Degradation behaviour in vitro of poly L-lactic acid (PLLA)/polycaprolactone (PCL) masterbatch

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ABSTRACT – REZUMAT

Degradation behaviour in vitro of poly L-lactic acid (PLLA)/polycaprolactone (PCL) masterbatch

In order to prepare the absorbable medical textile material with different degradation rates, two biopolymers of poly L-lactic acid (PLLA) and polycaprolactone (PCL) with different degradation rates, were mixed in different proportions, and made into PLLA/PCL masterbatch. The experiment of degradation in vitro was conducted to reveal the degradation behaviour of PLLA/PCL masterbatch, and the characteristics of masterbatch in degradation, such as surface morphology, chemical structure, crystallization, mass loss and strength, were analyzed. The results indicated that the surface of PLLA/PCL masterbatch was etched in degradation, and the larger proportion of PCL, the less etching and slower degradation. The ester bonds were hydrolyzed firstly, and the crystallization region in PLLA/PCL masterbatch was destroyed gradually to form a non-crystalline region in degradation. The degradation rate of PLLA in composite masterbatch was faster than that of PCL. With increasing of PCL involved in masterbatch, the mass loss rate of masterbatch in degradation decreased. In addition, the more PCL involved in composite masterbatch, the lower breaking strength.

Keywords: *poly L-lactic acid (PLLA), polycaprolactone (PCL), masterbatch, degradation behaviour, in vitro degradation*

Comportamentul de degradare in vitro al amestecului preliminar de acid poli-L-lactic (PLLA)/policaprolactonă (PCL)

În realizarea materialului textil absorbabil pentru domeniul medical ce prezintă diferite rate de degradare, doi biopolimeri de acid L-lactic (PLLA) și policaprolactonă (PCL) au fost combinați în diferite proporții și transformați în amestec preliminar de PLLA/PCL. Experimentul degradării in vitro a fost realizat pentru a investiga comportamentul de degradare al amestecului preliminar PLLA/PCL și au fost analizate caracteristicile amestecului preliminar în degradare, cum ar fi morfologia suprafaței, structura chimică, cristalizarea, pierderea de masă și rezistența la rupere. Rezultatele au indicat că suprafața amestecului prelimiar PLLA/PCL a fost corodată în timpul degradării, iar cu cât cantitatea de PCL a fost mai mare, cu atât degradarea a fost mai lentă. Legăturile esterice au fost hidrolizate primele, iar zona de cristalizare a amestecului preliminar PLLA/PCL a fost distrusă treptat pentru a forma o zonă necristalină în timpul degradării. Rata de degradare a PLLA în amestecul preliminar compozit a fost mai rapidă decât cea a PCL. Odată cu creșterea cantității de PCL în amestecul preliminar, pierderea de masă în timpul degradării a scăzut. În plus, cu cât cantitatea de PCL este mai mare în amestecul preliminar compozit, cu atât este mai mică rezistența la rupere.

Cuvinte-cheie: *acid poli-L-lactic (PLLA), policaprolactonă (PCL), amestec preliminar, comportament de degradare, degradare in vitro*

INTRODUCTION

The masterbatch of synthetic polymer biomaterials, including poly L-lactic acid (PLLA), polycaprolactone (PCL) and so on, possesses excellent biocompatibility, degradation absorptivity in body, good strength and others. They can be made into some absorbable textile products such as the tissue engineering scaffold, the absorbable suture and the temporary anti-adhesion membrane, using electrostatic spinning, melt spinning, three-dimensional woven, knitting and other technologies [1–3].

With the gradual degradation and absorption of the absorbable textile product implanted in the body, the tissue cells grow gradually clinging to the absorbable textile product, and the wound will be healed gradually [4–6]. The degradation of the absorbable textile product needs to be matched with the healing time of tissue.

In order to adjust degradation rate of these absorbable textile products, different methods are adopted.

