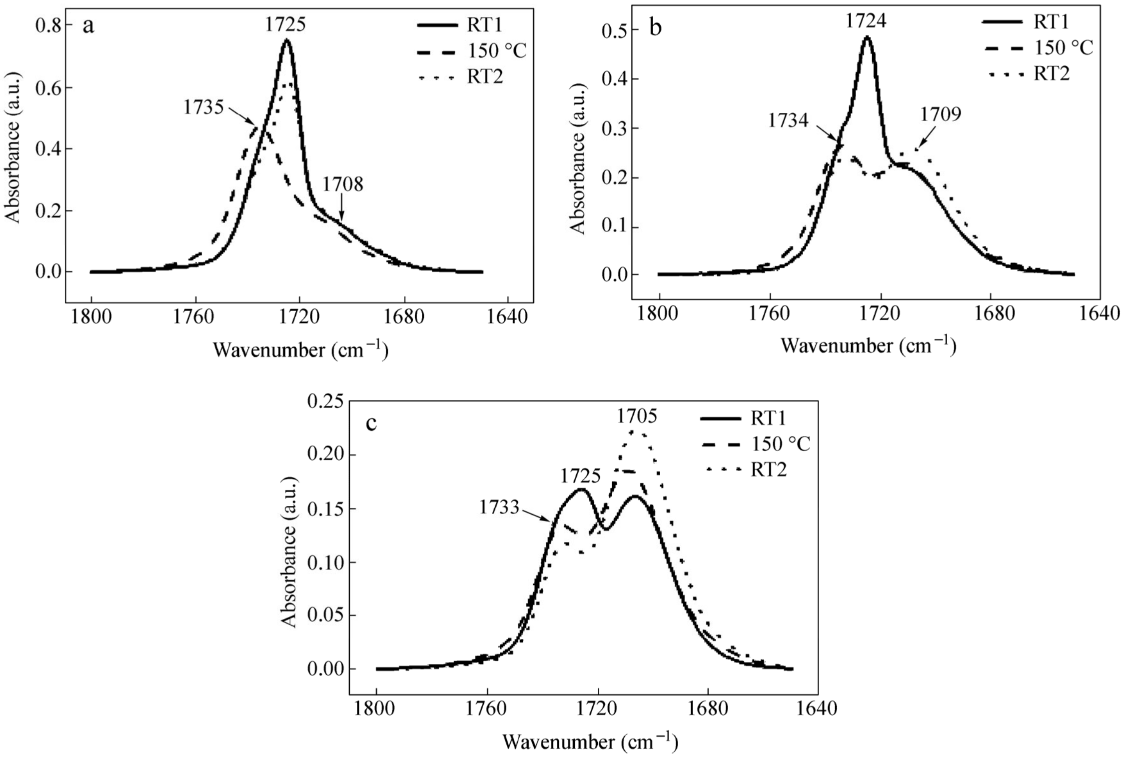

**Fig. 4** FTIR spectra in the region from 1800 cm$^{-1}$ to 1650 cm$^{-1}$ of PCL/PVPh films of different blend compositions: (a) 80/20, (b) 50/50 and (c) 20/80
The samples were first cast from THF and recorded at room temperature (solid line), then heated at 150 °C for 5 min (dashed line) and cooled to RT again (dotted line).

But the relative intensity of the 1708 $cm^{-1}$ increases at the expense of the 1725 $cm^{-1}$ band. At the same time, the intensity decrease of the 1725 $cm^{-1}$ band indicates a decrease of the crystallinity of PCL.

For the 50/50 PCL/PVPh blend, the crystalline band at 1724 $cm^{-1}$ can be clearly seen in the spectrum of the as-cast film (Fig. 4b). Also the 1709 $cm^{-1}$ band arising from carbonyl groups hydrogen bonded to the PVPh hydroxyl groups is more clearly seen compared with the 80/20 PCL/PVPh blend, indicating increased content of hydrogen bond. With careful inspection, some free carbonyl with absorption at 1734 $cm^{-1}$ can be identified. When the as-cast film was heated to 150 °C for 5 min, the band at 1724 $cm^{-1}$ corresponding to the PCL in crystalline phase disappears, leading to an apparent 1734 $cm^{-1}$ band of the amorphous PCL. The 1709 $cm^{-1}$ arising from carbonyl groups hydrogen bonded to the PVPh hydroxyl groups remains almost unchanged. After cooling the film to room temperature, similar spectrum as that taken at 150 °C is obtained. It is composed of stretching frequency from amorphous PCL and hydrogen bonded carbonyl groups. However, the fraction of hydrogen bonded carbonyl group is evidently increased. It is even more than the film at 150 °C. The disappearance of the crystalline sensitive band at 1724 $cm^{-1}$ implies the amorphous state of PCL.

