Modification of Polycarbonate by Adding Poly(L-lactide)

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ABSTRACT: In this study, the blend of polycarbonate (PC)/poly(L-lactide) (PLLA) (70/30) was prepared through the conventional extrusion-injection-molding process. The morphology of the blend was characterized using scanning electron microscope. Both differential scanning calorimetry and wide angle X-ray diffraction were used to investigate the crystallization behavior of PLLA component in the blend. The mechanical and thermal properties of the blend were comparatively investigated, and the hydrolytic degradation ability of the material was also evaluated. The results show that the dispersed-PLLA particles are in the amorphous state in the PC matrix. Although the blend is immiscible, the rigid PLLA particles exhibit the toughening and reinforcement effects on PC simultaneously. Specifically, the heat-distortion temperature of the blend is comparable to that of pure PC. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

Poly(L-lactide) (PLLA) is a biocompatible and biodegradable polymer, which can be obtained from renewable resources. As one of the typical semicrystalline polymers, it exhibits excellent modulus and tensile strength and attracts more attention in recent years. The disadvantage of PLLA for application is the poor fracture resistance and poor crystallization ability. Therefore, most of researches have been carried out to improve the crystallization behavior[1–11] and fracture resistance[12–14] of PLLA. Blending with other polymers is thought to be an efficient method to enlarge the application of PLLA. Factually, considering the biodegradation ability of PLLA, the addition of PLLA in other polymers possibly improves the biodegradation ability of the materials. This is very important and significant for the environmental protection. On one hand, the use of polymers which are obtained from petroleum resources will be reduced. On the other hand, the materials exhibit biodegradation ability to a certain extent, which is favorable for the reclaim of plastic waste.

Polycarbonate (PC) exhibits excellent physical properties including high fracture resistance, strength, heat-deformation temperature, electrical insulation, etc., and it has been one of the most important engineering plastics. Now, it has been widely used ranging from package, electronic elements to automobile. To further improve the performance of PC and provide more

application of the material, different PC blends have been developed, such as PC/polyethylene (PE),[15] PC/poly(ethylene terephthalate) (PET),[16] PC/polypropylene (PP),[17] PC/acrylonitrile–butadiene–styrene,[18] etc.

Recently, the blends of PLLA and PC attract the attention of researchers and several PLLA/PC blends have been developed.[19,20] Lee introduced different compatibilizers into PLLA/PC blends and found that the mechanical, morphological, rheological, and degradation properties are greatly dependent upon the type of the compatibilizer.[19] Kanzawa investigated the mechanical and morphology changes of ternary PLLA/PC/poly(butylenes adipate-co-terephthalate) blends through reactive processing. The results show that the tensile strain and impact strength of the ternary blends are greatly enhanced considerably.[20] Factually, the design and preparation of materials based on PC and PLLA is very significant. On one hand, the addition of PLLA reduces the amount of PC in articles, which weakens the dependence on the petroleum product. On the other hand, PLLA exhibits good hydrolytic degradation ability, which is favorable for the environmental protection. However, for most articles prepared from PC, the good thermal properties are required. As is well known, PLLA exhibits relatively low glass-transition temperature, therefore, the addition of PLLA possibly influences the thermal properties of PC articles. Unfortunately, the effect of PLLA on the thermal properties and hydrolytic

degradation ability of the blends has been less researched. As a part of serial work about the modification of PC induced by PLLA, in this study, PLLA (30 wt %) was introduced into PC and the physical properties as well as the hydrolysis behavior of the blend was comparatively researched in detail.

EXPERIMENTAL PART

Materials

PLLA (2002D, D-isomer content = 4.3%, M_w = 2.53 × 10^5 g/mol, melt flow rate (MFR) = 4–8 g/10 min (190°C/2.16 kg), and density of 1.24 g/cm^3) was purchased from NatureWorks®, USA. PC (S-2001R, M_η = 2.3 × 10^4 g/mol, MFR = 7.5–10.5 g/10 min (300°C/1.2 kg), and density of 1.2 g/cm^3) was obtained from Mitsubishi Engineering-Plastics.

