

Poly(methyl methacrylate)-induced Microstructure and Hydrolysis Behavior Changes of Poly(L-lactic acid)/Carbon Nanotubes Composites

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Abstract Poly(L-lactic acid) (PLLA)-based composites exhibit wide applications in many fields. However, most of hydrophilic fillers usually accelerate the hydrolytic degradation of PLLA, which is unfavorable for the prolonging of the service life of the articles. In this work, a small quantity of poly(methyl methacrylate) (PMMA) (2 wt%–10 wt%) was incorporated into the PLLA/carbon nanotubes (CNTs) composites. The effects of PMMA content on the dispersion of CNTs as well as the microstructure and hydrolytic degradation behaviors of the composites were systematically investigated. The results showed that PMMA promoted the dispersion of CNTs in the composites. Amorphous PLLA was obtained in all the composites. Largely enhanced hydrolytic degradation resistance was achieved by incorporating PMMA, especially at relatively high PMMA content. Incorporating 10 wt% PMMA led to a dramatic decrease in the hydrolytic degradation rate from 0.19 %/h of the PLLA/CNT composite sample to 0.059 %/h of the PLLA/PMMA-10/CNT composite sample. The microstructure evolution of the composites was also detected, and the results showed that no crystallization occurred in the PLLA matrix. Further results based on the interfacial tension calculation showed that the enhanced hydrolytic degradation resistance of the PLLA matrix was mainly attributed to the relatively strong interfacial affinity between PMMA and CNTs, which prevented the occurrence of hydrolytic degradation at the interface between PLLA and CNTs. This work provides an alternative method for tailoring the hydrolytic degradation ability of the PLLA-based composites.

Keywords Poly(L-lactic acid) composites; Poly(methyl methacrylate); Microstructure; Hydrolytic degradation

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INTRODUCTION

Poly(L-lactide) (PLLA), one of the green polymers that can be obtained from completely natural resources and also completely degrade through different strategies, has attracted increasing concerns since it was synthesized. The wide application of PLLA and its composites is of great significance because it not only reduces the dependence on petroleum-based polymers but also lowers the risk of environmental disruption.^[1] Among the various fascinating chemical/physical properties of PLLA, hydrolytic degradation ability is one of the very important indexes and it directly affects the long-service behavior and the reclamation of the PLLA-based articles. To promote the reclamation of PLLA materials or reduce the negative effect on the environment, high hydrolytic degradation ability is usually required.^[2] However, to prolong the service life of PLLA articles, reducing hydrolytic degradation

ability is also urgent.^[3–6] For example, in the application fields related to high temperature, high humidity, and high salinity, enhancing the hydrolytic degradation resistance of the PLLA-based articles is of great significance, which ensures that the comprehensive properties of the PLLA-based articles can be maintained at high level to satisfy the requirement of the real engineering application rather than be faced with deterioration induced by hydrolytic degradation. Therefore, fabricating the PLLA-based materials with tailorable hydrolytic degradation behavior is still challenging.

The hydrolytic degradation mechanisms of PLLA mainly include surface erosion and bulk erosion.^[7] Generally, when the hydrolytic degradation of PLLA occurs in the alkaline solution, the hydrolytic degradation obeys the surface erosion mechanism,^[8] while in the acidic solution, it accords to the bulk erosion mechanism.^[9] Furthermore, the hydrolytic degradation behavior of PLLA is also influenced by the environmental temperature. Obviously, higher temperature leads to greater hydrolytic degradation rate.^[10] PLLA is a well-known semi-crystalline polymer. The microstructure evolution during hydrolytic degradation is interesting. Generally, the hydrolytic

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degradation firstly occurs in the amorphous part due to the loose stacking of molecular chains and therefore, the crystalline PLLA materials show a gradually increased degree of crystallinity (X_c) with increasing hydrolytic degradation time in the early stage of the degradation process.^[11,12] Furthermore, in the PLLA materials with amorphous structure, the plasticizing effect of water and the reduction of molecular weight enhance the mobility of chain segments, which may promote the formation of locally ordered structure and/or crystalline structure in the early stage of degradation.^[13,14]

The hydrolytic degradation ability of PLLA can be easily tailored *via* various methods. Incorporating another polymer into PLLA has been demonstrated as an efficient way.^[15,16] Hydrolytic degradation behaviors of the PLLA blends are influenced by the miscibility between the components, the microstructure changes induced by the incorporated polymer, and the compositions of the blends,^[17–21] etc. Generally, immiscible PLLA blends possess apparent interfaces between components, which may induce the hydrolytic degradation of PLLA matrix at the interface region due to the lower entanglement density of molecular chains compared with the bulk components. Specifically, if the incorporated polymer exhibits excellent solubility in water, it may induce the change of hydrolytic degradation mechanism from surface erosion to bulk erosion in alkaline solution,^[22] and the mechanism is ascribed to the dissolution of the soluble polymer, which provides penetration channels for water molecules.

Incorporating nanofillers is another efficient way to tailor the hydrolytic degradation ability of PLLA. The hydrolytic degradation behavior of the PLLA composites not only depends on the microstructure changes induced by nanofillers, the content and dispersion state of nanofillers in the composites,^[23] but can also be influenced by the functional groups on the surface of nanofillers.^[24] The presence of hydrophobic groups usually enhances the hydrolytic resistance of the composites,^[25] while the hydrophilic groups promote the hydrolytic degradation of PLLA.^[26] To date, various nanofillers, such as organic montmorillonite (OMMT),^[23] hydrophilic silica (SiO_2),^[12] functionalized carbon nanotubes (CNTs),^[11] titanium dioxide (TiO_2),^[27] and graphene oxide (GO),^[28] have been incorporated into PLLA to tailor the hydrolytic degradation ability of the PLLA matrix. It has been accepted now that in the PLLA composites with hydrophilic nanofillers, the hydrolytic degradation firstly occurs at the interface between nanofillers and PLLA matrix because of the relatively high concentration of functional groups. Similarly, it is also observed that in the early stage of degradation, nanofillers may exhibit a nucleation effect on the crystallization of PLLA matrix at an appropriate environmental temperature, and the newly formed crystalline structures also influence the subsequent hydrolytic degradation behavior of the composites.^[27]

