

Greatly Enhanced Hydrolytic Degradation Ability of Poly(L-lactide) Achieved by Adding Poly(ethylene glycol)*

Yang-peng Wang, Xiao Wei, Jin Duan, Jing-hui Yang, Nan Zhang, Ting Huang and Yong Wang**

School of Materials Science and Engineering, Southwest Jiaotong University, Key Laboratory of Advanced Technologies of Materials, Ministry of Education of China, Chengdu 610031, China

Abstract Plasticized poly(L-lactide) (PLLA) materials have been applied in many fields and the microstructure performance of such materials attracts much attention of researchers. However, few reports declared the hydrolytic degradation ability of the plasticized PLLA materials. In this article, a small quantity of poly(ethylene glycol) (PEG) was introduced into PLLA, which aimed to understand the hydrolytic degradation behavior of the plasticized PLLA materials. The microstructures of the plasticized samples were comparatively investigated using scanning electron microscopy (SEM), wide angle X-ray diffraction (WAXD), differential scanning calorimetry (DSC) and Fourier transform infrared spectroscopy (FTIR), *etc.* The results demonstrated that PEG improved the hydrophilicity of sample surface, and the relatively high content of PEG enhanced the crystallization ability of PLLA matrix. The hydrolytic degradation measurement was carried out at 60 °C in an alkaline solution of pH = 12. The results demonstrated that the plasticized PLLA samples exhibited accelerated hydrolytic degradation compared with the pure PLLA sample, and the hydrolytic degradation was also dependent on the PEG content. Further results demonstrated that PEG induced the change of hydrolytic degradation mechanism possibly due to the good dissolution ability of PEG in water, which provided more paths for the penetration of water. Furthermore, the microstructure evolution of the plasticized PLLA during the hydrolytic degradation process was also investigated, and the results demonstrated the occurrence of PLLA crystallization, which was possibly contributed to the decreased hydrolytic degradation rate observed at relatively long hydrolytic degradation time. This work is of great significance and may open a new way for promoting the reclamation of PLLA waste material.

Keywords PLLA/PEG; Microstructure; Hydrolytic degradation

INTRODUCTION

As one of the biodegradable and biocompatible polyesters, poly(L-lactide) (PLLA) have attracted much attention in both academic and industrial fields ranging from food package, biomedical products, clothing to automotive materials^[1]. On one hand, the synthesis of PLLA is independent on the petroleum resources. The monomers (lactic acid) are prepared through the fermentation of completely natural resources such as corn, wheat and/or rice, *etc.*^[2]. On the other hand, the PLLA waste can be completely degraded to lactic acid monomer, carbon dioxide and water through different degradation methods^[3–5], which reduces the environmental pollution and meets the requirement of sustainable development. Furthermore, the PLLA materials exhibit better tensile strength and tensile modulus compared to most of the polyolefins^[6]. With the merits mentioned above, PLLA has become the well-known “green polymer” and it is of great interest as an alternative to the traditional plastic commodity.

However, PLLA also has many inherent shortages, including the relatively small crystallization rate and the

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** Corresponding author: Yong Wang (王勇), E-mail: yongwang1976@163.com

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poor fracture toughness, both of which are mainly related to the poor flexibility of the PLLA molecular chains. Although PLLA is a typical crystalline polymer, it usually maintains at the amorphous state during the common melt processing, such as extrusion and injection molding^[7]. The glass transition temperature (T_g) of PLLA is about 60 °C, therefore, it can be deduced that the PLLA products with amorphous state exhibit low heat distortion temperature (HDT), which inevitably limits the application of PLLA in the areas that experience relatively high environmental temperatures^[8]. Due to the intrinsic rigidity characteristic of molecular chains, it is very difficult to change their conformation under the load condition and consequently, PLLA usually possesses the brittle fracture mode, and the main mechanism for fracture energy absorption is crazing rather than that for shear yielding^[9].

To date, many strategies have been developed to improve the crystallization and fracture toughness of PLLA^[10–21]. Among these strategies, adding plasticizer is possibly an appropriate method because the plasticizer can simultaneously improve the crystallization and fracture toughness of the PLLA products^[22–24]. It is well known that plasticizers are widely used in plastic processing. Generally, a small quantity of plasticizer can greatly improve the flow ability of plastics through increasing free volume between molecular chains, reducing entanglement density of polymeric chains and the lubrication effect. During the crystallization process, the enhanced mobility of PLLA chain segment induced by plasticizer usually results in relatively high nucleation ability and higher crystallization rate compared with that of the pure PLLA^[7, 25]. So far, many kinds of plasticizers have been successfully applied in PLLA melt processing, including polyadipates^[26], star-structured polylactides^[27], compressed carbon dioxide^[28], poly(ethylene glycol)^[29], acetyl triethyl citrate^[7], triphenyl phosphate^[30, 31], acetyl tributyl citrate^[25] and triacetin^[25, 32], *etc.* Among these plasticizers, the most widely used plasticizer is poly(ethylene glycol) (PEG), which has the good miscibility with PLLA^[33]. For example, Kulinski *et al.*^[23] reported that adding a few PEG (< 10 wt%) in PLLA greatly enhanced the crystallization ability and tensile ductility especially, such effects were not influenced by the end groups of PEG. Nowadays, PEG is also introduced into the PLLA-based composites or blends to investigate the synergistic effects of PEG and other components on the crystallization and mechanical properties of the PLLA materials^[34].

Although PLLA is a biodegradable polymer and it can be completely degraded through different strategies, such as hydrolytic degradation process and enzymolysis process, it usually shows relatively low hydrolytic degradation rate, which also limits its application. Hence, enhancing the hydrolytic degradation ability of PLLA-based materials is very important from a viewpoint of accelerating the reclamation of PLLA waste material. So far, the studies on the hydrolytic degradation behavior of PLLA are mainly focused on the pure PLLA and/or the PLLA-based composites. For the pure PLLA, the hydrolytic degradation is influenced by many factors, such as (1) the microstructural factors including the content of D-isomer content^[35, 36], the molecular weight and the molecular weight distribution^[31], the degree of crystallinity^[37–44], the spherulite morphology^[45] and the end group of PLLA^[46, 47], *etc.*, and (2) the environmental factors including temperature^[45, 48, 49], pH value of solution^[43, 48, 50, 51] and the presence of ultraviolet light^[52], *etc.* For the PLLA-based composites, it has been demonstrated that the hydrolytic degradation occurs firstly at the interface between PLLA and the fillers. Therefore, besides the factors mentioned above, the hydrophilicity, dispersion and the content of fillers also influence the hydrolytic degradation behavior of the PLLA-based composites^[53–57]. However, the hydrolytic degradation behavior of the plasticized PLLA materials is rather few. Hu *et al.*^[58, 59] investigated the effect of aging on the microstructure and properties of the PLLA/PEG sample. Lemmouchi *et al.*^[60] reported that the plasticized PLLA containing tributyl citrate and block copolymers based on poly(D,L-lactide) and PEG exhibited accelerated hydrolytic degradation compared with the pure PLLA sample, but there are still many problems about the hydrolytic degradation of the plasticized PLLA material that need to be clarified. Loh *et al.*^[61] synthesized several polyester-based copolymers containing PEG segments and systematically investigated the hydrolytic degradation of such polyesters.

