Shape-Memory Behaviors of Biodegradable Poly(L-lactide-*co*-ε-caprolactone) Copolymers

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ABSTRACT: A series of biodegradable poly(L-lactide-*co*-ε-caprolactone) (PCLA) copolymers with different chemical compositions are synthesized and characterized. The mechanical properties and shape-memory behaviors of PCLA copolymers are studied. The mechanical properties are significantly affected by the copolymer compositions. With the ε-caprolactone (ε-CL) content increasing, the tensile strength of copolymers decreases linearly and the elongation at break increases gradually. By means of adjusting the compositions, the copolymers exhibit excellent shape-memory effects with shape-recovery and shape-retention rate exceeding 95%. The effects of composition, deformation strain, and the stretching conditions on the recovery stress are also investigated systematically. A maximum recovery stress around 6.2 MPa can be obtained at stretching at $T_g - 15°C$ to 200% deformation strain for the PCLA70 copolymer. The degradation results show that the copolymers with higher ε-CL content have faster degradation rates and shape-recovery rates, meanwhile, the recovery stress can maintain a relative high value after 30 days *in vitro* degradation. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 1109–1115, 2008

Key words: biodegradable; copolymerization; stimuli-sensitive polymers; tension

INTRODUCTION

Biodegradable polymers have significant potential in various fields of bioengineering, such as surgical sutures, tissue engineering, and drug delivery.[1–3] Because many biomedical devices are implanted in the body, these implants would ideally be made of biodegradable polymers which possess the shape-memory effects that can be implanted with the minimal shape and recover to its original shape when in the body. In recent years, biodegradable shape-memory polymers have attracted more and more attention and several kinds of biodegradable polymers have been reported.[4–6] Lendlein and Langer studied the shape-memory properties of multiblock copolymers based on oligo(ε-caprolactone) and oligo(*p*-dioxanone) segments.[7] Nagata and Sato have synthesized photocurable biodegradable multiblock copolymers with shape-memory effects.[8] Shape-memory behaviors of sensitizing radiation crosslinked polycaprolactone have been investigated systematically by Zhu et al.[9] But it is known that the synthesis and posttreatment methods of the polymers mentioned above are relatively complicated, and the mechanical properties are comparatively poor which results in low recovery stress. Moreover, most of researchers concentrate on the shape-recovery rate, and no systematic investigation on the recovery stress has been reported to date.

In contrast to the work mentioned earlier, our research work focuses on developing biodegradable shape-memory polymers with superior mechanical properties and high recovery stress. Poly(L-lactide) (PLLA) is one of the most intensively studied biodegradable polymers because of its good mechanical properties.[10,11] In previous publications, we have reported that PLLA showed shape-memory effects and the original shape could be recovered at 70°C.[12] However, the recovery strain of PLLA was relatively low and the recovery temperature was high for using in the human body. To improve the shape-memory properties and decrease the recovery temperature, copolymers with PCL are considered because the ε-CL appears to be a suitable comonomer for the preparation of copolymers with mechanical properties ranging from rigid to elastomeric. Moreover, PCL has a low-glass transition temperature about −50°C, thus, the recovery temperature of these copolymers can be modulated in a large range by altering the composition of the copolymers. During the past years, many research works are concentrated on the synthesis, biodegradability, and mechanical properties of these polymers.[13–15] However, to our knowledge, there have been very few reports

TABLE I
Thermal and Crystallization Properties of the Polymers

Samples	Monomer composition[a]	Copolymer composition[b]	$[\eta]$ (dL/g)	T_g (°C)	T_m (°C)	ΔH_m (J/g)	Crystallinity (%)
PCLA90	90 : 10	92 : 8	3.92	54	156	25.1	26.9
PCLA80	80 : 20	81 : 19	3.64	42	142	11.4	12.2
PCLA70	70 : 30	72 : 28	3.86	25	125	8.1	8.7
PCLA60	60 : 40	62 : 38	3.56	14	–	–	–

[a] Monomer composition from feed ratio of LA to CL (w : w).
[b] Copolymer composition (LA : CL) determined by ^{1}H NMR (mol : mol).

on shape-memory effects of PCLA copolymers especially on the recovery stress.

In this study, the PCLA copolymers with different compositions are synthesized by ring-opening polymerization, shape-recovery rate and shape-recovery stress are first investigated systematically. Meanwhile, the mass loss and the variation of shape-memory behaviors during hydrolysis are also discussed.

EXPERIMENTAL

Materials

L-Lactide was synthesized according to the literature,[16] and purified by recrystallization using ethyl acetate as solvent. ε-CL (Aldrich, USA) was dried over molecular sieve 4 Å and purified by distillation under reduced pressure. Stannous octanoate (Sigma, A. R., USA) was used as received. Chloroform and methanol were used as received.