To further understand the hydrolytic degradation behaviors of PLLA in complex systems, in this work, a small quantity of poly(methyl methacrylate) (PMMA) (2 wt%–10 wt%) was introduced into the PLLA/CNT composite that already contained 1 wt% CNTs. It has been demonstrated that PLLA was miscible with PMMA and the presence of PMMA greatly affected the crystallization of PLLA.^[29,30] Furthermore, research has shown that the hydrolytic degradation behavior of

PLLA/PMMA blends is also influenced by the compositions. Higher PMMA contents lead to faster hydrolytic degradation than crystallization of PLLA while higher PLLA contents lead to faster crystallization than hydrolytic degradation.^[31] Here, the interfacial interaction between components in the ternary PLLA/PMMA/CNT composites, the microstructure evolution induced by varying PMMA content as well as the hydrolytic degradation behaviors have been systematically investigated. It is interesting to observe that compared with the binary PLLA/CNT composite, largely enhanced hydrolytic degradation resistance of the PLLA matrix was achieved in the ternary PLLA/PMMA/CNT composites. The mechanisms are thoroughly discussed based on the interfacial interactions between components. This work indicates that the hydrolytic degradation behaviors of PLLA-based composites can be easily tailored through component designing and composition tailoring, which is of great significance because the PLLA articles need satisfy different requirements in different conditions.

EXPERIMENTAL

Materials

PLLA (2003D) was obtained from NatureWorks, USA. It had a D-isomer content of 4.3%, a weight-average molecular weight (M_w) of 2.53×10^5 g/mol, a melt flow rate of 5.6 g/10min (190 °C, 2.16 kg), and a density of 1.25 g/cm³. PMMA (VH001) was obtained from Mitsubishi Rayon Polymer Nantong Co., Ltd. Japan. CNTs (TNM5), which were partially functionalized, were obtained from Chengdu Institute of Organic Chemistry, Chinese Academy of Science (Chengdu, China). The content of oxygen-containing groups of CNTs was about 1.55 wt%.

Sample Preparation

Before sample preparation, all the components were dried at 40 °C for 24 h in a vacuum oven. The composites were prepared through melt-compounding processing, which was carried out using an internal mixer ZJL-300 (Changchun Zhineng Instrument, China). During the compounding processing, the melt temperature and screw speed were set at 190 °C and 60 r/min, respectively, and the mixing duration was 5 min. After that, the composites were compression-molded at the melt temperature of 195 °C and a pressure of 5 MPa to obtain sample slices with a thickness of 0.5 mm. The compression-molded sample was quenched in ice/water mixture. In this work, the content of CNTs was maintained at 1 wt%, while the content of PMMA was varied from 0 to 10 wt%. The sample notations are defined as PLLA/CNT and PLLA/PMMA-*x*/CNT, where *x* represents the content of PMMA in the sample. For example, the sample notation PLLA/PMMA-2/CNT means that the content of PMMA is 2 wt%.

Microstructure Characterizations

The dispersion states of CNTs and the surface morphologies of hydrolyzed samples were characterized using a scanning electron microscope (SEM) Fei inspect (FEI, the Netherlands). To characterize the dispersion state of CNTs, the cryogenically fractured sample surface was directly characterized without coating gold layer. However, to characterize the morphologies of the hydrolyzed samples, a thin layer of gold was coated on the sample surface before SEM characterization. The measurements were carried out at an operating voltage of 5 kV.

A wide-angle X-ray diffraction (WAXD) X'pert PRO diffractometer (Panalytical, the Netherlands) with Ni-filtered Cu K α radiation was used to characterize the crystalline structures of samples. The measurements were carried out at a continuous scanning angle range of 5°–55°.

Melting behaviors of the composites were investigated using a differential scanning calorimeter (DSC) STA449C Jupiter (Netzsch, Germany). About 8 mg of sample was heated from 30 °C to 200 °C at a heating rate of 5 °C/min and the measurements were carried out in nitrogen atmosphere. In this work, the main attention is focused on understanding the crystalline structure formed before and in the process of hydrolytic degradation and therefore, only heating scan was conducted. The degree of crystallinity (X_c) was calculated using the following relation:

$$X_c = \frac{\Delta H_m - \Delta H_{cc}}{\Delta H_m^0 \times \phi} \times 100\% \quad (1)$$

where ΔH_m and ΔH_{cc} represent the fusion enthalpy (J/g) and cold crystallization enthalpy of sample during the heating scan, respectively, ΔH_m^0 (93 J/g^[32]) is the fusion enthalpy of PLLA with 100% crystallinity, and ϕ is the weight fraction of PLLA in the sample.

Glass transition temperature of the composites was further investigated through using a dynamic mechanical analysis (DMA) Q800 analyzer (TA Instrument, USA). A sample with a length of 300 mm, a width of 5 mm, and a thickness of 0.5 mm, and it was prepared through compression molding processing as mentioned above. The measurements were carried out at a tensile mode, a frequency of 10 Hz, and a heating rate of 5 °C/min from 30 °C to 180 °C.

To further detect the microstructure changes in the hydrolyzed composites, a Fourier transform infrared spectroscope (FTIR) iS50 (Thermo Nicolet, USA) was used to characterize the samples in an attenuated total reflection (ATR) mode. The measurements were carried out in a wavenumber range of 400–4000 cm⁻¹ and the resolution was set at 4 cm⁻¹.

A polarized optical microscope (POM) DM2700P (Leica, Germany) with a hot stage LNP95 (Linkam Instrument, UK) was used to characterize the isothermal crystallization morphologies of samples. The isothermal crystallization was carried out at temperature of 130 °C for 1 h before the images of crystallization morphologies were taken.