Since the plasticized PLLA materials have already been widely used in many fields, systematically investigating the hydrolytic degradation behavior of this kind of PLLA materials becomes very significant. In the present work, PEG plasticized PLLA samples are prepared, and the effects of PEG content on crystallization and

hydrolytic degradation of PLLA matrix in alkaline solution are systematically investigated. Specifically, the microstructure evolution of PLLA matrix during the hydrolytic degradation process is also investigated. It is expected that the results reported in this work can provide guidance for the reclamation and disposal of PLLA waste material.

EXPERIMENTAL

Materials

PLLA (2003D, with a D-isomer content of 4.3 wt%, a melt flow rate (MFR) of 5.6 g/10min (190 °C/2.16 kg) and a density of 1.24 g/cm³) was purchased from Nature Works®, USA. PEG (Polyethylene glycol 4000, with M_w of 3000–4500 g/mol and a melting point (T_m) of 48–53 °C) was purchased from Keshi®, Chengdu.

Sample Preparation

Before melt compounding, PLLA was dried at 40 °C for 24 h to remove the interfering of moisture in thermal degradation of PLLA matrix. Different contents of PEG (2 wt%, 5 wt% and 10 wt%) were introduced into PLLA through melt compounding processing that was conducted on an internal mixer. The melt compounding was carried out at a melt temperature of 190 °C, a screw speed of 60 r/min and a mixing duration of 6 min. After that, the blends were compression-molded at 190 °C and 5 MPa to obtain the sheet-like samples with a thickness of about 0.5 mm for subsequent microstructure characterization and hydrolytic degradation measurements. The sample notation is defined as PLLA/PEG- x , where x represents the PEG content. For making a comparison, the pure PLLA sample was also prepared by the same procedures mentioned above.

Characterization

The morphology of the sample was characterized using a scanning electron microscope (SEM) Fei inspect (FEI, the Netherlands) at an accelerating voltage of 5.0 kV. To characterize the sample surface morphology, the hydrolyzed sample was directly used. To understand the possible change of morphology in the inner part of the sample before and after hydrolytic degradation, samples were firstly immersed into liquid nitrogen for 30 min, and then they were cryogenically fractured. Either for the cryo-fractured surfaces or for the surfaces of the hydrolyzed samples, they were coated with a thin layer of gold before SEM characterization.

The crystalline structure of PLLA matrix was investigated using a wide angle X-ray diffraction (WAXD) X'pert PRO diffractometer (Panalytical, the Netherlands) with Ni-filtered Cu K α radiation. The continuous scanning angle range used in this study was from 5° to 55° at 35 kV and 25 mA. The degree of crystallinity (X_{c-WAXD}) was calculated according to the following Eq. (1):

$$X_{c-WAXD} = \frac{\sum A_c}{\sum A_c + \sum A_a} \times 100\% \quad (1)$$

where A_c and A_a represent the integrated intensities under the diffraction peaks and the integrated intensities under the amorphous halo.

The melting behaviors of the samples were detected using a differential scanning calorimetry (DSC) STA 449C Jupiter (Netzsch, Germany) instrument. A sample of about 8 mg was heated from 30 °C to 200 °C at a heating rate of 10 K/min. The measurement was carried out in nitrogen atmosphere. The degree of crystallinity (X_{c-DSC}) was calculated according to the following Eq. (2):

$$X_{c-DSC} = \frac{\Delta H_m - \Delta H_{cc}}{\Delta H_m^0 \times \phi} \times 100\% \quad (2)$$

where ΔH_m is the DSC measured value of fusion enthalpy, ΔH_{cc} is the cold crystallization enthalpy obtained during the DSC heating process, ΔH_m^0 is the fusion enthalpy of the completely crystallized PLLA, and ϕ is the relative weight fraction of PLLA in the plasticized samples. Here, ΔH_m^0 of PLLA is selected at 93 J/g^[62].

A Fourier transform infrared (FTIR) AVATAR 360 (Thermo Nicolet, USA) spectroscope was used to

detect the formation of oriented structure and/or crystalline structure of PLLA before and after being hydrolyzed. During the measurements, an attenuated total reflection (ATR) mode was used. The resolution was set at 2 cm^{-1} and the wavenumber range was from 600 cm^{-1} to 4000 cm^{-1} . The measurements were carried out at room temperature ($23\text{ }^{\circ}\text{C}$).

The hydrophilicity of the sample was evaluated by measuring the static contact angle of double distilled water on the sample surface. The measurement was conducted on a drop shape analysis system DSA 100 (KRÜSS, Germany) at an environmental temperature of $20\text{ }^{\circ}\text{C}$. Measurement of a given contact angle was carried out for at least 5 times and the value close to an average value was given.

Hydrolytic degradation measurement was carried out in a solution of sodium hydroxide (NaOH) with original pH value of 12 and the temperature of $(60 \pm 0.2)\text{ }^{\circ}\text{C}$. Before hydrolytic degradation, the weight of each sample was carefully weighed. Then, the sample was immersed into a NaOH solution and the hydrolytic degradation occurred accordingly. After being hydrolyzed for a certain time, the sample was taken out, washed with fresh water and dried through the cryodesiccation at $-18\text{ }^{\circ}\text{C}$ for 24 h to insure the complete removal of water, and then the residual weight of the hydrolyzed sample was carefully weighed to detect the weight loss of the sample during the hydrolytic degradation process. After that, the hydrolyzed sample was further hydrolyzed in the NaOH solution, and the similar procedures were repeated until the morphology of the sample could not be well maintained. Subsequently, the variation of the residual weight fraction (Φ) as a function of hydrolytic degradation time (t, h) was illustrated. Here, Φ was calculated by the following Eq. (3):

$$\Phi = \frac{w_t}{w_0} \times 100\% \quad (3)$$

where w_0 and w_t represent the initial weight (g) of sample before hydrolytic degradation and the residual weight (g) after hydrolysis for a certain time (h).

