

Effects of Hydrogen Bond Interaction on the Miscibility of Poly (D, L-lactide) Composites Materials

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Abstract. Blend materials of poly (D, L-lactide)/ poly (vinyl alcohol) (PDLA/PVA), poly (D, L-lactide)/poly (ethylene glycol)₃₀₀ (PDLA/PEG₃₀₀) and poly (D, L-lactide)/poly(ϵ -caprolactone) (PDLA/PCL), obtained by solvent-casting, have been studied by differential scanning calorimetry (DSC) and Fourier transform infrared spectroscopy (FT-IR). DSC results showed that PDLA/PVA and PDLA/PEG₃₀₀ are miscible in entire composition range and PDLA/PCL blends are immiscible. FT-IR results indicated that there are hydrogen bond interactions in these blends except PDLA/PCL. The miscibility of blends is enhanced; however, the plasticizing role is not affected by hydrogen bond interaction through hydroxyl end groups. With the increase of PEG₃₀₀, the plasticizing role become obvious in PDLA/PEG₃₀₀. The effects of hydrogen bond interaction between poly (D, L-lactide) and other polymer chain were studied, the effects of the mixed temperature and solvent of the blends were also discussed.

1. Introduction

Generally, synthetic polymers from petrochemical products were not easily degraded in the environment. In recent years, biodegradable polymers attracted great interest for their environmental friendly application [1-3]. The most popular and important biodegradable polymers were aliphatic polyesters, such as polylactide (PLA), poly (glycolic acid) (PGA), poly (ϵ -caprolactone) (PCL) and poly (3-hydroxy butyrate) (PHB). Poly (lactide) was thermoplastic polyester that was studied extensively owing to its source accessible, non-toxic, easy processing, biodegradable, biocompatibility and excellent thermal/mechanical properties, which was known as the most promising biodegradable material [4-6]. Currently, PLA has already been applied in the plastic industry, biomedical, pharmaceutical and other fields. Their applications mainly included drug delivery systems, artificial organs, surgical devices, biosensors, materials for orthopedics and biodegradable packaging [7-11].

PDLA was a sort of amorphous polyester with a T_g varied from around 50 to 60 °C and a wide range of melting temperatures, generally depending on its molecular weight and distribution [12]. But there were still a lot of restrictions due to its crisp and heat instability. To overcome these drawbacks, many approaches have been investigated, and most excellent PLA materials were prepared by copolymerization and blending [13-16]. Miscibility, mechanical properties and

crystallization of PLA blends have been studied in several papers [17-21], and it was considered that PLA is immiscible with other polymers many times.

Zhang [22] studied the miscibility of poly (D, L-lactide)/poly (vinylphenol) (PDLLA/PVPh) blend, finding phase separation in blends over a wide composition. In contrast, Owen [23] indicated the blends were completely miscible with solution/precipitation and higher temperature. On the other hand, some blends which were known as as-prepared before may be improved the miscibility by using different blending methods and temperatures.

Recently, many investigations have been also performed to enhance the impact resistance PLA and compete with low cost commodity polymers. In this study, PVA, PEG₃₀₀ and PCL were used for blending with PDLLA (Figure 1), and blends of poly (D, L-lactide)/poly (vinyl alcohol) (PDLLA/PVA), poly (D, L-lactide)/poly (ethylene glycol)₃₀₀ (PDLLA/PEG₃₀₀) and poly (D, L-lactide)/poly(ϵ -caprolactone) (PDLLA/PCL) obtained by solvent-casting were analyzed by differential scanning calorimeter (DSC) and Fourier transform infrared spectroscopy (FT-IR). The changes of T_g were investigated, and the miscibility and hydrogen bonds of blends have been also discussed.

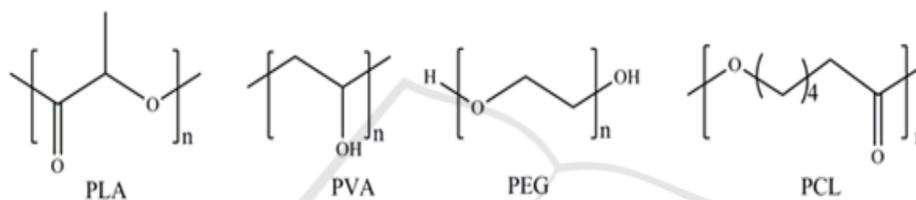


Figure 1. Chemical structures of PLA, PVA, PEG and PCL.