Hydrolytic Degradation Measurements

The hydrolytic degradation measurements were carried out in alkaline solution (NaOH/H₂O, pH = 13) with a solution temperature of 37 °C. In the degradation process, the sample was periodically taken out, cautiously washed and freeze-dried at -18 °C for 24 h, and then carefully weighed. It should be pointed out that the hydrolytic medium maintained invariant during the whole process of hydrolytic degradation. Two parameters, *i.e.* residual weight fraction (Φ) and hydrolytic degradation rate (R , %/h), are calculated according to the following relations:

$$\Phi = \frac{w_t}{w_0} \times 100\% \quad (2)$$

$$R = \frac{1 - \Phi}{t} \quad (3)$$

where w_0 and w_t represent the weights (g) of sample before and after being hydrolyzed for time t (h).

RESULTS AND DISCUSSION

Microstructure of the Composites

The dispersion states of CNTs in the representative PLLA/CNT and PLLA/PMMA-10/CNT composites were firstly characterized using SEM, and the results are shown in Fig. 1. It is worth noting that these samples were directly characterized using SEM without coating gold layer. Therefore, only the region that contains many CNTs can be characterized due to the relatively high local electrical conductivity, while the other regions containing no or few CNTs cannot be characterized. From Fig. 1 more CNTs are clearly observed in the PLLA/CNT composites, while fewer CNTs can be observed in the PLLA/PMMA-10/CNT composites. This indicates that CNTs had better dispersion in the PLLA/PMMA-10/CNT composites and it was relatively difficult for CNTs to form local electrical conductive path. In other words, incorporating PMMA improved the dispersion of CNTs in the PLLA/CNT composites. The similar scenario that incorporating another polymer component to tailor the dispersion state of nanoparticles in the polymer matrix has also been reported elsewhere.^[33] Here, the mechanism for the improved dispersion of CNTs will be further discussed in the following section.

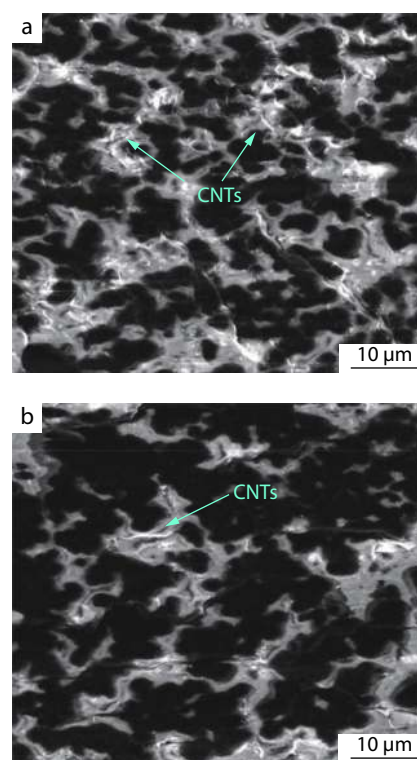


Fig. 1 SEM images showing the dispersion states of CNTs in (a) PLLA/CNT and (b) PLLA/PMMA-10/CNT composites.

CNTs have been demonstrated as an efficient nucleating agent for the crystallization of semi-crystalline polymers. The presence of a few CNTs may induce greatly accelerated crystallization of the polymer matrix.^[34] Furthermore, the hydrolytic degradation rate of PLLA is also largely influenced by X_c ^[35] In this work, 1 wt% CNTs were incorporated into PLLA and therefore, it is interesting to find out whether CNTs induced the crystallization of PLLA matrix or not. Fig. 2(a) shows

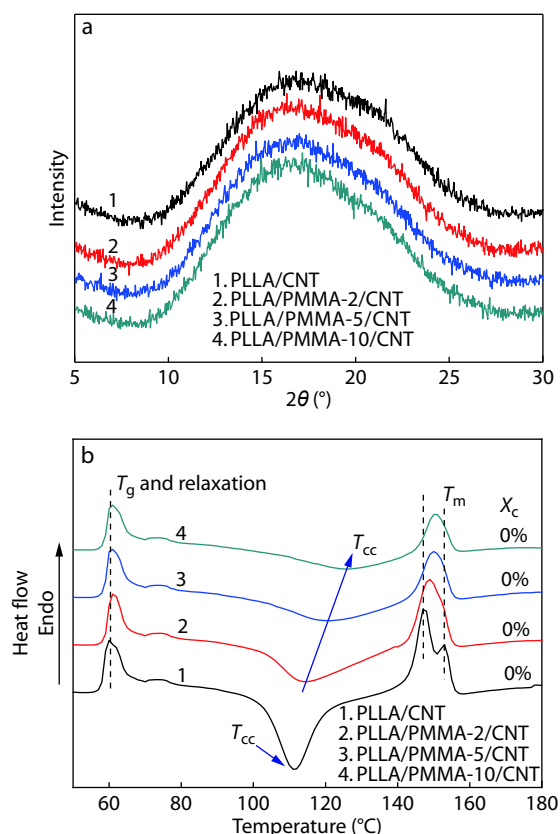


Fig. 2 (a) WAXD patterns of binary PLLA/CNT and ternary PLLA/PMMA/CNT composites, and (b) DSC curves showing the glass transition, cold crystallization, and melting behaviors of samples during the heating scan.

the WAXD profiles of all the composites investigated, where all of them show the typical WAXD profiles of the amorphous polymer. This indicates that the PLLA matrix was in the amorphous state or the content of crystalline structure was too small to be detected by WAXD measurement.