The number-average (M_n), weight-average (M_w) molecular weights and the polydispersity ($\bar{D} = M_w/M_n$) of the samples before and after hydrolysis were measured using a gel permeation chromatography (GPC) HLC-8320 GPC (TOSOH, Japan) instrument with polystyrene as a standard. During the measurement, the sample was dissolved in *N,N*-dimethylformamide (DMF).

RESULTS AND DISCUSSION

Effect of PEG on the Microstructure of PLLA

The as-prepared sample is crucial for studying the microstructures to understand the subsequent hydrolytic degradation behaviors. Here, the cryogenically fractured surface morphology of the plasticized PLLA sample was firstly investigated using SEM. As shown in Fig. 1, the PLLA/PEG-5 sample exhibits very homogeneous morphology without phase separation, which confirms the good miscibility between PLLA and PEG components^[33].

The crystalline structures of the pure PLLA sample and the plasticized PLLA samples were characterized using WAXD. As shown in Fig. 2, the pure PLLA sample shows the typical WAXD profile of amorphous polymers without any characteristic diffraction peak, which indicates that the pure PLLA sample from the compression molding is amorphous. The similar phenomenon is also observed for the PLLA/PEG-2 sample, indicating that adding a small quantity of PEG (2 wt%) does not apparently promote the crystallization of PLLA. However, the PLLA/PEG-5 sample displays a weak diffraction peak at $2\theta = 16.7^{\circ}$, attributing to the diffractions of (110)/(200) crystal planes of α -form PLLA^[63]. Such result clearly indicates the presence of PLLA crystallites in the sample. For the PLLA/PEG-10 sample, besides the diffractions of (110)/(200) crystal planes, the diffraction peak of (203) crystal plane at $2\theta = 19.2^{\circ}$ appears, indicating the presence of more integrated PLLA crystallites in the plasticized sample. Obviously, the crystallization ability of the PLLA matrix during the compression molding processing is greatly enhanced by adding more PEG.

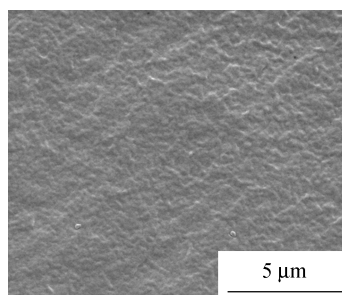


Fig. 1 SEM image showing the typical cryo-fractured surface morphology of the representative PLLA/PEG-5 sample

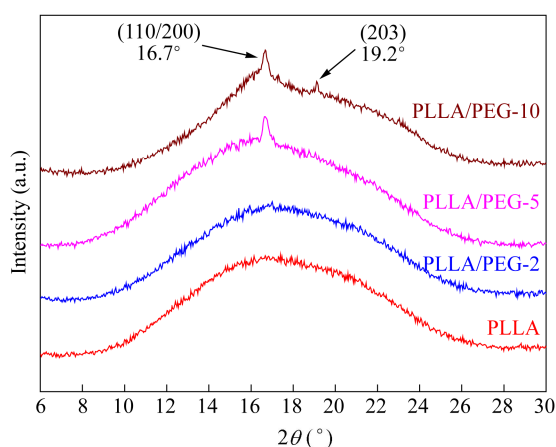


Fig. 2 WAXD profiles showing the crystalline structures of the pure PLLA sample (red line) and the plasticized PLLA samples (blue, pink and brown line) (The online version is colorful.)

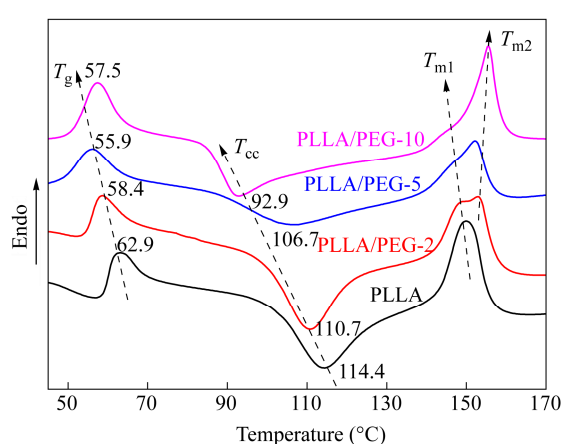


Fig. 3 DSC heating curves showing the melting behavior of the pure PLLA sample (black line) and the plasticized PLLA samples (red, blue and pink line) as prepared from compression molding processing (The online version is colorful.)

Figure 3 shows the DSC heating curves of all the samples prepared in this work and the corresponding thermal properties are listed in Table 1. The pure PLLA sample has three transitions at 62.9, 114.4 and 150.0 °C, which are mainly related to the glass transition (T_g), cold crystallization (T_{cc}) and the fusion of crystallites (T_m) of PLLA, respectively. The previous WAXD measurements have also demonstrated that the pure PLLA sample is amorphous. Therefore, it can be deduced that the crystallites detected by the DSC measurement are mainly induced by the cold crystallization process during the DSC heating scan. The similar transitions are also observed for all the plasticized PLLA samples. However, some differences need to be noticed. Firstly, the glass transition of the plasticized PLLA samples shifts to the lower temperatures and T_g gradually decreases with increasing the PEG content up to 5 wt%. For example, the PLLA/PEG-2 and PLLA/PEG-5 samples exhibit T_g of 58.4 and 55.9 °C, respectively, both of which are much lower than that of the pure PLLA sample. This clearly demonstrates the excellent plasticizing effect of PEG, which greatly enhances the mobility of the PLLA molecular chains. However, the PLLA/PEG-10 sample shows a slightly increased T_g possibly due to the restriction effect of crystalline part on the motion of amorphous domains. Secondly, T_{cc} also decreases with increasing the PEG content. Generally, the PLLA polymers with higher crystallization ability give the lower T_{cc} . It is well known that the cold crystallization ability is mainly related to the presence of nucleus and/or the chain segment mobility of polymer matrix. In our case, the PLLA/PEG-2 sample exhibits the amorphous structure as demonstrated by previous WAXD measurement. Therefore, it can be deduced that the enhanced cold

crystallization ability is mainly related to the enhanced mobility of the PLLA molecular chains due to the plasticizing effect of PEG. For the PLLA/PEG-5 and PLLA/PEG-10 samples, besides the enhanced mobility of the chain segment, the pre-existent crystallites also contribute to the decrease of T_{cc} because they play the nucleation role and promote the crystallization of the adjacent chains. Thirdly, the PLLA/PEG-2 sample has the double endothermic peaks at 148.8 °C (T_{m1}) and 153.2 °C (T_{m2}). With increasing the PEG content, T_{m1} decreases gradually and the intensity of the endothermic peak also decreases, while T_{m2} changes slightly. This indicates that T_{m1} is mainly related to the fusion of crystallites formed through the cold crystallization process, while T_{m2} is correlated with the fusion of crystallites formed through melt-recrystallization process at relatively high temperatures^[64].