Through adjusting size of the absorbable textile products, the degradation rate can be controlled. For instance, Scaffaro et al. [7] adjusted the fiber's fineness to change the degradation rate of poly (lactic acid) membrane. However, the size of bioabsorbable products, such as absorbable suture, vascular stent and so on, just have a narrow adjustable range, so the adjustable range of degradation rate is very narrow.

The degradation rate is adjusted by grafting some simple chemical groups onto the molecular chain

segment of the absorbable textile products. For instance, Qian et al. [8] grafted the polar groups onto the end groups or pendant groups of polyester molecular chains, so that the hydrolysis rate of polyester polymers was accelerated, and the number of polar groups was positively correlated with the polymer hydrolysis rate. However, this method involves a complex chemical process, and it is difficult to control the degradation rate with high precision and accuracy.

Some substances, such as plasticizer, hydrophilic agent and so on, are mixed with the absorbable textile products to change the degradation rate. For instance, Choi et al. [9] added poly(ethylene glycol) into poly(lactic acid), and accelerated the degradation of poly(lactic acid). However, the substances added in the absorbable products are mostly low molecular weight, so that the mechanical properties of the absorbable products are often worsened and decreased.

In this article, we selected two biomaterials of poly L-lactic acid (PLLA) and polycaprolactone (PCL) with different degradation rates, to blend and then form PLLA/PCL composite masterbatch. Both PLLA and PCL possess many advantages, such as good biocompatibility in vivo, small tissue reaction and no rejection reaction [10–11]. Besides, the degradation rate of PLLA is faster than that of PCL, and the degradation rate of PLLA/PCL composite masterbatch can be adjusted by changing the mixing ratio of PLLA and PCL. In addition, PLLA and PCL are both polyester biomaterials and have good compatibility, so they are easy to mix with each other, which is in favour of getting sufficient mechanical properties for composite masterbatch [12–13].

EXPERIMENTAL WORK

Materials

The poly L-lactic acid (PLLA, $(C_6H_8O_4)_n$) with 51500 viscous molecular weight, and the polycaprolactone (PCL, $(C_6H_{10}O_2)_n$) with 48900 viscous molecular weight, are both produced by Natureworks Company (USA).

Experimental process

The PLLA and PCL are mixed in different proportions, such as 100/0, 90/10, 80/20, 70/30, 60/40, 50/50, 40/60, 30/70, 20/80, 10/90 and 0/100. 5 g mixture of PLLA/PCL is put into 60 mL dichloromethane (CH_2Cl_2), and they are vibrated in a Water-bathing Constant Temperature Vibrator (SHA-C, Ningbo Textile Instrument Factory) at 25°C for 4 h, to dissolve the PLLA and PCL fully. After that, the solution of PLLA and PCL is poured into a glass trough, and they are horizontally put into ventilation under normal temperature, to make the solvent of dichloromethane (CH_2Cl_2) volatilize completely. So the PLLA/PCL composite materials are cut into masterbatch (1 mm × 2 mm × length), and then the structure and property of the masterbatch are tested and measured.

Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) investigations were performed on a JEM2100F (Kabuskiki Kaisha, Japan) at 7kV accelerating voltage to evaluate the morphologies of PLLA/PCL masterbatch samples.

Fourier transform infrared spectroscopy (FTIR)

The chemical structure of PLLA/PCL masterbatch samples were dedicated by FTIR. The infrared spectra were obtained via Fourier Transform Infrared Spectroscopy (FTIR; TL-8000) with a resolution of 4 cm^{-1} that scanned 50 times from 600 to 4000 cm^{-1} at room temperature.

X-ray diffraction (XRD)

X-ray diffractometer (TD-3700, Dandong Tongda Technology Co., LTD.) was used to measure the XRD spectrum of PLLA/PCL masterbatch samples, under conditions of 2θ angle of 10°–50°, 0.05° step-angle, 30 KV tube-voltage and 25 mA tube current intensity.