Sample Preparation

Both PC and PLLA were first dried at 70°C for 10 h. Then the blend of PC/PLLA (70/30) was prepared on a twin-screw extruder (SHJ-30, China) at the screw speed of 100 rpm and the temperatures of 170–200–220–240–255–255–250°C from hopper to die. After making droplets, the pellets were injection-molded and the standard specimens for physical properties measurements were prepared using an injection-molding machine (NISSEI-PS40E5A5E, Japan) with the melt temperatures of 240–255–255–250°C from hopper to nozzle and mold temperature of 25°C. The injection speed was 6.3 g/s and the holding pressure was 35 MPa. To make a comparison, both PC and PLLA samples were prepared according to the same processing procedures.

Differential Scanning Calorimetry

Differential scanning calorimetry (DSC, Netzsch STA449C Jupiter, Germany) was used to investigate the melting and crystallization behaviors of the samples. A sample of about 8 mg was first heated from 0 to 280°C at a heating rate of 10°C/min and maintained at 280°C for 3 min to erase any thermal history, then the sample was cooled down to 0°C at a cooling rate of 5°C/min. All the measurements were carried out in nitrogen atmosphere.

Scanning Electron Microscope

The dispersion of PLLA in the blend and the tensile-fractured surface morphologies of samples were characterized using a scanning electron microscope (SEM, Fei Inspect FEI, the Netherlands) with an accelerating voltage of 5.0 kV. To characterize the morphology of the blend, the sample was cryogenically fractured in liquid nitrogen perpendicularly to the flow direction, and then the fractured surface was coated with a thin-gold layer before SEM characterization. The core zone of an injection-molded bar was characterized.

Wide angle X-ray diffraction

The crystalline structure of the sample was investigated using a wide angle X-ray diffraction (WAXD, Panalytical X'pert PRO diffractometer with Ni-filtered Cu Kα radiation, the Netherlands). The continuous scanning angle range used in this study was from 5 to 40° at 40 kV and 40 mA.
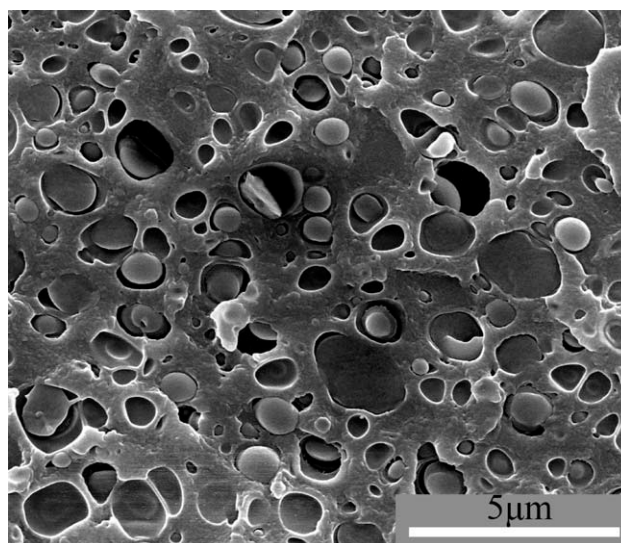

Figure 1. SEM image shows the morphology of PC/PLLA (70/30) blend.

Physical Properties Measurements

Universal tensile properties were measured at room temperature (23°C) using an SHIMADZU AGS-J tensile testing machine (Japan) according to ASTM D638. A crosshead speed of 50 mm/min was used. For each sample, the average value reported was derived from at least five specimens. Dynamic mechanical analysis (DMA) testing was carried out using a DMA Q800 analyzer (USA). The single cantilever mode was selected, and the measurement was carried out on a rectangular cross-sectional bar (with length of 50 mm, width of 10 mm, and thickness of 4 mm) from 0 to 200°C at a heating rate of 3°C/min and a frequency of 1 Hz. For pure PLLA, the temperature range for the DMA measurement was set from 0 to 140°C.