Table 1 Thermal properties of the pure PLLA sample and the plasticized PLLA samples before and after hydrolysis for different time *

Samples	Hydrolysis time (h)	T_g (°C)	T_{cc} (°C)	T_m (°C)	ΔH_{cc} (J/g)	ΔH_m (J/g)	X_c (%)
PLLA	0	60.2	113.9	149.8	-21.7	22.7	0.0
	24	63.9	—	152.7	—	8.2	8.9
	72	61.7	—	155.4	—	20.9	22.5
PLLA/PEG-2	0	56.1	110.5	152.9	-21.2	20.0	0.0
	24	60.8	—	154.1	—	13.5	14.8
	72	60.2	—	155.0	—	19.3	21.8
PLLA/PEG-5	0	52.1	105.5	152.1	-13.1	12.8	0.0
	24	59.5	—	154.7	—	21.0	23.7
	72	59.7	—	155.2	—	23.7	26.8
PLLA/PEG-10	0	54.3	92.7	155.5	-19.6	18.5	0.0
	24	60.2	—	154.6	—	22.7	26.8
	72	58.6	—	154.9	—	24.9	29.5

* The data were obtained through DSC measurement.

It is well known that the FTIR measurement not only provides the information about the presence of chemical functional groups and/or the interactions between functional groups, but also offers the information about the crystalline and/or the oriented structures. For the PLLA sample, the absorption bands at about 921 and 956 cm^{-1} are usually assigned to the crystalline α -form (or α' -form) with a 10_3 helix conformation and the amorphous phase, respectively^[65]. Furthermore, the absorption band at about 867 cm^{-1} is demonstrated to be very sensitive to the intermolecular packing in the PLLA^[66]. Generally, the increase of intermolecular packing results in the increase of the dipole-dipole interactions, so the band shifts to relatively high wavenumbers. As shown in Fig. 4, both the pure PLLA sample and the PLLA/PEG-2 samples exhibit strong absorption bands at 956 and 867 cm^{-1} . This demonstrates that the samples are completely amorphous. Interestingly, obviously changes are observed for the PLLA/PEG-5 and the PLLA/PEG-10 samples, which show a weak absorption band at 921 cm^{-1} , and the absorption band attributing to the intermolecular packing shifts to 871 cm^{-1} . This clearly indicates the presence of ordered and/or crystalline structure of PLLA in the samples. These observations agree well with the results obtained from WAXD and DSC measurements. In conclusion, the pure PLLA sample and the plasticized PLLA samples containing relatively low PEG content (2 wt%) are completely amorphous, while a relatively high PEG content (5 wt% and 10 wt%) promotes the crystallization of PLLA.

Hydrophilicity of the Samples

Besides the microstructure of the sample, the hydrophilicity of the sample surface is another factor that determines the hydrolytic degradation ability of PLLA. Usually, the high wettability of the sample surface is favorable for the absorption and penetration of water molecules, which facilitates the hydrolytic degradation of the samples. In our case, although PLLA is known as a hydrophilic polymer due to the presence of a large amount of polar groups in the main chain, the hydrophilicity is still low^[67]. PEG is a polar material with the excellent interaction ability with water. Therefore, it can be hypothesized that adding PEG is favorable for the

improvement of PLLA hydrophilicity. As shown in Fig. 5, the pure PLLA sample displays a static contact angle of about 72°. While relatively low contact angles are obtained for all the plasticized PLLA samples, indicating the increased hydrophilicity of the sample surface. Specifically, the contact angle decreases gradually with increasing the PEG content, indicating that the high content of PEG enhances the hydrophilicity of the sample surface.

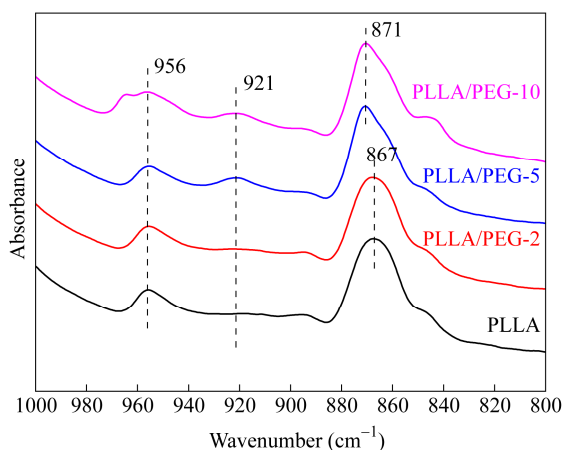


Fig. 4 FTIR spectra showing the microstructure of the pure PLLA sample and the plasticized PLLA samples