Mass loss rate testing

The mass of PLLA/PCL masterbatch sample, before the degradation test in vitro, was recorded as M_0. After the degradation test in vitro, the drying mass of sample was recorded as M_1. So the mass loss rate, recorded as W, was calculated according to equation (1).

$$W = \frac{M_0 - M_1}{M_0} \times 100\% \quad (1)$$

Mechanics performance testing

The mechanical properties of PLLA/PCL masterbatch samples (1 mm × 2 mm × 100 mm) were obtained via a Strength Tester (TG(B)026D, Wenzhou Darong Textile Standard Instrument Factory).

Degradation test in vitro

The degradation behaviour of PLLA/PCL masterbatch samples was characterized through degradation-test in vitro. The “Hanks” solution, which simulated the body fluid, was prepared according to the recipe of 1.0 g/L $C_6H_6O_6$, 8.0 g/L NaCl, 0.4 g/L KCl, 0.14 g/L CaCl, 0.1 g/L $MgCl{\cdot}6H_2O$, 0.06 g/L $MgSO_4{\cdot}7H_2O$, 0.06 g/L KH_2PO_4, 0.06 g/L Na_2HPO_4 and 0.35 g/L Na_2HCO_3 [14–16]. After that, the masterbatch samples (1 mm × 2 mm × 100 mm) were placed into the body simulation fluid of “Hanks” solution, and they were put into a Thermostatic Water Bath (HH-8, Ningbo Textile Instrument Factory) at 37°C which simulated the human body temperature [17]. In the process of degradation test, the “Hanks” solution should be replaced regularly to simulate the body fluid circulation. The PLLA/PCL masterbatch samples will be degraded gradually in “Hanks” solution. After a certain amount of time, the samples were taken out and dried, and then the structure and properties were measured.

RESULTS AND DISCUSSION

The surface morphology of PLLA/PCL masterbatch in degradation

In the process of degradation, the surface morphology of masterbatch in different proportions of PLLA/PCL will change, as shown in figure 1.

Figure 1, *a–c*, which are the masterbatchs in 90/10 proportion of PLLA/PCL, shows that the surface of masterbatch was etched more and more seriously with the time, even many large gullies were appeared on the surface of masterbatch (yellow arrows in figure 1, *c*. Figure 1, *d–f*, which are the masterbatchs in 90/10 proportion of PLLA/PCL, shows that with the further degradation, the surface of masterbatch was etched more and more seriously and even appeared many potholes (red arrows in figure 1, *e–f*). Figure 1, *g–i*, which are the masterbatchs in 10/90 proportion of PLLA/PCL, shows that the surface of masterbatch was etched slightly in degradation.

In addition, we compared these images in different proportions vertically, and found that the larger proportion of PLLA, the greater etching effect on surface of masterbatch, and the greater proportion of PCL, the less etching effect on surface of masterbatch. This indicated that the degradation rate of PCL was slower than that of PLLA, and the more PCL in the masterbatch, the slower degradation rate and the longer degradation period of the masterbatch.