Heat distortion temperature (HDT) was measured on a Heat Distortion/Vicat softening point instrument (RV-300, Chengde, China) in accordance with ISO75. The standard pressure was calculated as 1.4 MPa and the heating rate was 120°C/h.

Hydrolytic Degradation

Hydrolytic degradation of the sample was carried out at 50°C in a solution of sodium hydroxide (NaOH, pH = 13). The weight of the sample was carefully measured before the measurement. After being placed into the solution, the sample was periodically removed, washed with fresh water and dried in an oven for 4 h, and then the sample was carefully weighed to obtain the weight loss. The variation of the weight loss as a function of hydrolysis degradation time was then graphed.

RESULTS AND DISCUSSION

Morphology of the Blend

Figure 1 shows the morphology of the blend. It can be seen that the fractured surface exhibits a typical surface morphology of an immiscible blend that has no interfacial bonding. In the blend, PLLA exhibits the dispersed particles, whereas PC is the matrix and the average diameter of PLLA particles is about 0.62 μm. The apparent interface between PLLA particles and PC
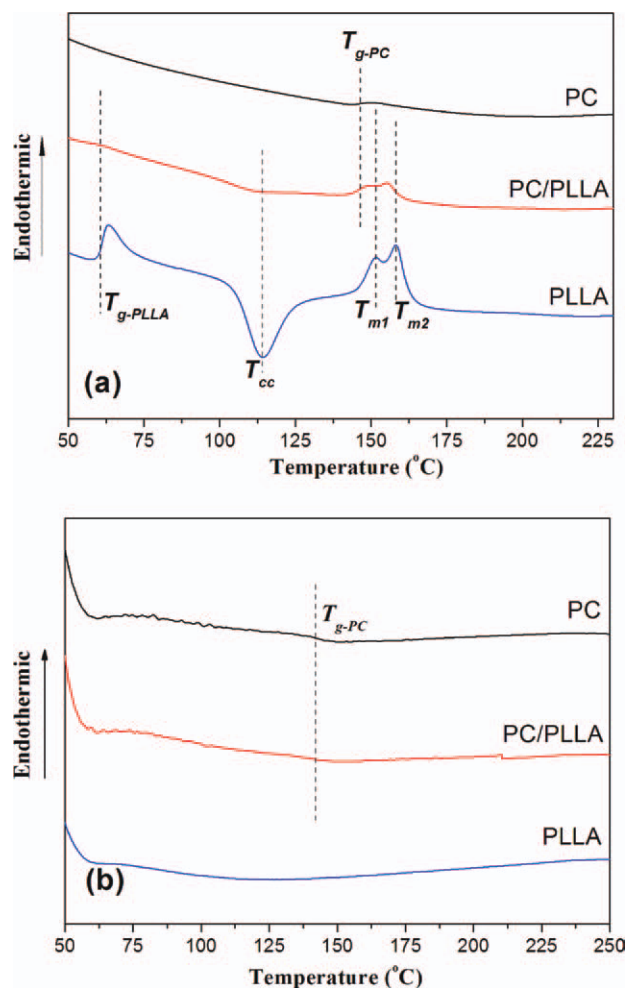
Figure 2. DSC heating curves (a) and cooling curves (b) of samples. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

matrix indicates the weak interfacial interaction between PLLA and PC. The similar results have been reported elsewhere.[19]

Crystallization Behavior of the Blend

Figure 2 shows the melting and crystallization behaviors of samples. To make a comparison, the results of both pure PC and PLLA are also shown. Pure PC is in the amorphous state and therefore, only the glass-transition behavior can be differentiated from the DSC heating curve. The glass transition-temperature (T_g) of PC is about 147.2°C. For pure PLLA, besides the glass transition with T_g of 61.3°C, one can observe the other two transitions including cold crystallization behavior T_{cc} and melting behavior T_m. Specifically, one can observe double-melting peaks at 151.7 (T_{m1}) and 158.3°C (T_{m2}). Now, it is widely accepted that the double-melting peaks are attributed to the melting–recrystallization–melting process of PLLA lamellae. The first-melting peak is attributed to the fusion of thin lamellae formed during the cooling process or during the DSC-heating process, and the second one to the fusion of lamellae formed during the DSC-heating process through the melting–recrystallization process of thin lamellae occurred at relatively lower temperature.[21] In the