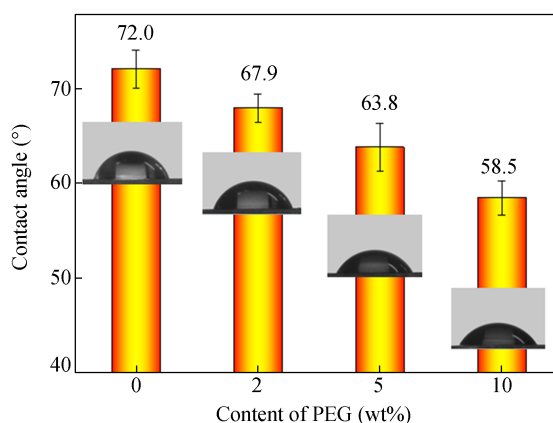


Fig. 5 Variation of contact angle versus the content of PEG in the samples

Hydrolytic Degradation

The hydrolytic degradation behaviors of the samples were measured in the alkaline solution of pH = 12 at 60 °C. The determination of degradation conditions was mainly based on the consideration of accelerating the reclamation and disposal of PLLA waste products. The variation of residual weight fraction (Φ) versus hydrolytic degradation time (t) is illustrated in Fig. 6. Generally, the hydrolytic degradation rate of the sample can be deduced from the slope of the curve. As shown in Fig. 6, there are several features that need to be noticed. Firstly, all samples exhibit gradually decreased Φ with increasing t , which is easily to be understood and the similar phenomenon is widely reported elsewhere. Secondly, the plasticized PLLA samples exhibit accelerated hydrolytic degradation compared with the pure PLLA sample, especially the sample with more PEG. For example, after being hydrolyzed for 312 h, the pure PLLA sample still exhibits Φ of 98.0%, indicating the rather low hydrolytic degradation rate even at relatively high temperature and high pH value. However, at the same hydrolytic degradation conditions, the PLLA/PEG-5 and PLLA/PEG-10 samples exhibit Φ of 91.1% and 87.9%, respectively. Thirdly, all the samples display the similar variation trends of Φ versus t . Namely, the whole hydrolytic degradation process can be divided into three stages as shown in Fig. 6. In the stage I and stage III, samples exhibit faster hydrolytic degradation rate. Specifically, the slop of the curve increases with increasing the PEG content in stage I. This further indicates the enhanced hydrolytic degradation rate of PLLA possibly due to the improved hydrophilicity of the sample surface by incorporating PEG.

To further demonstrate the degradation of PLLA samples, the variation of molecular weight of the representative samples after hydrolysis for 72 h was measured by GPC. Figure 7 shows the GPC profiles, and the corresponding data are listed in Table 2. For comparison, the results of the pure PLLA sample before hydrolysis are also shown in Fig. 7 and Table 2. Compared with the pure PLLA sample without hydrolysis, the hydrolyzed samples have the lower molecular weight. A new peak in the GPC profile is observed, which is possibly attributed to the presence of the oligomer of PLLA generated by the hydrolysis. It is clear that the more the PEG in the sample is, the more change the molecular weight is. Furthermore, the intensity of the new peak greatly reduces with increasing the PEG content, demonstrating the accelerated hydrolytic degradation of PLLA induced by PEG. The data shown in Table 2 also confirm that the presence of PEG promotes the reduction of both M_n

and M_w , and the increase of $\bar{D}$. Obviously, the hydrolytic degradation of PLLA matrix is greatly enhanced by adding PEG.

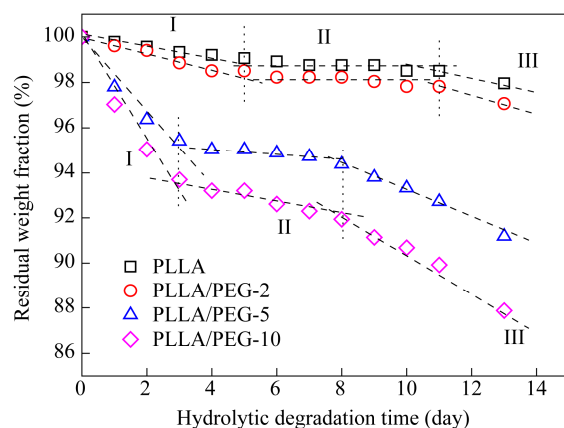


Fig. 6 Variation of residual weight fraction (%) of different samples versus the hydrolytic degradation time (day) (The hydrolytic degradation was carried out at 60 °C and pH = 12.)

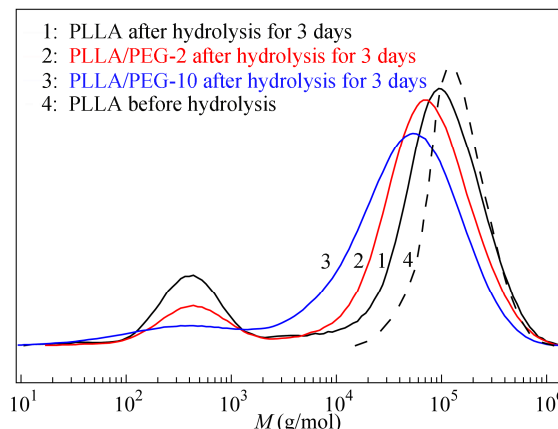


Fig. 7 GPC profiles of the pure PLLA (black line) and the PLLA/PEG samples after hydrolysis at 60 °C for 72 h

Table 2 Number-average (M_n) and weight-average (M_w) molecular weights and the polydispersity ($\bar{D}$) of the samples *

Samples	$M_n \times 10^{-4}$ (g/mol)	$M_w \times 10^{-4}$ (g/mol)	$\bar{D}$
PLLA-before hydrolysis	11.06	16.78	1.52
PLLA	5.54	14.20	2.56
PLLA/PEG-2	4.26	11.28	2.65
PLLA/PEG-10	2.21	8.00	3.62

* Samples were hydrolyzed at 60 °C for 72 h. For making a comparison, the data of the pure PLLA sample before hydrolysis are also involved in the Table.

Studying the surface morphology of the hydrolyzed sample is favorable for understanding the hydrolytic degradation mechanism. In this work, the evolutions of surface morphologies of the pure PLLA and the PLLA/PEG-5 samples with increasing hydrolytic degradation time were comparatively investigated using SEM. The results are shown in Fig. 8. It can be seen that for both of the pure PLLA and the PLLA/PEG-5 samples, their surfaces become coarse after hydrolytic degradation, and the surface roughness is more serious with increasing the hydrolytic degradation time. Notably, the surface of PLLA/PEG-5 sample shows more roughness with many holes as compared with that of the pure PLLA sample, which further confirms the more serious degradation in the plasticized sample. To better understand the hydrolytic degradation of the plasticized PLLA sample, the cross-section of the broken hydrolyzed PLLA/PEG-5 sample was also characterized, and the corresponding cryo-fractured surface morphology is shown in Fig. 9. Even in the center of the hydrolyzed sample, we still observe many tiny holes. There are two possibilities that contribute to the presence of such holes. One possibility is related to the dissolution of PEG in water when the fractured sample is taken out from liquid nitrogen, and the other possibility is the synergy effect of the hydrolytic degradation of PLLA and the dissolution of PEG during the hydrolytic degradation process. However, considering that the cryo-fractured surface morphology of the PLLA/PEG-5 sample (Fig. 1) shows the homogeneous morphology without any tiny holes, it can be deduced that the tiny holes observed in Fig. 9 are really related to the hydrolytic degradation of the PLLA matrix. It has been demonstrated that in the alkaline solution, the main hydrolytic degradation mechanism of PLLA and/or PLLA-based composites is the surface erosion mechanism^[43, 50, 54–56]. Namely, the hydrolytic degradation occurs from the surface to the center of the sample. Obviously, the phenomena observed in the present work are quite different from the literature report^[43, 50, 54–56]. It seems that the plasticized PLLA

sample exhibits bulk erosion mechanism^[68].