The samples were further measured using DSC and the results are shown in Fig. 2(b). There are several transitions in the DSC heating curves, attributable to the glass transition (T_g), the cold crystallization (T_{cc}), and the melting of crystalline structures (T_m). However, the glass transition overlaps the relaxation peak and consequently, the determination of T_g value becomes difficult through DSC measurements. Here, T_g was determined through DMA measurement as reported in the next section. Furthermore, the PLLA/CNT composite exhibits T_{cc} at 111.5 °C and double endothermic peaks at 147.1 and 153.1 °C. The presence of the double endothermic peaks can be attributed to the melting-recrystallization-melting behaviors of the crystalline structures with defects during the DSC heating scan.^[36] Fig. 2(a) already shows that PLLA matrix was in the amorphous state. Therefore, the crystalline structure was mainly formed in the DSC heating process. Since the chain mobility of PLLA matrix is very small and the cold crystallization occurs at relatively low temperature, many defects were induced in the crystallites. Similar to the PLLA/CNT composite, the glass transition of the ternary composites still overlaps the relaxation peak and T_g cannot be well determined.

However, it is found that the ternary PLLA/PMMA/CNT composites show gradually enhanced T_{cc} with increasing PMMA content, and invariant T_m at about 148.9 °C. Obviously, the presence of PMMA suppressed the cold crystallization of the PLLA matrix, and the suppression effect became more apparent with increasing PMMA content. Since the cold crystallization occurs at relatively high temperature, more integrated crystalline structures are achieved and consequently, these crystalline structures show single endothermic peak at relatively high temperature. According to Eq. (1), X_c of all samples are calculated and the results are also shown in the graph. All of them showed X_c of 0%, indicating that the PLLA matrix in all samples as prepared were amorphous. In other words, the crystalline structures detected at 145–155 °C were mainly induced through the cold crystallization process during the DSC heating scan.

The effect of PMMA on T_g of the composite samples was further detected using DMA, and the results are shown in Fig. 3. It is clearly seen that incorporating PMMA did not make much difference to the PLLA matrix, and T_g of all the composites was in the range of 87.4–89.5 °C. It is well known that PMMA exhibits higher T_g compared with PLLA on the one hand. On the other hand, PLLA is miscible with PMMA. Therefore, it is expected that incorporating PMMA may induce an enhancement of T_g as reported in literature.^[31,37,38] Interestingly, in this work, the ternary PLLA/PMMA/CNT composites had very slightly enhanced T_g compared with the binary PLLA/CNT composite. The similar phenomenon has also been reported by Hao *et al.*^[38] In their work, the PLLA/PMMA blend containing 10 wt% PMMA showed T_g of 62 °C, which was slightly higher than that of the neat PLLA (60 °C). While increasing PMMA content up to 30 wt%, T_g was apparently enhanced up to 67 °C. Here, the slight enhancement of T_g is possibly attributed to the low PMMA content in the composites and the presence of CNTs that weakened the effect of PMMA on mobility of PLLA molecular chains. This will be further discussed in the following section.

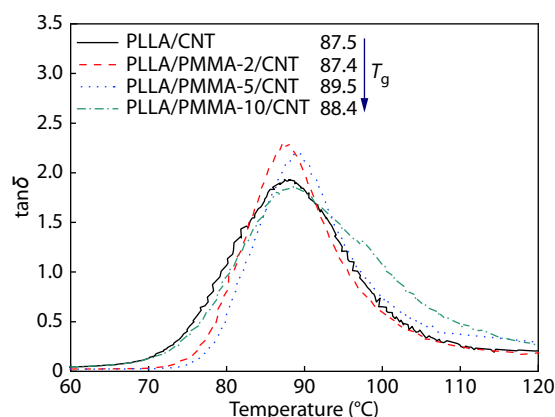


Fig. 3 Loss factor ($\tan\delta$) of the binary PLLA/CNT and the ternary PLLA/PMMA/CNT composite samples.

Hydrolytic Degradation Behavior

Fig. 4 shows the variations of residual weight fraction (Φ) and hydrolytic degradation rate (R) with increasing hydrolytic degradation time (t). From Fig. 4(a) one can see that all the composite samples show a linear decrease of Φ with increasing t .

The binary PLLA/CNT composite sample shows the smallest Φ . After being hydrolyzed for 240 h, Φ was greatly decreased to 54.3%. This confirms the high hydrolytic degradation ability of the PLLA/CNT composites. The similar phenomenon has been previously reported in our group,^[11] and the high degradation ability is mainly ascribed to the increased hydrophilicity of sample surface and the presence of a large number of interfaces in the composite. Largely enhanced Φ was achieved for all the ternary PLLA/PMMA/CNT composite samples, which indicates that incorporating PMMA was beneficial to improving the hydrolytic degradation resistance of the PLLA composites, and higher PMMA content led to better hydrolytic degradation resistance. For example, after being hydrolyzed for 240 h, the PLLA/PMMA-2/CNT composite sample showed Φ of 73.8%, which is higher than that of the PLLA/CNT composite sample. As for the PLLA/PMMA-10/CNT composite sample, Φ was dramatically increased up to 85.9%. As shown in Fig. 4(b), after being hydrolyzed for 240 h, the PLLA/CNT composite sample showed R of 0.19 %/h, while a largely decreased R was obtained for the PLLA/PMMA/CNT composite samples. The higher the PMMA content in the composite sample, the smaller the R is. For example, R of the PLLA/PMMA-2/CNT composite sample was 0.109 %/h, while it decreased dramatically to 0.059 %/h for the PLLA/PMMA-10/CNT composite sample. This clearly confirms that the hydrolytic degradation resistance of the PLLA/PMMA/CNT composite samples was markedly enhanced com-

pared with that PLLA/CNT composite sample.