2. Experimental

2.1. Materials

PDLLA was synthesized in the way similar to that described in the literature [24-26]. PCL was obtained by ring-opening polymerization of ϵ -CL using tin octoate as catalyst at 160°C. Both PDLLA and PCL were purified as literature described [27]. The molecular weight and molecular weight distribution was measured at 25°C by gel permeation chromatography (GPC) with tetrahydrofuran (THF) as eluent (1.0 mL/min) using multi-angle laser light scattering and refractive index (Figure 2). PVA ($M_n=6.97 \times 10^4$, % hydrolyzed) and PEG₃₀₀ ($M_n=285\sim 310$) were supplied by Sigma-Aldrich. Polymers were dried in a vacuum oven at 40°C overnight previous use, and all other reagents were used as received.

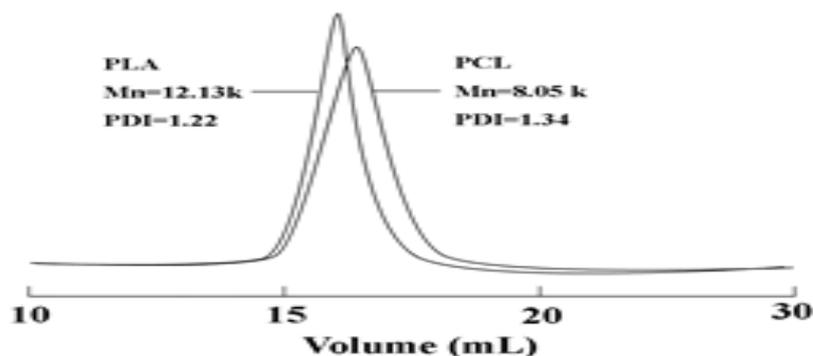


Figure 2. GPC profiles of PDLLA ($M_n=121\ 300$, $PDI=1.22$) and PCL ($M_n=80\ 500$, $PDI=1.34$).

2.2. Preparation of blends

PDLLA/PEG₃₀₀ were mixed in the desired amounts then dissolved in THF at room temperature. After dissolved completely (about 12 h), the solution was cast on glass slide, solvent were volatilized for 48 h, then the blend film was dried in vacuum oven at 40°C for 48 h. PDLLA/PCL blend prepared in a similar way. PDLLA/ PVA were dissolved in dimethyl formamide (DMF) at 140°C for 12 h, then the solvent was allowed to evaporate at 100°C for 48 h; the films were dried in a vacuum oven at 60°C for 96 h.

2.3. Differential scanning calorimeter

Thermal analysis of the blend samples was performed using Mettler Instrument, model DSC822e. The instrument was calibrated using indium and all experiments were carried out under a nitrogen atmosphere. Approximately 5~6 mg of each blend was weighed and sealed in an aluminum pan. All specimens were heated to 200°C at a rate of 100 K/min and held for 5 min to eliminate the thermal history, followed by cooling to 20°C at a rate of 10 K/min. Then two consecutive scans were performed with the scan rate of 10 K/min. The midpoints of heat capacity change in the DSC thermal diagram obtained in the second heating run were taken as the glass transition temperature (T_g).

2.4. Infrared spectroscopy

Infrared spectra of blends were recorded on a Nicolet AVATER 370 Fourier transform infrared spectrophotometer (FTIR) at room temperature. A small quantity of sample was mixed with KBr, carefully ground in a mill, and pressed to a pellet. The absorbance of all the studied samples was within the absorbance range in which the Lambert-Beer law is obeyed. Second-derivative spectra were smoothed with a quartic 15-point Savitzky-Golay smoothing filter. Care was taken on the degree of distortion introduced by the smoothing algorithm, which was checked according to the procedure reported elsewhere.

3. Results and discussion

3.1. DSC analysis

DSC is a well-known method to study the miscibility of polymer composite, based on the criterion of a single glass transition temperature (T_g) intermediate between those of pure polymers [28-32]. The definition for miscible and partially miscible blends has been well established. There was usually only one T_g will appear in DSC thermograms at an intermediate temperature compared to that of the T_g value of each pure polymer if components were miscible. The single T_g of blend should obey the Fox equation describing the relationship between the T_g value, of the blend and its composition, as well as T_g values of components in the pure state. The T_g value of each component phase should be affected by the other one, even if two components were only partially miscible, and it was usually depended on composition.