blend, the cold crystallization behavior of PLLA component still can be differentiated at the similar temperature range when compared with pure PLLA. However, the area of the exothermic peak is reduced greatly when compared with pure PLLA. The enthalpy of cold crystallization was calculated as 2.1 J/g, much smaller than the 26.0 J/g of pure PLLA. Even if the composition of the blend is considered, the crystallization enthalpy of PLLA component (7.0 J/g) is still much smaller than that of pure PLLA. This suggests that the cold crystallization of PLLA component in the blend is prevented by PC matrix to a certain extent. Although the melting peak of PLLA overlaps with the glass transition of PC matrix, the peak at relatively higher temperature (155.6°C) still can be attributed to the fusion of PLLA lamellae. Compared with the T_m of pure PLLA, the relatively lower T_m value of PLLA component in the blend also suggests the restriction of PC matrix on the mobility of chain segments of PLLA component, which prevents the crystallization of PLLA.

Figure 2(b) exhibits the cooling curves of samples obtained from DSC measurement at the cooling rate of 5°C/min. Besides the glass transition of PC at temperature range of 130–150°C, which can be differentiated in both pure PC and PC/PLLA blend, whether for pure PLLA or for PLLA component of the blend, no crystallization phenomenon is detected during the cooling process. The presence of PC matrix shows no influence on the crystallization behavior of PLLA. In other words, both PLLA and PC are in the amorphous state. This is most likely ascribed to the relative high-cooling rate during the injection-molding process, which endows little time for the nucleation and growth of PLLA crystallites. This can be further proved by WAXD measurement. As shown in Figure 3, all samples exhibit the typical WAXD patterns of amorphous state. This suggests that the following physical properties had to be analyzed based on the fact that both PLLA and PC are amorphous.

Physical Properties

The tensile properties of the samples were first measured and the corresponding results are shown in Figures 4–6. In general, the engineering stress–strain curve of polymer can be delineated:
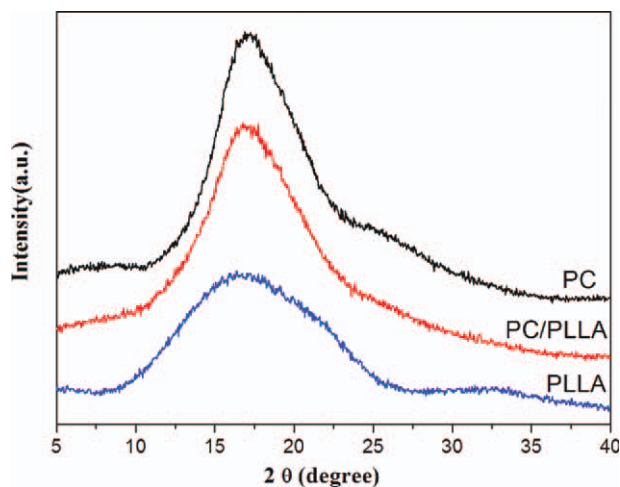
Figure 3. WAXD pattern of samples. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
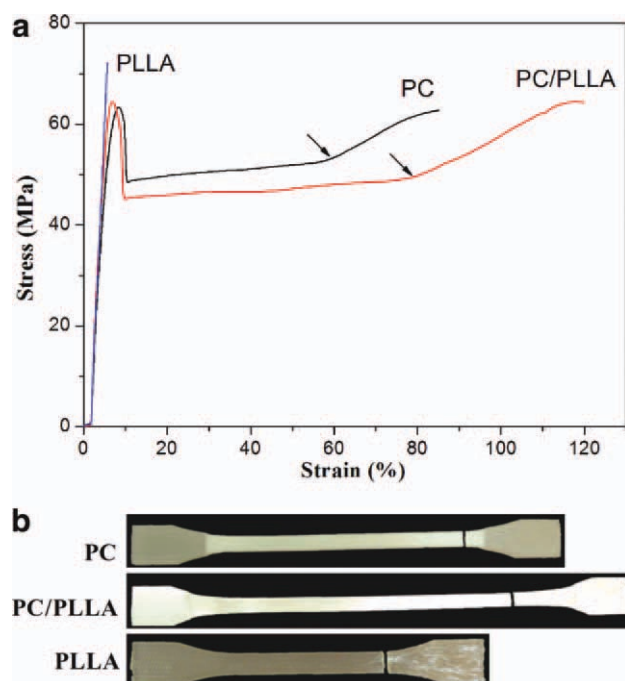
Figure 4. (a) The typical stress–strain curves of samples. (b) The optical images show the appearance of the fractured samples. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