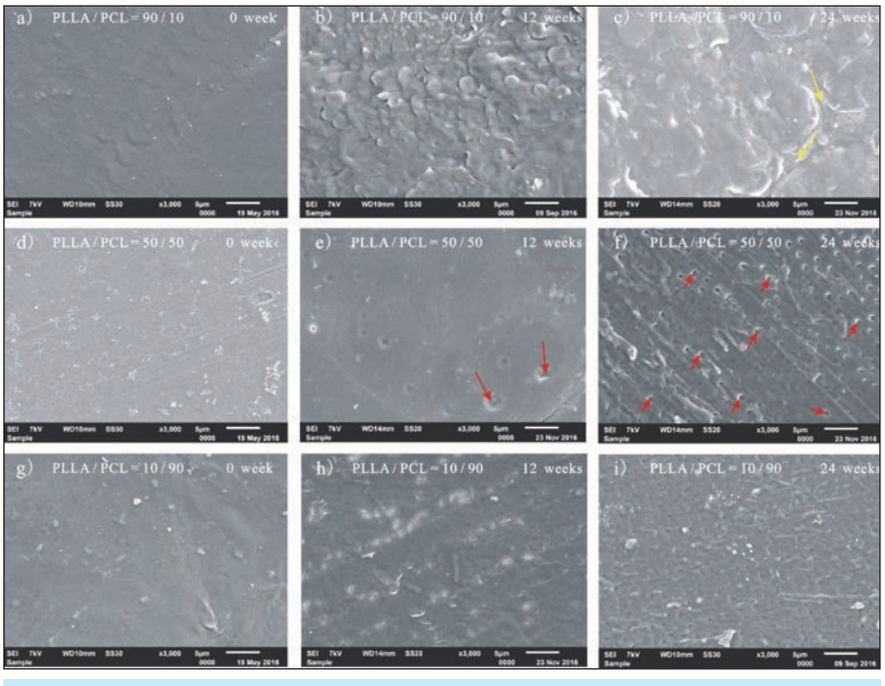

Fig. 1. The surface morphology of PLLA/PCL masterbatch

The chemical structure of PLLA/PCL masterbatch in degradation

The infrared spectra of masterbatch in degradation were shown in figure 2.

Figure 2 shows that with the further degradation, the absorption peak value of "–C=O" at 1752 cm^{-1} in ester group was smaller and smaller, which indicated that the ester group in the masterbatch decreased in the process of 20 weeks degradation. However, the value of deformation vibration absorption peak of "–CH_2–" at 1454 cm^{-1}, 2861 cm^{-1} and 2930 cm^{-1} hardly changed in the process of 20 weeks degradation, which shows that the group of "–CH_2–" was not broken down or degraded in the 20 weeks degradation. The results above suggested that the ester bonds, which exist in both PCL and PLLA molecules, were easily broken down by water and degraded firstly during the process of the degradation of PLLA/PCL masterbatch in vitro, but the groups of "–CH_2–" and others was stable and not easy to be degraded.

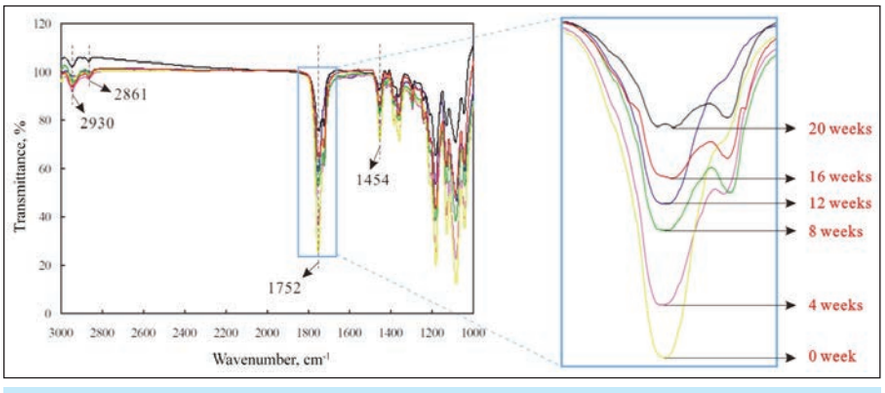

Fig. 2. FTIR of PLLA/PCL masterbatch with 70/30 proportion in degradation

The crystallization of PLLA/PCL masterbatch in degradation

The XRD of masterbatch in different proportions of PLLA/PCL is shown in figure 3.

Figure 3 shows that the characteristic diffraction peak of pure PLLA, in 100/0 proportion of PLLA/PCL, was located at 16.87° and 19.19°, and the characteristic diffraction peak of pure PCL, in 0/100 proportion of PLLA/PCL, was located at 21.76°, 22.31° and 23.96°. Through comparing all XRD patterns from 100/0 to 0/100 proportions of PLLA/PCL, we found that with the increasing content of PCL and the decreasing content of PLLA, the characteristic diffraction peak of PCL at 21.76°, 22.31° and 23.96° was bigger and bigger, on the contrary, the characteristic