With further increase of the PVPh component for a 20/80 PCL/PVPh blend, the crystalline band at 1725 $cm^{-1}$ together with a strong 1705 $cm^{-1}$ band related to the carbonyls groups hydrogen bonded to PVPh hydroxyls groups are observed in the spectrum of the solution cast film (see Fig. 4c). The spectrum taken at 150 °C is composed of only two bands attributed to the free and hydrogen bonded carbonyls, respectively. After cooling the film to room temperature again, we see still only the bands originating from the free and hydrogen bonded carbonyls. The obvious difference between the spectra taken at 150 °C and after cooling to room temperature is the ratio of absorbance between the hydrogen bonded carbonyls and free carbonyls. The re-cooled film contains more fractions of hydrogen bonded carbonyls than the molten film at 150 °C. This result can indicate the better miscibility between PVPh and PCL after heat treatment process.

From the above results, it can be concluded that the formation of hydrogen bond inhibits the crystallization of PCL in the PCL/PVPh blend. In order to explain the influence of hydrogen bond on the crystallization of PCL, the amount of hydrogen bonding formed in the PCL/PVPh blends with different blend ratios and under different preparation conditions was quantitatively calculated through a curve-fitting procedure. The curve-fitting process decomposes the IR spectra in the C=O stretching region into the elemental vibration bands. In the fitting process, the shape of the peaks was assumed to be Gaussian. Band widths and heights were treated as adjustable parameters. The fraction of hydrogen bonding C=O was calculated on the basis of

$$f_{\mathrm{k}} = (A_{\mathrm{k}}/\varepsilon_{\mathrm{k}}) / \sum_{\mathrm{k}} (A_{\mathrm{k}} / \varepsilon_{\mathrm{k}}) \qquad (2)$$

where $A_{\mathrm{k}}$ and $\varepsilon_{\mathrm{k}}$ are the absorbance and absorption coefficient of the elemental spectrum. The k corresponding to free, crystalline, and hydrogen-bonded components were abbreviated as free, crys and H-B, respectively. For this blend system, $\varepsilon_{\mathrm{H-B}}/\varepsilon_{\mathrm{free}} = \varepsilon_{\mathrm{H-B}}/\varepsilon_{\mathrm{crys}} = 1.5$ was used[27, 29–31]. As an example, Figure 5 shows the experimental (light solid line) and fitted (dotted line) spectra of a 80/20 PCL/PVPh blend in the carbonyl vibration region. The spectrum was decomposed into three bands, *i.e.*, free, crystalline, and hydrogen-bonded components. It can be seen that there is good agreement between the experimental and the fitted spectra. According to the curve-fitting results, the fractions of hydrogen-bonded, free and crystalline carbonyl groups can be obtained and are present in Table 3.

It can be clearly seen from Table 3 that the fraction of carbonyls depends strongly on the state of the sample. According to the fractional change of the carbonyls, the different crystallization behaviors can be explained in the following way. Even though the PVPh and PCL are well mixed both in solution and melt, the intermolecular interactions developed during solution crystallization and melt crystallization are different. During the evaporation of the solvent, the residual solvent acts as a plasticizer and interacts with both PCL and PVPh[13, 14]. Accordingly, the interaction between PVPh and PCL may be reduced. In this case, the PCL in its PCL/PVPh blends with different blend ratios can crystallize. With increasing PVPh content in the blends, the fraction of hydrogen-bonded carbonyl groups increases. This results in a reduced crystallization ability of PCL.