Investigating the surface morphologies of the hydrolyzed samples is beneficial to understanding the hydrolytic degradation mechanism of the samples. Here, surface morphologies of the representative samples obtained after being hydrolyzed for 240 h were comparatively investigated. As shown in Fig. 5(a), many CNTs can be clearly seen from the hydrolyzed PLLA/CNT sample, which confirms that some PLLA was hydrolyzed and removed from sample surface and then CNTs were exposed after hydrolytic degradation, while for PLLA/PMMA-10/CNT observed (Fig. 5b), the sample surface is still very smooth and only a few CNTs can be observed. At higher magnifications, many small holes can be distinguished, confirming the occurrence of PLLA hydrolytic degradation. The variations of sample surface morphologies clearly show that the hydrolytic degradation of PLLA in the PLLA/CNT and PLLA/PMMA-10/CNT composites still obeyed the surface erosion mechanism and the presence of PMMA did not induce any change to the hydrolytic degradation mechanism. Besides, SEM characterizations further confirmed that the presence of PMMA greatly improved the hydrolytic degradation resistance of PLLA.

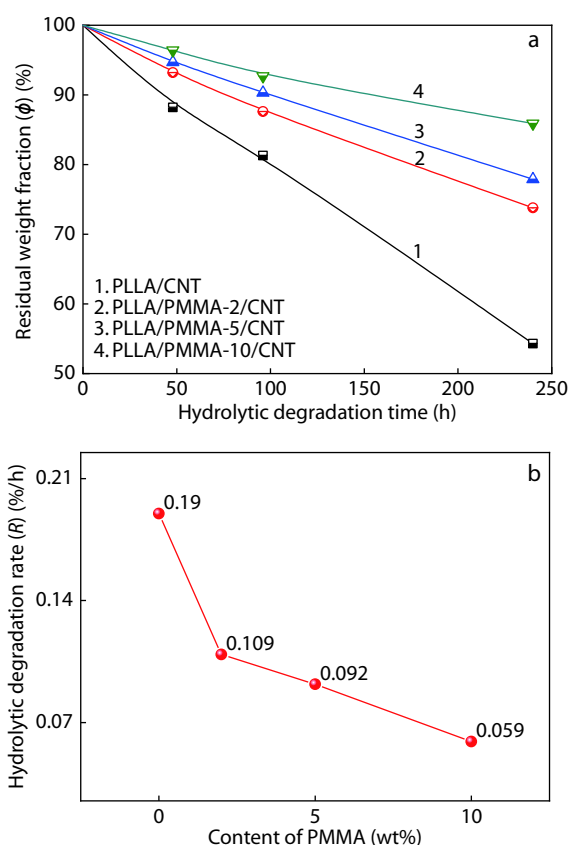


Fig. 4 (a) Variation of residual weight fraction (Φ) of samples with increasing hydrolytic degradation time, and (b) variation of hydrolytic degradation rate (R) of samples at hydrolytic degradation time of 240 h with increasing PMMA content.

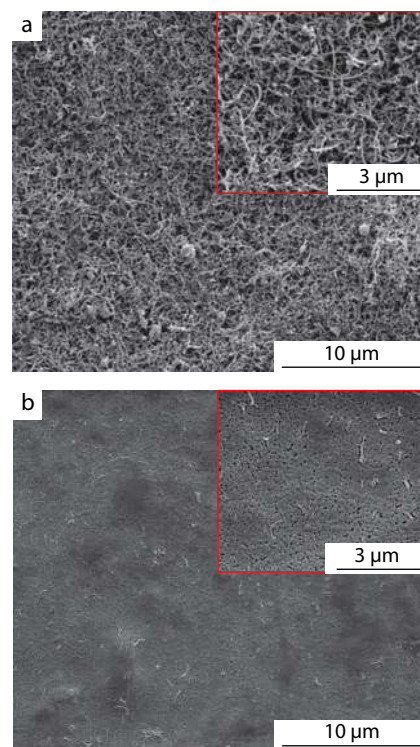


Fig. 5 SEM images showing the morphologies of (a) PLLA/CNT and (b) PLLA/PMMA-10/CNT samples obtained after being hydrolyzed for 240 h.

Microstructure Evolution in the Hydrolytic Degradation Process

PLLA is a well-known semicrystalline polymer and its crystallization behaviors are greatly dependent upon many factors, including the interior factors such as the content of D-isomer, nucleating agent, plasticizer, and molecular weight, etc., and external factors such as crystallization temperature and cooling

rate, etc. For the hydrolyzed samples, with the proceeding of hydrolytic degradation, molecular weight of the matrix becomes smaller and the distribution of molecular weight becomes broader, both of which are favorable for the crystallization of the PLLA matrix. Furthermore, once the new crystalline structure is induced in the hydrolyzed PLLA samples, hydrolytic degradation might be influenced to a certain extent. Therefore, investigating the microstructure evolution of PLLA in the hydrolytic degradation process is of great significance.

Fig. 6 shows the FTIR spectra of the representative PLLA/CNT and PLLA/PMMA-10/CNT composite samples. The characteristic absorption band at 1748 cm^{-1} as shown in Fig. 6(a) is mainly attributed to the stretching vibration of the C=O groups on PLLA molecular chains.^[39] With the increase of hydrolytic degradation time, the intensity of the absorption band becomes weaker and it nearly disappears at the hydrolytic degradation time of 240 h. This indicates that the ester groups in the molecular chains of PLLA were easily degraded.^[2] The similar variation trends are also observed for the absorption bands at 956 and 867 cm^{-1} as shown in Fig. 6(b), which are mainly related to the C—C backbone stretching vibration.^[40,41] So far, it is still not clear why the characteristic absorption bands of the PLLA matrix cannot be detected. Possibly the disappearance of the characteristic absorption bands at t of 240 h is mainly attributed to the exposure of a large number of CNTs on the surface of the hydrolyzed sample, which influences the detection of the PLLA matrix.