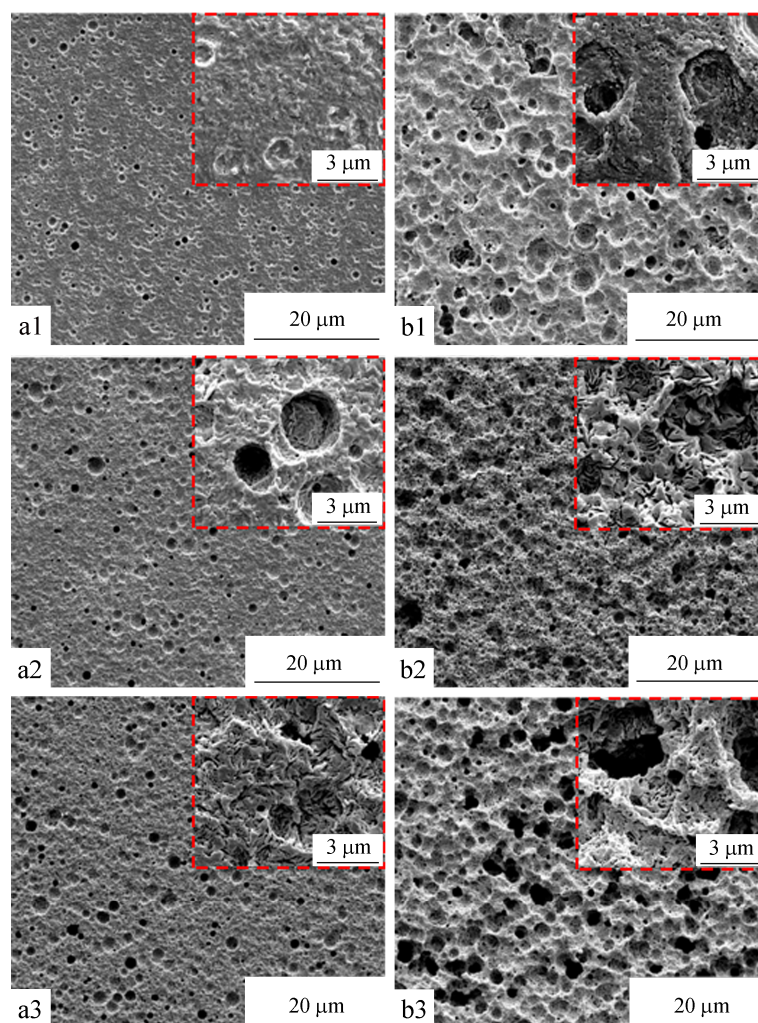


Fig. 8 SEM images showing the surface morphologies of the pure PLLA (a1–a3) sample and the PLLA/PEG-5 (b1–b3) samples after degradation at 60 °C for different time: (a1, b1) 24 h, (a2, b2) 72 h and (a3, b3) 264 h (The inserted images showing the morphologies obtained at higher magnifications.)

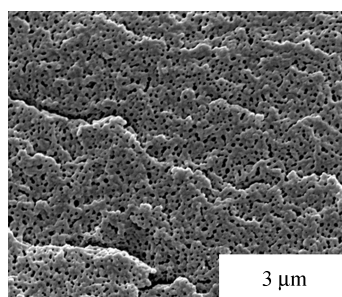


Fig. 9 SEM image showing the surface morphology in the cross-section of the PLLA/PEG-5 sample after degradation at 60 °C for 264 h

To further demonstrate the role of PEG in the hydrolytic degradation of PLLA, some representative samples

were also characterized using FTIR. The results are shown in Fig. 10. The PLLA/PEG-10 sample shows a characteristic absorption band at 2883 cm^{-1} before hydrolytic degradation, attributing to the C—H stretching vibration in the CH_2 groups^[69]. However, after being hydrolyzed for 24 h, its absorption band becomes very weak, which indicates that there is no PEG in the sample or the content of PEG is very low.

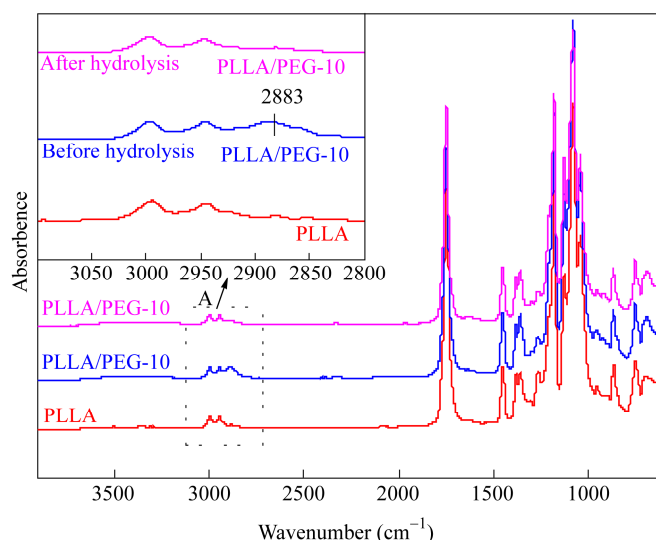


Fig. 10 FTIR spectra showing the comparison of characteristic absorption bands at $2800\text{--}3100\text{ cm}^{-1}$ of the representative samples (red line for PLLA, blue line and pink line for PLLA/PEG-10 before and after hydrolysis, respectively) (Inset: the amplification for the wavelength from 2800 cm^{-1} to 3050 cm^{-1})

Considering the good dissolution ability of PEG in water and the results of SEM and FTIR measurements, more visualized illustrations are proposed in Fig. 11 for explaining the hydrolytic degradation mechanism of the plasticized PLLA samples. For comparison, the hydrolytic degradation mechanism of pure PLLA is also included. It is well known that the hydrolytic degradation of pure PLLA in alkaline solution obeys the surface erosion mechanism^[43, 50]. Namely, the hydrolytic degradation firstly occurs on the sample surface, and then proceeds to the center part with the gradually changes in size and morphology when the hydrolytic degradation time increases. However, for the plasticized PLLA sample, the presence of PEG improves the hydrophilicity of sample surface, which enhances the wettability of sample. The dissolution of PEG firstly occurs, which provides