(a) the elastic region (linear increase in engineering stress with engineering strain), (b) yield point (maximum yield stress on the stress–strain curve), (c) stress softening region (dramatic decrease in engineering stress with almost invariant engineering strain), (d) cold-drawing region (almost invariant engineering stress with engineering strain), (e) strain hardening region (gradually increased engineering stress with engineering strain), and (f) fracture point. According to the analysis of engineering stress–strain curve, the fracture mode of sample can be deduced. As shown in Figure 4, specimen of pure PC experiences the whole regions as delineated earlier, and it exhibits the typical ductile fracture mode with apparent necking phenomenon during the tensile process. The elongation at break is about 83.8% as seen in Figure 5. Specifically, an apparent stress whitening phenomenon is observed, which is the result of the nucleation and formation of large amounts of cavities during the tensile process. However, pure PLLA specimen exhibits the typical brittle fracture mode without apparent yielding phenomenon, and the elongation at break is only 5.7%. The stress whitening phenomenon nearly disappears, suggesting that the nucleation and propagation of crack occur in a very short time. With the presence of 30 wt % PLLA in PC matrix, the specimen exhibits the similar engineering stress–strain curve when compared with pure PC. The difference is that the addition of PLLA enlarges the cold-drawing region and delays the strain hardening to relatively higher strain. Specifically, it is interesting to observe that PLLA exhibits simultaneous toughening and reinforcement effects on PC. As shown in Figure 5, the tensile strength is increased from 63.5 MPa of pure PC to 65.1 MPa of the blend, and the tensile modulus is also increased from 1751.1 to 2040.6 MPa. The reinforcement mechanism of PLLA for PC can be attributed to the relatively higher strength and modulus of PLLA particles when compared with PC matrix. Although the blend is immiscible and there is apparent interface between PLLA particles and PC matrix as proved by SEM results, the elongation at break (%) is still enhanced from 83.8% of pure PC to 119.6% of the blend. Since the presence of PLLA particles results in the formation of multiphase structure in the blend, leading to the change of the appearance of specimen, it is difficult to differentiate the stress whitening phenomenon of the blend during the tensile process.