From Figs. 6(c) and 6(d) one can see that the characteristic absorption bands at 1748 and 867 cm^{-1} become very weak while new absorption bands are present at 1725 and 840 cm^{-1} . The intense absorption band at 1725 cm^{-1} indicates the presence of PMMA and it can be attributed to the stretching vibration of C=O groups.^[42,43] In other words, with the occurrence of hydrolytic degradation, PLLA was degraded while the insoluble PMMA was exposed. Furthermore, no molecular ordering or crystallization occurred in the PLLA matrix during hydrolytic degradation, which is different from the other PLLA-based systems in which local molecular ordering and/or for mation of new crystallites took place in the earlier stage of the hydrolytic degradation process.^[13,14] Obviously, the presence of PMMA, which restricts the movement of chain segments in PLLA matrix, is the main reason for the suppressed molecular ordering and/or crystallization of the PLLA matrix.

To further confirm the microstructure evolution of the hydrolyzed samples, DSC measurements were carried out, and the results are shown in Fig. 7. For comparison, the results of samples before hydrolytic degradation are also illustrated. There are several changes that need to be noticed. First, the peak of the hydrolyzed samples, which is observed at about $60\text{--}70\text{ }^{\circ}\text{C}$, shifts to higher temperatures. The above hydrolytic degradation measurements show that after being hydrolyzed for 240 h, the weight loss of the PLLA/CNT composite sample was about 45.7%, which indicates that the relative concentration of CNTs in the residual sample was greatly en-

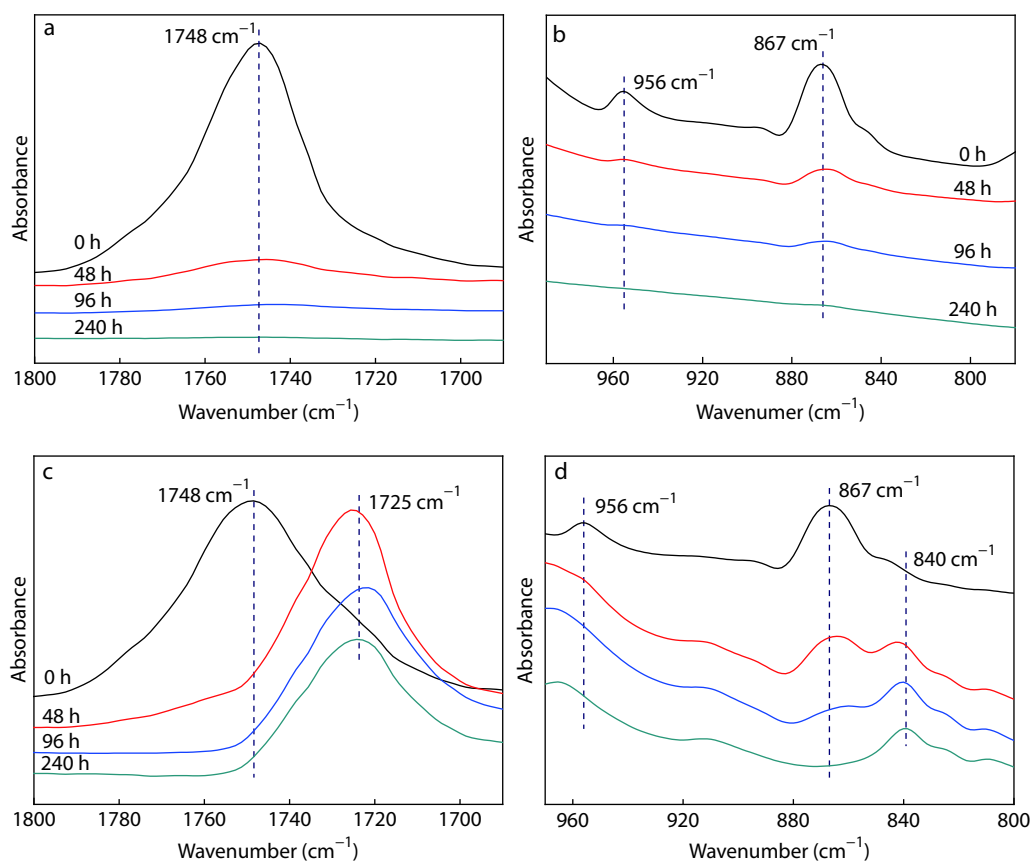


Fig. 6 Evolution of FTIR spectra of (a, b) PLLA/CNT and (c, d) PLLA/PMMA-10/CNT samples with increasing hydrolytic degradation time as indicated in the graphs.

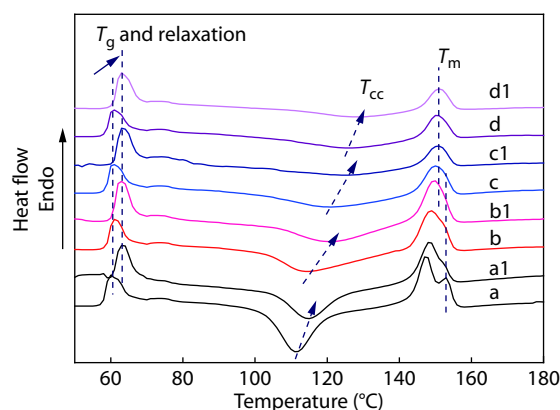


Fig. 7 Comparison of the DSC heating curves of samples (a–d) before and (a1–d1) after being hydrolyzed for 240 h: (a, a1) PLLA/CNT, (b, b1) PLLA/PMMA-2/CNT, (c, c1) PLLA/PMMA-5/CNT, and (d, d1) PLLA/PMMA-10/CNT.

hanced. Therefore, it is believed that the variation of the peak is mainly attributed to the restriction effect of CNTs on the residual PLLA matrix. As for the PLLA/PMMA/CNT composites, besides the restriction effect of CNTs, the presence of PMMA also restricted the movement of the residual PLLA molecular chains. Second, the hydrolyzed samples showed higher T_{cc} . As mentioned above, the hydrolyzed PLLA samples usually exhibit reduced molecular weight and increased distribution of molecular weight, which are believed to be favorable for the crystallization of PLLA. However, it is interesting to observe that the hydrolyzed PLLA/CNT and PLLA/PMMA/CNT samples showed higher T_{cc} . This indicates that the restriction effects, which originate from the enhanced concentrations of PMMA molecular chains and CNTs on the nucleation and growth of crystallites during the DSC heating scan, outdid the promotion effect of the reduced molecular weight of the PLLA matrix. The more the PMMA in the sample, the more apparent the restriction effect of PMMA on PLLA crystallization and consequently, the higher the T_{cc} . Since the cold crystallization was delayed to high temperatures and more integrated crystallites were formed at the lower supercooling degree, single endothermic peak is achieved for the hydrolyzed samples.