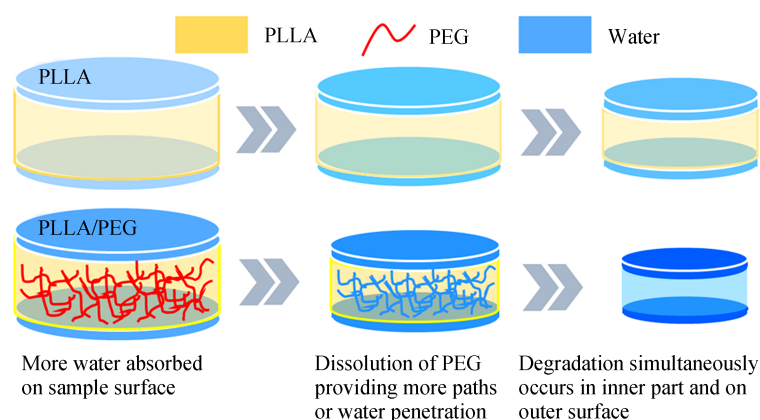


Fig. 11 Schematic representations showing the different hydrolytic degradation mechanisms for the pure PLLA and the plasticized PLLA samples

more paths for the penetration of water, consequently, the hydrolytic degradation of PLLA matrix is greatly accelerated. Obviously, the more the PEG in the sample is, the faster the hydrolytic degradation of PLLA matrix is. Because the dispersion of PEG in the plasticized PLLA is very homogeneous due to the good miscibility between PLLA and PEG, the hydrolytic degradation possibly occurs simultaneously on the sample surface and in the center part.

Microstructure Evolution of PLLA Matrix during the Hydrolytic Degradation Process

The microstructure evolution of PLLA during the hydrolytic degradation is also very interesting, since it facilitates to further understand the hydrolytic degradation behaviors of the samples. The previous reports have demonstrated that during the hydrolytic degradation process, the solvent of water exhibits a plasticizing effect, which enhances the mobility of PLLA chain segments. The average molecular weight reduces and the molecular weight distribution increases with the proceeding of hydrolytic degradation, which also enhances the mobility of residual PLLA chain segments. Consequently, molecular ordering and crystallization of PLLA usually occur during the hydrolytic degradation process^[43, 50]. With the presence of nanofillers, the crystallization of PLLA can be further promoted^[54, 70]. In the present work, the hydrolytic degradation was carried out at 60 °C, which was higher than T_g of the plasticized PLLA. Although PEG firstly dissolves into water during the hydrolytic degradation process, the plasticizing effect of PEG still exists. This indicates that the crystallization of PLLA matrix can be possibly promoted during the hydrolytic degradation process.

The DSC heating curves of the samples after hydrolysis for different time are shown in Fig. 12, and the corresponding thermal properties are also listed in Table 1. For comparison, the results of the samples before hydrolysis are also shown in Fig. 12 and Table 1. There are several features that need to be pointed out. Firstly, compared with the samples before hydrolysis, all the hydrolyzed samples show the increased T_g , which can not be attributed to the reduced average molecular weight and/or increased molecular weight distribution^[71]. Secondly, different from the cold crystallization phenomenon of un-hydrolyzed samples observed during the DSC heating scan, the cold crystallization is not detected from the hydrolyzed samples. Thirdly, a weak exothermic peak (shown by arrow) is observed at the left side of the main endothermic peak of PLLA crystallites. It has been demonstrated that the presence of such exothermic peak is mainly related to the transformation of the unstable α' -form PLLA to the more stable α -form during the heating scan^[72]. This indicates that the hydrolyzed samples, especially containing a relatively low PEG, display the α' -form PLLA after hydrolysis for a certain time^[54]. Finally, although all the samples exhibit intense endothermic peaks at about 150–152 °C, the mechanism for the origination of crystallites is different. For the un-hydrolyzed samples, the endothermic peaks are mainly related to the crystallites formed by cold crystallization during the DSC heating process. While for the hydrolyzed samples, the crystallites are mainly induced during the hydrolytic degradation process rather than the subsequent DSC heating process. In other words, during the hydrolytic degradation process, a large number of PLLA crystallites are induced.

Furthermore, the pure PLLA sample and the PLLA/PEG-2 sample present X_{c-DSC} of 8.9% and 14.8% (Table 1) respectively after they are hydrolyzed for 24 h. Further increasing the PEG content to 5 wt% and 10 wt%, X_{c-DSC} is increased to 23.7% and 26.8%, respectively. Clearly, the plasticized PLLA samples show more pronounced crystallization during the hydrolytic degradation process, indicating the role of PEG in promoting the crystallization of PLLA matrix. However, such function of PEG becomes inconspicuous when the hydrolytic degradation time increases up to 72 h.

To further understand the crystallization of PLLA matrix during the hydrolytic degradation process, another measurement, *i.e.* annealing treatment, was also applied to treat the plasticized PLLA sample. The PLLA/PEG-10 was selected and the sample was directly annealed at 60 °C for 6 h. The crystalline structure of the annealed sample was also detected using DSC and WAXD. For a comparison, the sample obtained after being hydrolyzed for 6 h was also characterized. As shown in Fig. 13(a), the annealed sample has the T_g of about 53.5 °C and T_{cc} of about 110.3 °C, while the T_g of the hydrolyzed sample increases to 63.8 °C and a weak exothermic peak appears at 89.5 °C. In addition, a weak exothermic peak attributed to the transformation of α' -form to α -form is