To further understand the toughening effect of PLLA on PC, the tensile-fractured surface morphology was characterized using SEM and the result is shown in Figure 6. To make a comparison, the results of pure PC and PLLA are also shown. PC specimen exhibits intense plastic deformation morphology along the stress direction, indicating the ductile fracture mode during the tensile measurement. As expected, the tensile-fractured surface of PLLA specimen is very smooth without apparent plastic deformation phenomenon, further indicating the brittle fracture mode of the specimen. However, a rough surface with large amounts of tearing or deformation is observed for the blend specimen. This means that the presence of PLLA particles change the stress state of the specimen, and more PC matrix is provoked to deform during the tensile process. As proved in Figure 5, PLLA exhibits much higher elastic modulus than PC, and therefore, it can be thought that the rigid PLLA particles disperse in the ductile PC matrix. During the tensile process, a triaxial stress is provoked around PLLA particles, leading to debonding at the PLLA–PC interface. The formation of the voids at the interfaces changes the stress state in the PC matrix surrounding the voids, resulting in operative shear yielding mechanism. On one hand, the latter is believed to be favorable for the energy absorption upon fracture.[22] On the other hand, although PLLA is a typical brittle polymer, it exhibits relatively lower T_g. During the tensile process, the enhancement of local temperature of the specimen possibly is higher than the T_g of PLLA component, leading to the enhancement of mobility of PLLA chain segments. This is also favorable for the improvement of the ductility of the specimen.
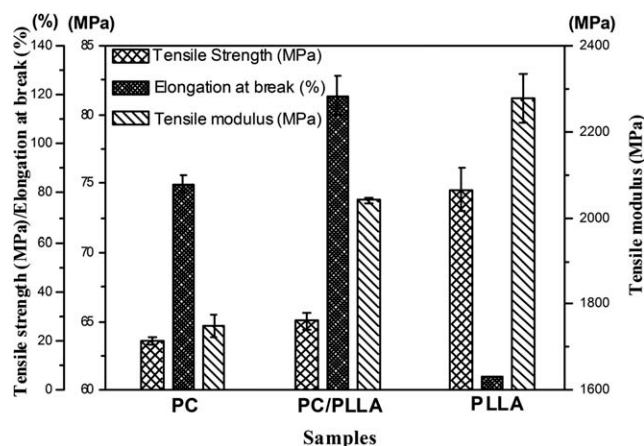
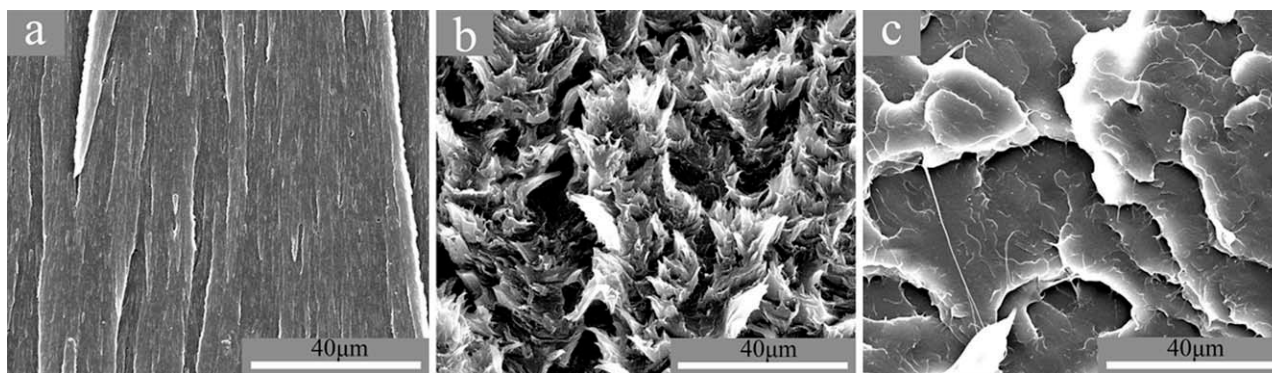**Figure 5.** Comparison of tensile properties of samples.

Figure 6. SEM images show the tensile-fractured surface morphologies. (a) PC, (b) PC/PLLA, and (c) PLLA

Figure 7 shows the dynamic mechanical properties of the pure specimens and the blend. Below the T_g of PLLA, pure PLLA exhibits the biggest storage modulus (E') and PC shows the smallest one. Due to the presence of rigid PLLA particles, the E' of the blend is enhanced greatly. Specifically, at temperature range of 100–130°C, whether for pure PLLA or for the blend,