Shuai et al. [33] studied the miscibility of PLLA/PVA blends, finding immiscibility or partially miscible because DSC measurements detected two series of isolated and rather composition-independent T_g . They used hexafluoro isopropanol as solvents, and blend solutions were cast onto Teflon dishes after polymers were codissolved. The solvent was allowed to evaporate at room temperature for 2 weeks, and films were dried in vacuo for 3 weeks at 60°C. But in this progress, DMF was used as PDLLA/PVA mixed solvents, and polymers were codissolved at 140°C. Figures 3 and 4 were the first and second scans of PDLLA/PVA blends, respectively. All results of PDLLA/PVA blends showed similar traces, it can be seen from Figure 3 and Figure 4 that there was only one T_g (also see Table 1.) in each blend. The glass transition temperature of the blends rose with the increasing of PVA which all temperatures were higher than those of neat PDLLA (59°C). We can also see that PDLLA and PVA were miscible, and the compatibility in the second scan was better

than that in the first one, especially when the component of PDLLA was low. Nevertheless, FTIR results (see the following section) were much more conclusive than DSC ones, supporting nearly pure phases.

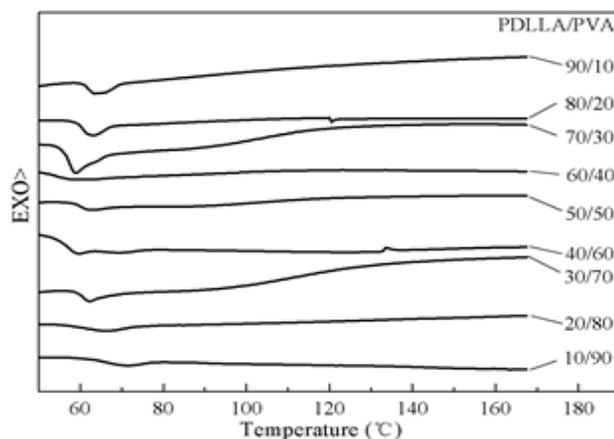


Figure 3. First scan DSC traces of PDLLA/PVA blends.

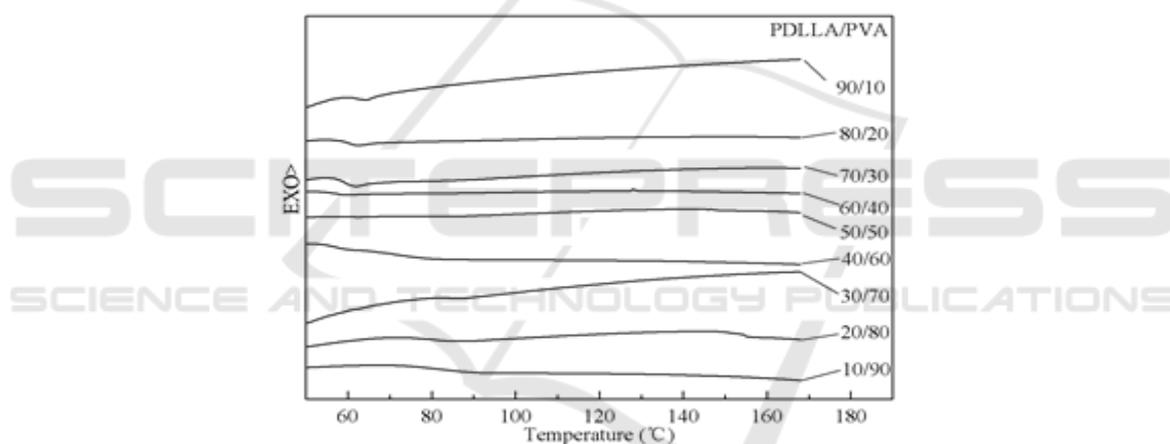


Figure 4. Second scan DSC traces of PDLLA/PVA blends.

Table 1. DSC results for PDLLA/PVA blends with different composition.

PDLLA/PVA (wt%)	T_g -first (°C)	T_g -second (°C)
100/0	59	59
90/10	62	61
80/20	61	60
70/30	58	59
60/40	-	59
50/50	59	71
40/60	57	-
30/70	61	81
20/80	63	80
10/90	67	79
0/100	85	85

PEG₆₀₀ was used to plasticized poly (L-lactide) by Kulinski et al. [34]. It indicated that T_g was decreased with increasing of plasticizers. The DSC data for the amorphous PLA also showed clearly a decrease of T_g due to enhanced of segmental mobility of PLA chains caused by the presence of plasticizer, increasing with the PEG₃₀₀ in this study. As can be seen from Figure 5, at low mixed temperature (40°C), the first and second heating scan showed good compatibility for PDLA/PEG₃₀₀ blends. No significant differences were found during two heating scans. The results suggested that as-casting PDLA/PEG₃₀₀ blends were miscible in nearly pure polymer.