**Table 3.** Curve-fitting results of the C=O stretching vibration bands in the PCL/PVPh blends

| PCL/PVPh (wt%) | RT1 | | | 150 °C | | | RT2 | | |
|---|---|---|---|---|---|---|---|---|---|
| | H-B | Crys | Free | H-B | Crys | free | H-B | Crys | Free |
| 80/20 | 21.7 | 40.4 | 37.9 | 23.1 | 0 | 76.9 | 25.9 | 33.7 | 40.5 |
| 50/50 | 38.5 | 24.9 | 36.6 | 53.7 | 0 | 46.3 | 60.8 | 0 | 39.2 |
| 20/80 | 52.5 | 7.5 | 40.0 | 62.5 | 0 | 37.5 | 72.8 | 0 | 27.2 |

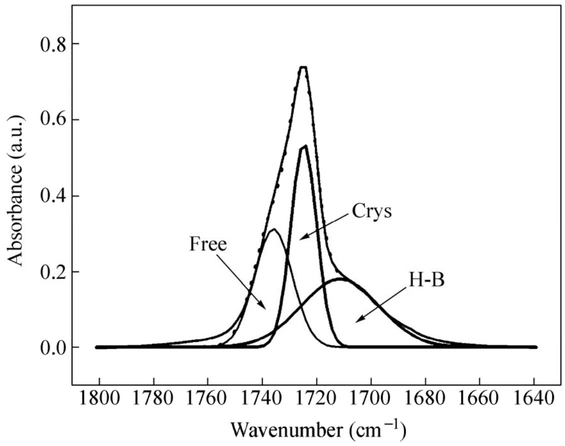

**Fig. 5** Curve-fitting of FTIR spectra in the C=O stretching region for the PVPh/PCL blend (20:80, wt% )

Nevertheless, crystallization of PCL in the blends always takes place. After crystallization of PCL, the fraction of free carbonyl groups in all blends is almost the same. During the melting process, the PCL solution crystallized crystals are destroyed and this causes a tremendous increment of the free carbonyl groups. On the other hand, the good miscibility and the absence of solvent encourage the interaction between PCL and PVPh, which leads to an increased amount of hydrogen-bonded carbonyl groups. It should be pointed out that, for the 80/20 PCL/PVPh blend, the maximum amount of hydrogen-bonded carbonyl groups is about 23%. During the cooling process, a further increase of the hydrogen-bonded carbonyl groups at the expense of the free carbonyl groups was seen. It is still only one fourth of the total carbonyl groups due to the limited PVPh content in the blend. In this case, the crystallization of hydrogen bonded PCL molecules may be prohibited by the PVPh molecules since they are in the glassy state. The free PCL molecules then crystallize when the sample was cooled to room temperature again. As a result, all the absorption bands related to free, crystalline and hydrogen-bonded carbonyl appear again after cooling to room temperature. For the 50/50 and 20/80 PCL/PVPh blends, the free carbonyl groups decrease while the hydrogen-bonded carbonyl groups increase with increasing PVPh content, indicating more and more PCL molecules interact with the PVPh. During the cooling process, further increase of the hydrogen-bonded carbonyl groups at the expense of the free carbonyl groups is evident. When the sample was cooled to room temperature again, the amount of hydrogen-bonded carbonyl groups is over 60%, while the amount of free carbonyl groups reduces remarkably. This implies that most of the PCL molecules are associated with PVPh molecules through intermolecular hydrogen bonding. Considering that the crystallization temperature of PCL is much lower than the glass transition temperature ($T_g$) of PVPh, the PCL hydrogen bonded with PVPh will lose chain mobility. These PCL molecules can therefore not be arranged into crystalline entities due to the restricted mobility, which results in a miscible blend film. Comparing the fraction of hydrogen bonded carbonyl groups in solution cast 20/80 PCL/PVPh film (~52%) with that in the melt recooled 50/50 PCL/PVPh film (~60%), it seems that the PCL will lose its crystallization ability when the fraction of hydrogen bonded carbonyl groups exceeds 60%.

## CONCLUSIONS

The development of crystallinity and intermolecular interactions in PCL/PVPh blends with different blend ratios under different preparation conditions can be depicted. In the as-cast film, crystallization of PCL takes place even in the blend containing only 20% PCL. This may be attributed to the solvent effect, which reduces the interaction between the PCL and PVPh. After heat treatment process, more PCL chains are hydrogen bonded with the PVPh molecules and the interaction between PCL and PVPh is enhanced. Since the crystallization temperature of PCL is much lower than the $T_g$ of PVPh, the PCL chains interacted with PVPh through hydrogen bond lose mobility for packing into crystalline entities and, therefore, reduces the crystallization ability of PCL. When the PCL weight fraction in the blend is 50% or lower, the samples changed from semicrystalline to compatible amorphous blends, and the miscibility between PCL and PVPh of the obtained films is promoted by heat treatment process.

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