one can observe the increase of E', which can be attributed to the cold crystallization of PLLA during the heating process. The variation of the loss factor (tan δ) of specimen is shown in Figure 7(b). For pure PLLA, besides the main peak at about 67.4°C attributing to the glass transition of chain segments of PLLA, one can observe some weak peaks at about 100–130°C, which can also be ascribed to the cold crystallization of PLLA. The T_g of PLLA component in the blend is slightly higher than that in pure PLLA possibly due to the restriction of PC matrix on the relaxation of chain segments of PLLA. However, the blend specimen and pure PC specimen exhibit the similar T_g values, further indicating the weak interfacial interaction between PC and PLLA.
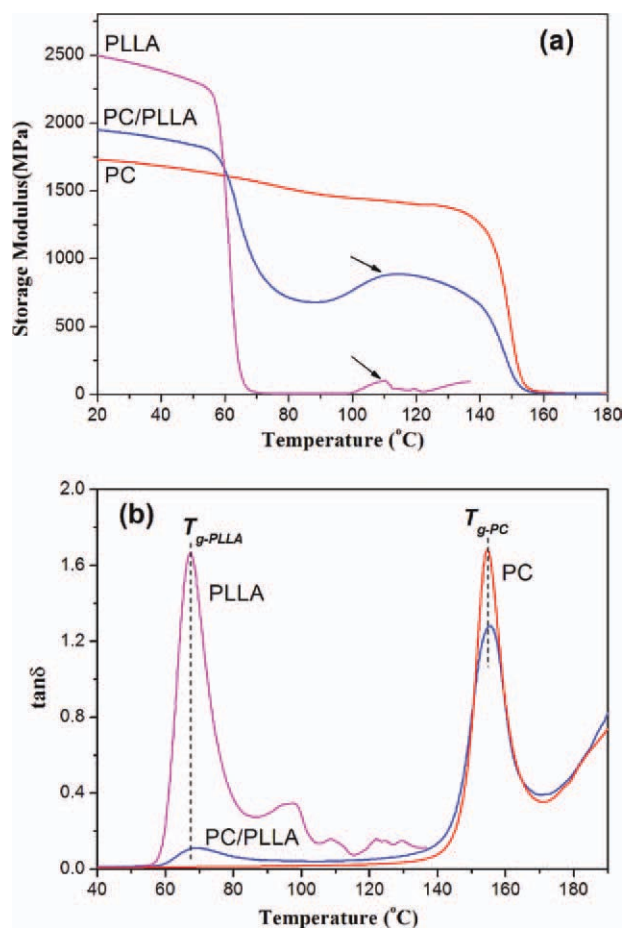
The thermal properties of the specimens were evaluated through the measurement of HDT. As shown in Figure 8, pure PC exhibits the biggest HDT (128.5°C) and pure PLLA exhibits the smallest one (only 58.8°C). Interestingly, the HDT of the blend (124.2°C) is comparable to that of pure PC. The measurements were repeated for several times and the similar results were obtained. This is very significant for application of PC/PLLA articles. Although the HDT of PLLA is very small, it exhibits very weak influence on thermal property of the sample. In general, the HDT of sample depends on thermal property of the matrix. Herein, as shown in Figure 1, even if the content of
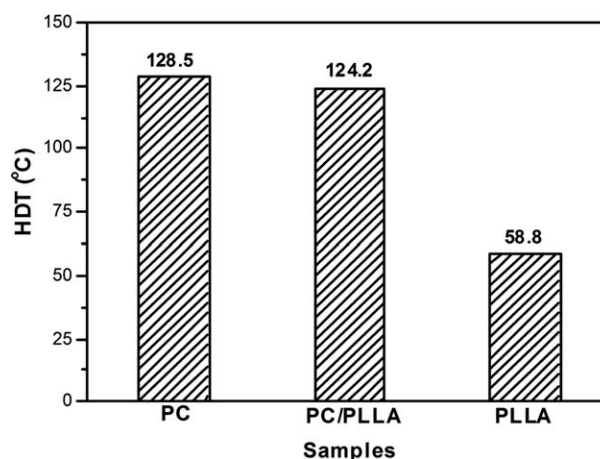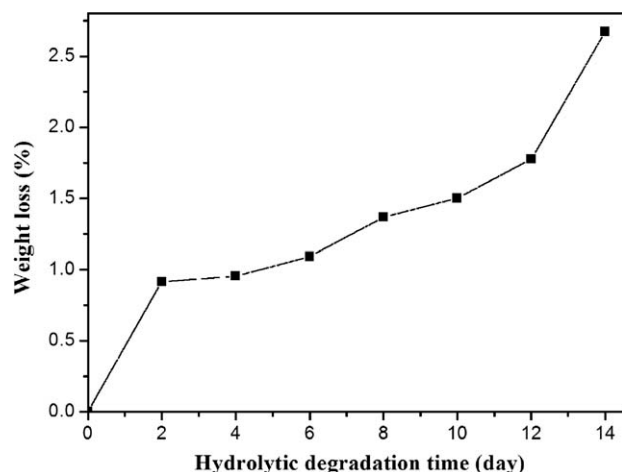