Further Understanding about the Hydrolytic Degradation Mechanisms

The above results clearly show that the presence of PMMA greatly improved the hydrolytic degradation resistance of PLLA; especially, higher PMMA contents led to better degradation resistance. It is well known that in the PLLA-based composites, hydrolytic degradation firstly occurs at the interface between PLLA matrix and fillers due to the relatively low chain entanglement density and high concentration of functional groups compared with the bulk polymer.^[44,45] This indicates that tailoring the microstructure and interfacial interaction can efficiently tailor the hydrolytic degradation behavior of the PLLA matrix.

In this work, although PMMA is non-degradable in alkaline solution, the presence of PMMA might restrict the mobility of PLLA chain segments on the one hand. On the other hand, the PLLA/PMMA blend was miscible and CNTs did not show the selective location feature, which is usually observed in the immiscible polymer blends.^[46] However, the concentration of

molecular chains of PLLA or PMMA in the zone close to CNTs is still very important because it may influence the hydrolytic degradation of the PLLA matrix. Generally, concentration of PLLA or PMMA molecular chains nearby CNTs is mainly determined by the interfacial tensions between components. Obviously, the polymer that exhibits low interfacial tension with CNTs has higher molecular chain concentration in the region close to CNT surface.^[47,48] It is then believed that the enhanced degradation resistance of the PLLA/PMMA/CNT composites is mainly related to the change of the interfacial state. To confirm the above hypothesis, the interfacial tensions between components are discussed in detail.

The interfacial tensions can be calculated according to the harmonic-mean equation and geometric-mean equation as follows:^[49,50]

Harmonic-mean equation:

$$\gamma_{12} = \gamma_1 + \gamma_2 - 4 \left(\frac{\gamma_1^d \gamma_2^d}{\gamma_1^d + \gamma_2^d} + \frac{\gamma_1^p \gamma_2^p}{\gamma_1^p + \gamma_2^p} \right) \quad (4)$$

Geometric-mean equation:

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2 \left(\sqrt{\gamma_1^d \gamma_2^d} + \sqrt{\gamma_1^p \gamma_2^p} \right) \quad (5)$$

where γ_i represents the surface energy of component i . Accordingly, γ_i^d and γ_i^p represent the dispersive and polar parts of the surface energy of component i . The surface energies of the components, including PLLA, PMMA, and CNTs, can be cited from literature^[51–53] and the data are listed in Table 1. And then, the interfacial tensions between polymers and CNTs are calculated and listed in Table 2.

Table 1 Surface energies of the components investigated in this work.

Sample	γ (mJ/m ²)	γ^d (mJ/m ²)	γ^p (mJ/m ²)	Ref.
PLLA	38	36.3	1.7	[51]
PMMA	41.1	29.6	11.5	[52]
CNTs	45.3	18.4	26.9	[53]

Table 2 Interfacial tensions between components calculated using harmonic- and geometric-mean equations.

Component couple	Interfacial tension (mJ/m ²)	
	Harmonic-mean equation	Geometric-mean equation
$\gamma_{\text{PLLA-CNT}}$	28.1	18.1
$\gamma_{\text{PMMA-CNT}}$	8.8	4.6

It is clearly seen that the interfacial tension between PMMA and CNTs is apparently smaller than that between PLLA and CNTs. This indicates that PMMA molecular chains are easier to be adsorbed on the surface of CNTs. PMMA is non-degradable in alkaline solution and consequently, the promotion effect of interface on PLLA hydrolytic degradation, which is observed in the PLLA/CNT composites, is greatly weakened in the PLLA/PMMA/CNT composites. The more the PMMA in the composites, the higher the concentration of PMMA molecular chains at the interface, and consequently, the more apparent the suppression effect of PLLA on hydrolytic degradation. Tailoring the interfacial interaction of the PLLA-based composites to enhance the hydrolytic degradation resistance of the PLLA matrix has also been reported elsewhere. For example, Kyutoku *et al.*^[54] prepared the modified cellulose fiber

(CF) through using the epoxy-based surface treatment agents, and they found that the surface treatment agent not only improved the interfacial adhesion between CF and PLLA but also inhibited the degradation of the PLLA matrix.

Furthermore, the improved dispersion of CNTs in the PLLA/PMMA/CNT composites can be also explained by the interfacial tensions between components. Here, PMMA shows higher interfacial affinity to CNTs and simultaneously, PMMA is also miscible with the PLLA matrix. Therefore, in the process of sample preparation, homogeneous dispersion of CNTs can be achieved with the aid of PMMA component thanks to the diffusion of PMMA molecular chains in the composite. Incorporating PMMA into PLLA usually leads to the enhancement of T_g as mentioned above. However, in this work, the effect of PMMA on T_g of the composites is inconspicuous. It is also believed that the local accumulation of PMMA at the interface region is possibly one of the reasons that determine the change of T_g , because the accumulated PMMA exhibits lower effect on the mobility of PLLA molecular chains compared with the homogeneously dispersed PMMA.