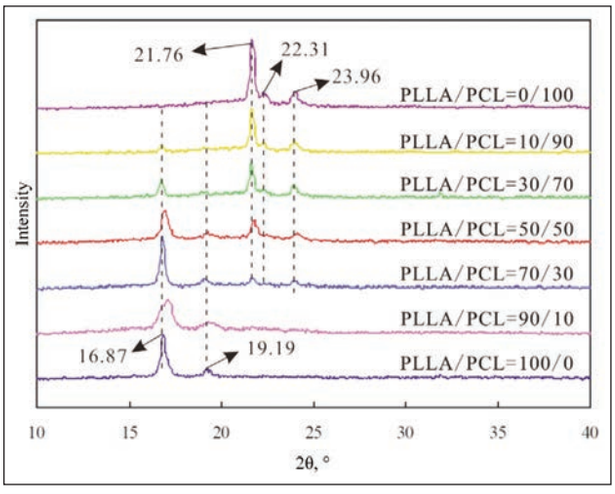

Fig. 3. XRD of PLLA/PCL masterbatchs in different proportions

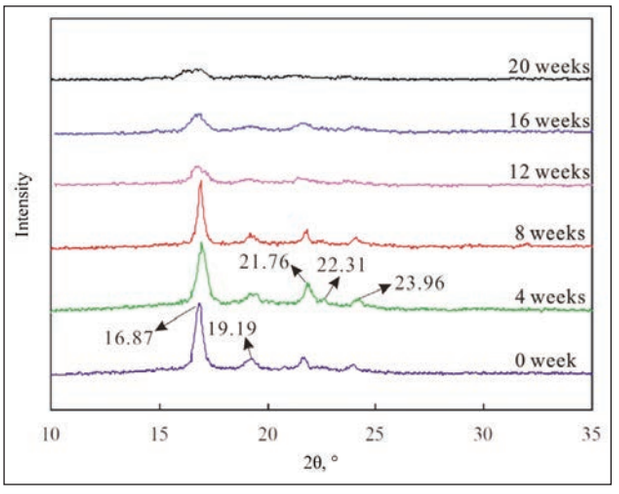

Fig. 4. XRD of 70/30 PLLA/PCL masterbatch in degradation

diffraction peak of PLLA at 16.87° and 19.19° was smaller and smaller. The rule of peak variation was consistent with that of proportion of PLLA/PCL samples.

In the process of degradation, the crystallization of PLLA/PCL masterbatch would change, and the XRD patterns of PLLA/PCL masterbatch in degradation were shown in figure 4.

Figure 4 shows that the characteristic diffraction peaks of PLLA at 16.87° and 19.19°, and the characteristic diffraction peaks of PCL at 21.76°, 22.31° and 23.96°, were weakened gradually as the masterbatch was degraded, which indicated that the crystalline region in PLLA/PCL masterbatch or the degree of crystallinity decreased gradually in the process of degradation. It was because that the ester bonds in molecular chains of PLLA and PCL masterbatch would be hydrolyzed by the water in the simulated body fluid, and the molecular chain was broken, so that the orderly arrangement of molecular chains in the crystalline regions was destroyed, and then the crystalline state was transformed into amorphous form, that was, non-crystalline state.

The mass loss rate of PLLA/PCL masterbatch in degradation

In process of degradation, the mass of PLLA/PCL masterbatch will lose, and the mass loss rate of masterbatch is shown in figure 5.

Figure 5 shows that with the time of degradation, the mass lose rate increased gradually. It is because that the macromolecules in PLLA/PCL masterbatch would break into micro-molecule, and then the micro-molecules would further degrade into CO_2 and H_2O, therefore the mass of masterbatch would lose, and the mass loss rate increased. It is also known from figure 5 that the larger proportion of PCL in the masterbatch, the lower mass loss rate of masterbatch in degradation. It is because that the degradation rate of PCL was slower than that of PLLA, which was proved in the above crystallization analysis in this paper. Hence, with the proportion of PCL increased in