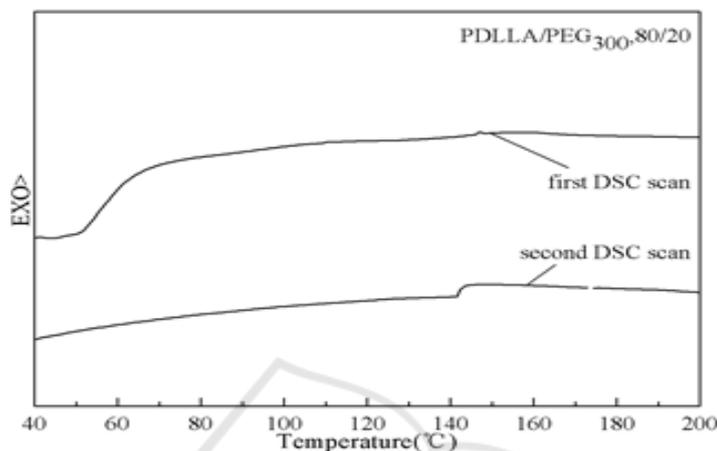


Figure 5. First and second scan DSC traces of PDLA/PEG₃₀₀ blends.

Many scholars have already proved that PLA and PCL are immiscible or partially miscible [17, 35-38]. Figure 6 and Figure 7 showed that the first scan was consistent with the second one. PDLA was immiscible with PCL when the mixed temperature was low. Even after the blends were heated, the results were still unsatisfactory. However, Solid-state NMR studies indicated the presence of phase separation. In addition, it may be not remove all residual crystals during first heating which the glass transition of PDLA and melting of PCL were overlapped in some DSC thermograms showing in Figure 6.

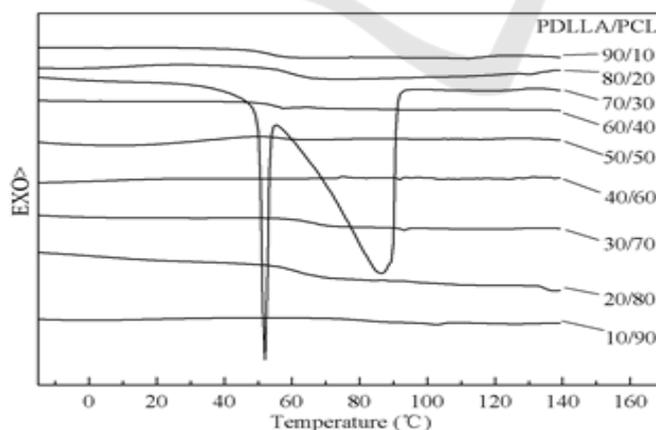


Figure 6. First scan DSC traces of PDLA/PCL blends.

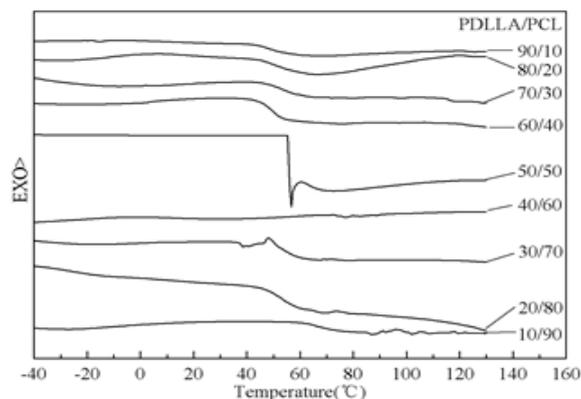


Figure 7. Second scan DSC traces of PDLLA/PCL blends.

3.2. FT-IR results

FT-IR were widely used to study hydrogen bonding in blends of polymers [39]. From the chemical structures in Figure 1 we can see that PDLLA is easier to form hydrogen bonding with PVA and PEG than PCL. Shuai et al. also proved that hydrogen bonding appeared between PLLA and PVA by FT-IR and Solid-state NMR.