The accumulation of PMMA molecular chains in the region nearby CNTs can be further confirmed through the change of isothermal crystallization behaviors. Fig. 8 shows the morphologies of samples after being isothermally crystallized at 130 °C for 1 h. As shown in Fig. 8(a), a large number of PLLA spherulites with average diameter of about 35 μm are observed in the PLLA/CNT composite sample, indicating the excellent heterogeneous nucleation effect of CNTs on PLLA crystallization. Interestingly, the PLLA/PMMA/CNT composite samples show largely reduced spherulite numbers, which means that the nucleation density of PLLA in the PLLA/PMMA/CNT composite samples was much smaller than that in the PLLA/CNT composite sample. In other words, the he-

terogeneous nucleation effect of CNTs was greatly suppressed when PMMA was present in the composites. One possibility is related to the suppression of both PLLA chain mobility and PLLA nucleation on the surface of CNTs due to the presence of PMMA. The other one is related to the adsorption of PMMA molecular chains on the surface of CNTs given the relatively strong interfacial interaction between PMMA and CNTs compared with that between PLLA and CNTs. In this condition, the nucleation effect of CNTs on the crystallization of PLLA matrix was greatly suppressed. It is also interesting to observe that in the PLLA/PMMA/CNT composite samples, the average diameter of the PLLA spherulites varied at 32, 31, and 24 μm at PMMA content of 2 wt%, 5 wt%, and 10 wt%, respectively. The gradually reduced spherulite diameter in the PLLA/PMMA/CNT composite samples can be possibly attributed to the lower nucleation ability of PLLA in a certain crystallization time.

The above results clearly show that incorporating PMMA into PLLA/CNT composites is an efficient way to enhance the hydrolytic degradation resistance of the composites, which is of great significance from a viewpoint of prolonging the service life of the articles. However, there are still some problems that need to be further clarified in the future work. Although the crystallization of PLLA is not apparently influenced by adding PMMA in this work due to the relatively low PMMA content and high cooling rate, it is easily to be deduced that the crystallization ability of PLLA can be greatly influenced at high PMMA content even if the appropriate crystallization condition is provided. In this condition, higher PMMA content may lead to lower PLLA crystallinity. Since the hydrolytic degradation of PLLA is also greatly influenced by the crystallinity with lower crystallinity leading to higher hydrolytic degradation rate of PLLA, higher PMMA content may

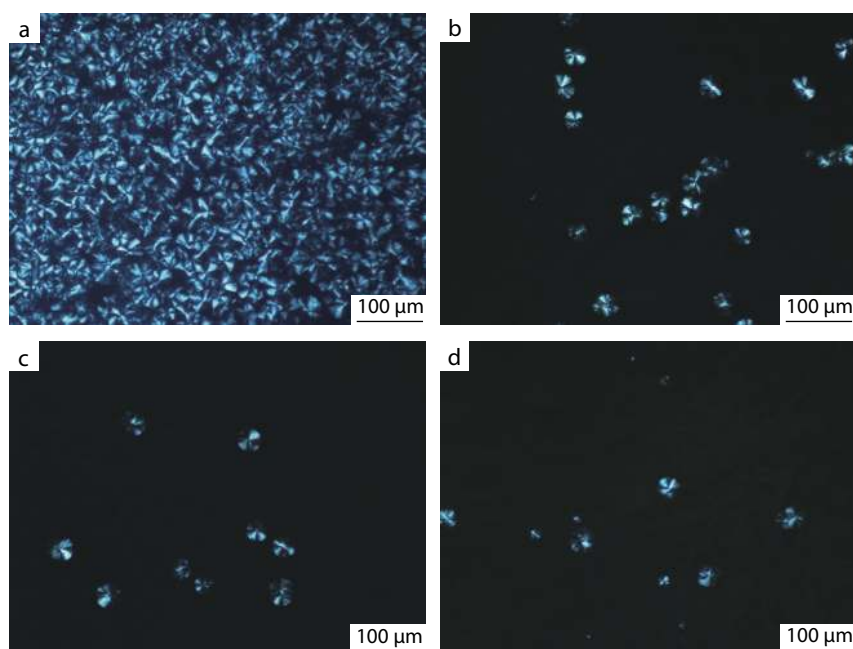


Fig. 8 POM images showing the isothermal crystallization morphologies of the binary PLLA/CNT and ternary composites as indicated. Isothermal crystallization was carried out at 130 °C for 1 h: (a) PLLA/CNT, (b) PLLA/PMMA-2/CNT, (c) PLLA/PMMA-5/CNT, and (d) PLLA/PMMA-10/CNT.

promote the hydrolytic degradation of PLLA from a viewpoint of crystallinity. Therefore, the first work that should be carried out is to further examine the effect of PMMA content (>10 wt%) on the crystallization of PLLA in the PLLA/PMMA/CNT composites and the resultant hydrolytic degradation behaviors of the composites. Second, the concentration fluctuation of the miscible PLLA/PMMA blends induced by CNTs should be further confirmed. Third, variations of the mechanical properties of the composites with increasing hydrolytic degradation time is interesting. Furthermore, the evolution of surface resistance of hydrolyzed sample during hydrolytic degradation should also be investigated. It is believed that once the relationship of erosion degree-mechanical properties-surface resistance is founded, the service status of the composite articles can be monitored and then, people may know whether the articles should be replaced or not.

CONCLUSIONS

In summary, a small quantity of PMMA (2 wt%–10 wt%) has been incorporated into the PLLA/CNT composites. The microstructure characterizations show that PMMA facilitated the dispersion of CNTs in the composites on the one hand. On the other hand, PLLA matrix existed in the amorphous state in all the composites as prepared. Hydrolytic degradation measurements show that the presence of PMMA greatly improved the hydrolytic degradation resistance of the composites, especially at high PMMA content. Further results show that no molecular ordering or crystallization occurred in the PLLA matrix in the hydrolytic degradation process. The suppressed nucleation effect of CNTs and the enhanced hydrolytic degradation resistance are mainly attributed to the accumulation of PMMA molecules around CNTs because of the stronger interfacial interaction between PMMA and CNTs. This work demonstrates that the hydrolytic degradation ability of the PLLA-based composites can be well tailored through adding a few miscible PMMA component, which is of great significance in designing and fabricating the PLLA-based articles with promising hydrolytic degradation ability.

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