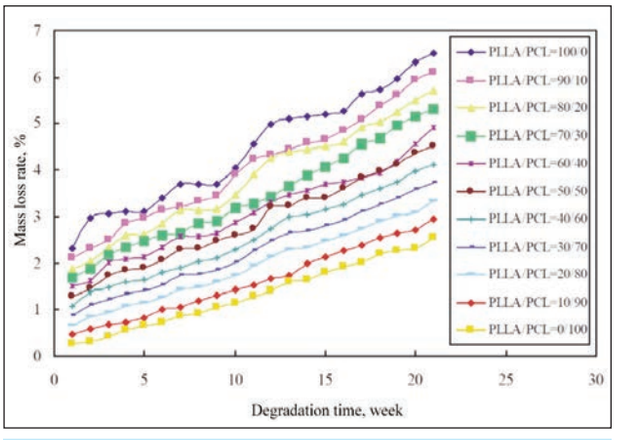

Fig. 5. Mass loss rate of PLLA/PCL masterbatchs in degradation

the masterbatch, the mass loss rate of masterbatch decreased.

The breaking strength of PLLA/PCL masterbatch in degradation

The mechanical properties of masterbatch will affect the mechanical properties of the textile medical products. So the breaking strength of masterbatch in process of degradation were investigated, as shown in figure 6.

Before degradation (at 0 week), the breaking strength of pure PCL, at 1/100 proportion of PLLA/PCL, is far lower than that of pure PLLA at 100/1 proportion of PLLA/PCL, and with the increase of PCL in the masterbatch, the breaking strength of masterbatch decreased. This is because that PCL macromolecule was a linear molecule without branched chains and the interaction among molecules was small, so the molecules were easy to slip, which led to the poor strength and good toughness of PCL. Therefore, the more PCL involved in masterbatch, the lower breaking strength for the PLLA/PCL masterbatch.

Figure 6 also shows that with the time of degradation, the breaking strength of PLLA/PCL masterbatchs

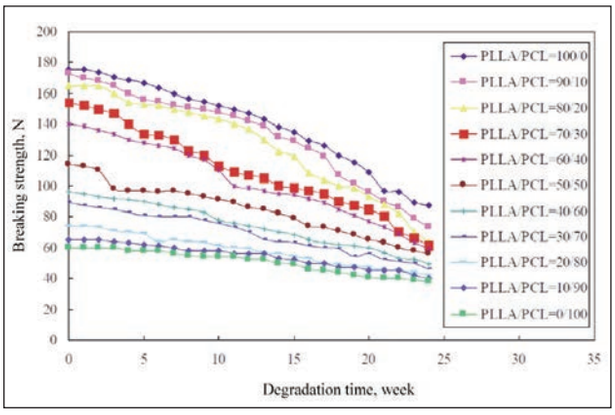

Fig. 6. Breaking strength of PLLA/PCL masterbatchs in degradation

declined rapidly, owing to the continuous degradation of masterbatchs. And it can be also known that with the proportion of PCL in masterbatch increased, the rate of decline of breaking strength, which could be expressed by the slope of tangent line, decreased. This is because that the PCL had a lower degradation rate relatively to PLLA, as the proportion of PCL increased in masterbatch, the degradation rate of masterbatch would slow down, thence the breaking strength would decline in a slower rate. In particular, the change rule of breaking strength was consistent with that of mass loss rate.

CONCLUSION

In this work, the surface of PLLA/PCL masterbatch was etched and degraded in the process of degradation, and the mixing ratio of PLLA and PCL influenced the degradation of masterbatch mainly. The larger proportion of PCL in masterbatch led to the less etching and slower degradation. In degradation, the ester bonds would be hydrolyzed firstly, and the crystallization region in PLLA/PCL masterbatch would be destroyed gradually to form a non-crystalline region. And the degradation rate of PLLA in masterbatch was faster than that of PCL. The mass of PLLA/PCL masterbatch decreased with the degradation, and with the proportion of PCL involved in masterbatch increased, the mass loss rate of masterbatch in degradation decreased. The more PCL involved in masterbatch, the lower breaking strength. With the degradation, the breaking strength of masterbatch declined rapidly, and with the proportion of PCL in masterbatch increased, the rate of decline of breaking strength decreased.

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