Infrared spectroscopy has been widely used to investigate specific interactions in polymer blends in which the driving force for miscibility was hydrogen bonding. All these studied blends have been analyzed, and hydrogen bonding were confirmed during PDLLA/PVA and PDLLA/PEG₃₀₀ blends. Figure 8 and Figure 9 were IR spectra of PDLLA/PVA blends after the second DSC scan. It can be seen from the results that as PVA is increased, hydroxyl group does more and more effect on carboxyl band (C=O). Figure 8 shows the peak of carboxyl become smaller and smaller. Figure 9 shows that the hydrogen bond (O-H...O=C) makes the peak of hydroxyl band (O-H) become wider and shift to red. However, for the blends of PDLLA and PCL, both of the two IR peaks are almost unchanged, indicating that no hydrogen bond is formed between them.

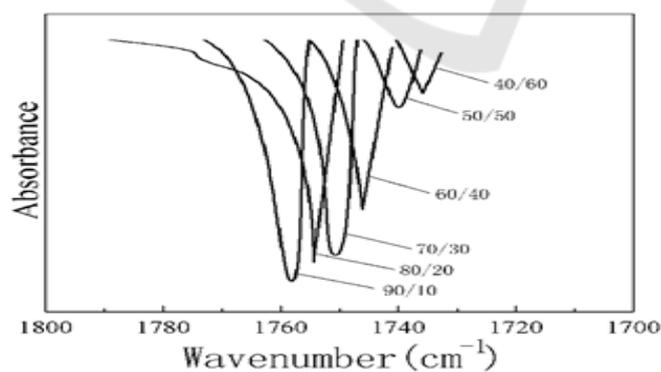


Figure 8. FTIR of PDLLA/PVA blends from 1700-1800 cm^{-1} .

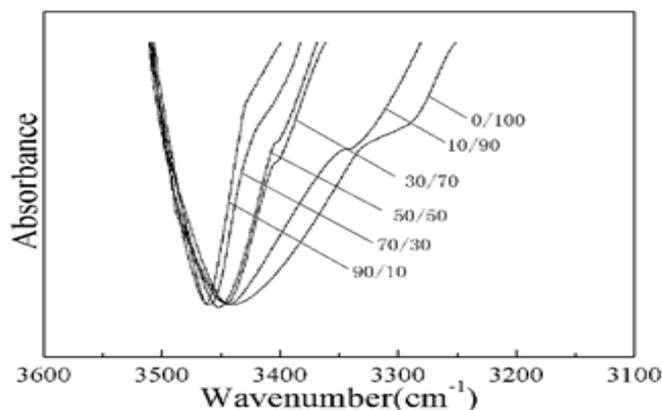


Figure 9. FTIR of PDLLA/PVA blends from 3100-3600 cm^{-1} .

3.3. Blend miscibility

According to DSC data and FTIR results, miscibility of PDLLA/PVA, PDLLA/PEG₃₀₀ and PDLLA/PCL were studied. The solitary T_g of PDLLA/PVA and PDLLA/PEG₃₀₀ blends indicated good miscibility. The chemical structures of the blending polymers support the DSC results also. There were hydroxyl groups at PVA main chain and PEG end group. Miscibility should become better due to hydrogen bonding (O-H...O=C) which produced from hydroxyl groups and carboxyl groups. Hence, miscibility would be weakened because there was no hydrogen bonding during PDLLA and PCL. During heating, thermal motion increased both chain mobility and the probability of hydrogen bonding contacts. Rigidity of main chain would affect miscibility for blends, and second heating results of PDLLA/PVA blends showed better miscibility than first scans also. Lesser molecular weight of PEG would increase miscibility of PDLLA/PEG₃₀₀, and also enhance plasticizing agent role.

4. Conclusions

DSC results show that PDLLA/PVA and PDLLA/PEG₃₀₀ were miscible in whole composition range and PDLLA/PCL blends were immiscible. Miscibility of PDLLA/PVA after twice heating scan was better than as-casting blends because thermal motion increased both chain mobility and the probability of hydrogen bonding contacts. With increasing of PEG₃₀₀ its plasticizing agent role were obvious in blends of PDLLA/PEG₃₀₀ due to lesser molecular weight. According to FT-IR analysis, results of DSC were confirmed. There were hydrogen bonds in blends of PDLLA/PVA and PDLLA/PEG₃₀₀, but there were no hydrogen bonds in PDLLA/PCL. Hence, miscibility of PDLLA/PVA and PDLLA/PEG₃₀₀ were enhanced by hydrogen bonding. As a result, the effect of hydrogen bonding and the mixed temperature are very important in the miscibility of blends.

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