Figure 7. Storage modulus (a) and loss factor (b) of samples. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 8. Comparison of HDT of samples.

Figure 9. The weight loss (%) of PC/PLLA blend as the function of time.

PLLA in the blend is up to 30 wt %, it is still present as the dispersed particles. Therefore, the blend still exhibits excellent thermal property.

The hydrolytic degradation ability of the sample was also investigated. As is well known that PC has no hydrolysis and therefore there is no any weight loss in NaOH solution. In our study, the weight of PC keeps invariant when it was immersed in NaOH solution for about 2 weeks (not shown in this article). For PLLA, it exhibits relatively better hydrolytic degradation ability and its hydrolysis behavior has been widely investigated in the published reports.[23–25] For example, Zhao found that the weight loss of pure PLLA is up to 50% when it was immersed in NaOH solution (37°C) for about 16 days.[23] In our study, the solution temperature is increased up to 50°C, therefore, the hydrolytic degradation ability can be further enhanced. Factually, in our study, the PLLA sample became soft and disappeared in a very short time when it was immersed in NaOH solution. Therefore, only the hydrolysis behavior of blend was investigated and the variation of weight loss as a function of time is shown in Figure 9. It can be seen that with the increase of time, the weight loss of the samples increases gradually, indicating the hydrolysis of PLLA component. However, it had to be noticed that the rate of hydrolysis of PLLA component is very small. For example, when the sample was immersed in NaOH solution for 14 days, the weight loss is only about 2.7%, much smaller than the content of PLLA component (30 wt %) in the blend. This indicates that only a small portion of PLLA component is hydrolyzed. Factually, this can be explained by the morphology of the blend. As shown in Figure 1, PLLA exhibits the dispersed particles and these particles are surrounded by PC matrix. In general, chemical properties including hydrolytic ability depend on contact area with solvent. In this article, when PLLA particles are surrounded by PC matrix, the contact area with solvent is relatively small. Therefore, it is very difficult for the solvent to contact the PLLA particles, and only the PLLA particles which contact with solvent can be attacked and exhibit the hydrolysis behavior. This is very similar to the dissolution characteristics of dispersed particles in blends.

However, it proved at least that the presence of PLLA component in PC endows the material, the hydrolytic degradation ability to a certain extent. It can also be deduced that with the further increase of PLLA content, the hydrolytic degradation ability of PC/PLLA material will be further enhanced. Obviously, this is very important and significant in environmental protection.

CONCLUSION

In summary, a certain content of PLLA (30 wt %) is introduced into PC. The morphology characterization shows that PLLA exhibits the dispersed particles in the PC matrix. Both DSC and WAXD results show that the crystallization behavior of PLLA component is not influenced by amorphous PC. Through the common processing methods, both PLLA and PC are amorphous. The mechanical measurements show that PLLA exhibits the toughening and reinforcement effects on PC simultaneously. Furthermore, the HDT of the blend is comparable to that of pure PC, although the content of PLLA is as high as 30 wt %. Finally, the hydrolytic degradation ability measurement shows that the presence of PLLA endows the PC material the hydrolysis behavior to a certain extent.

ACKNOWLEDGMENTS

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