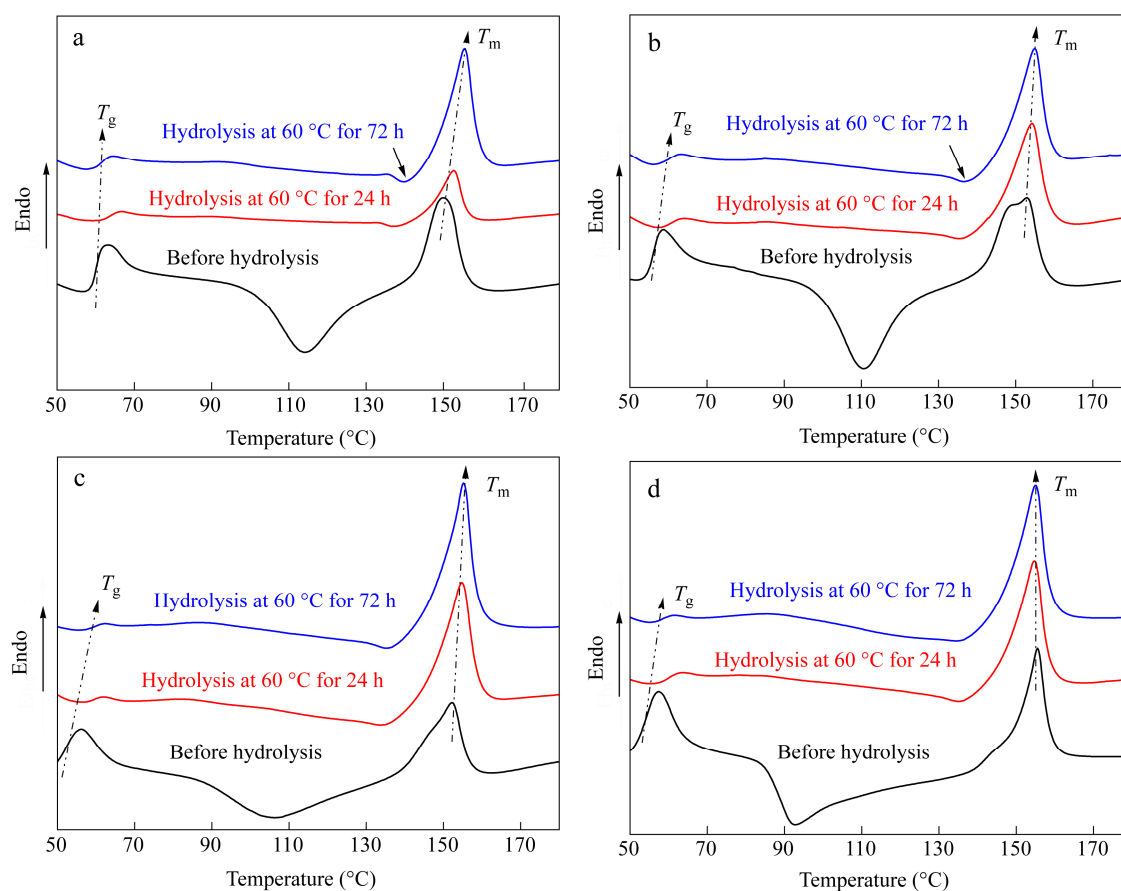


Fig. 12 DSC heating curves showing the melting behavior of the samples before and after hydrolysis for different time: (a) pure PLLA, (b) PLLA/PEG-2, (c) PLLA/PEG-5, and (d) PLLA/PEG-10

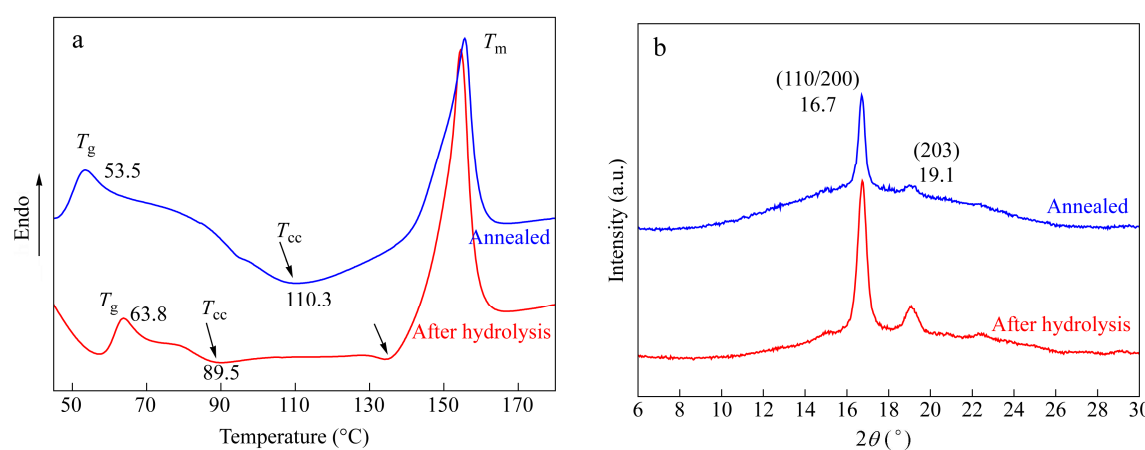


Fig. 13 (a) DSC heating curves and (b) WAXD patterns showing the crystalline structures of the representative PLLA/PEG-10 sample by the annealing treatment and hydrolysis (The annealing time and hydrolysis time are 6 h)

also observed. The hydrolyzed sample shows higher X_{c-DSC} compared with the annealed sample. Due to the increased restriction effect of the crystalline part on the motion of amorphous chains and the increased nucleation effect of existent crystallites on cold crystallization, the hydrolyzed sample displays enhanced T_g and

decreased T_{cc} compared with the annealed sample. The difference in the degree of crystallinity between the hydrolyzed sample and the annealed sample can be further demonstrated through WAXD measurement as shown in Fig. 13(b). The hydrolyzed sample shows more intensified diffraction peaks compared with the annealed sample. Furthermore, X_{c-WAXD} of the hydrolyzed sample is 28.8%, which is much higher than the annealed sample (10.0%). The results clearly confirm that the crystallization of PLLA really occurs during the hydrolytic degradation process.

CONCLUSIONS

In summary, PEG plasticized PLLA samples containing different PEG contents have been prepared. It is found that the crystallization ability of PLLA is enhanced with relatively high PEG content (5 wt% and 10 wt%). The plasticized PLLA samples exhibit improved hydrophilicity compared with the pure PLLA sample. The hydrolytic degradation measurements show that the hydrolytic degradation of plasticized PLLA samples is accelerated. Under the same hydrolytic degradation conditions, the hydrolytic degradation of PLLA is obviously faster with more PEG in the plasticized samples. The PEG induces the change of hydrolytic degradation mechanism from surface erosion to bulk erosion, which is possibly related to the dissolution of PEG in water, providing more paths for the penetration of water. Furthermore, it is found that the plasticized PLLA samples exhibit crystallization during the hydrolytic degradation process.

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