Preparation of copolymers

PCLA copolymers were prepared by simultaneous addition of the calculated amounts of two monomers (L-LA and ε-CL) into a flask in the presence of stannous octanoate at 130°C for 48 h. The product was dissolved in chloroform and precipitated by pouring the polymer solution into excess methanol and then dried under vacuum. The copolymer films were prepared by casting chloroform solutions of copolymers with a concentration of 8 wt % onto a mold. After solvent evaporation at room temperature, the films were removed from the mold and dried under vacuum to optimize solvent removal.

Characterization

Intrinsic viscosities of PCLA copolymers were measured with a Ubbelohde viscometer in chloroform at 25°C, and the results are listed in Table I. ^{1}H NMR spectroscopy was carried out with a Bruker DMX 300 spectrometer and chloroform was used as the solvent. The mole fraction of PCL in the copolymers was determined from the area of the peak at δ = 4.05 ppm corresponding to the ethylene hydrogen attached to the oxygen in a repeating CL unit divided by the sum of the area of the peak at δ = 4.05 ppm, and the area of the peak at δ = 5.15 ppm corresponding to methane hydrogen in —[OCH(CH₃)]. Differential scanning calorimeter (DSC) measurements were performed on a Perkin-Elmer Diamond DSC at heating rate of 10°C/min. The glass transition temperature (T_g), melting temperature (T_m), and heat of fusion (ΔH_m) were measured. X-ray diffraction spectra was carried out with a Rigaku D/max-rb rotating anode X-ray diffractometer at the conditions of Cu Kα, 50 kV, and 40 mA.

Mechanical properties

The tensile tests were performed with a WDS-5 tensile tester (Changchun Chaoyang), equipped with a constant-temperature heating chamber; the crosshead speed was 50 mm/min. The tensile test specimens had dimensions of 40 mm in length, 5 mm in width, and 0.4 mm in thickness.

Shape-memory behaviors

Shape-memory behaviors of copolymers were investigated by the tensile test. The test procedure for investigating the shape-memory behaviors was as follows: (1) applying a deformation (ε_m) to the sample at a constant crosshead speed of 50 mm/min at T_k, (2) cooling the sample to T_1 with the same ε_m, (3) maintaining the sample at T_1 for 5 min after removal of the load, and (4) raising the temperature from T_1 to T_k then maintain at the latter for 5 min. Under these conditions, shape-retention rate (R_f) and shape-recovery rate (R_r) are defined as follows[17]:

$$\text{Shape-retention rate (\%)} = \varepsilon_u \times 100/\varepsilon_m$$

$$\text{Shape-recovery rate (\%)} = (\varepsilon_m - \varepsilon_p) \times 100/\varepsilon_m$$

where $T_k = T_g + 15°C$, $T_1 = T_g - 15°C$, ε_m is the elongation strain, ε_u is the retention strain at T_1, and ε_p is the recovery strain at T_k.

For measurement of the recovery stress, the test procedure was similar to the above-mentioned (1)–(3), the difference was the last step (4), the specimen
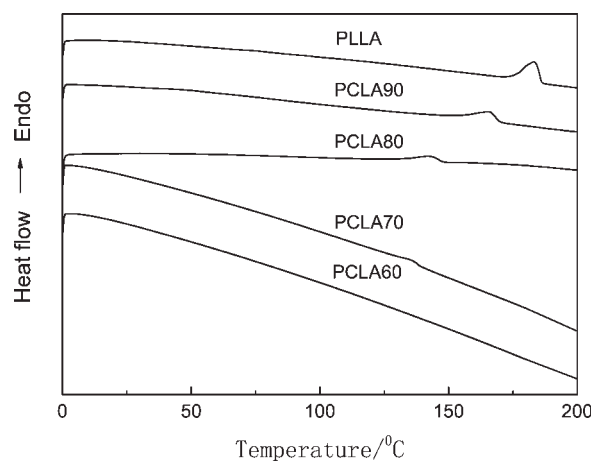
Figure 1 DSC curves of PCLA copolymers obtained on heating.

Figure 2 X-ray diffraction profiles of PCLA copolymers.

was clamped with its length fixed and then was heated until T_k, and the tensile stress was recorded as the recovery stress.

Degradation test

Pieces of accurately weighed sample films were immersed in phosphate buffer solution (PBS, pH 7.4) and thermostated at 37°C. The PBS was renewed every week. After predetermined intervals of time, the samples were taken out, washed with distilled water, and then dried under vacuum at room temperature until constant weight.

RESULTS AND DISCUSSION

Thermal properties and crystalline structure of PCLA copolymers

Figure 1 shows the DSC curves of PCLA copolymers, and their thermal data are listed in Table I. It can be seen that copolymerization with ε-CL has a dramatic impact on thermal properties: the T_g, T_m, and ΔH_m of copolymers gradually decrease with the amount of the ε-CL increasing. PCLA90 and PCLA80 are semicrystalline exhibiting an apparent melting peak at 156 and 142°C, respectively, which corresponds to the melting of PLLA crystal. PCLA70 is semicrystalline showing only a small melting peak around 125°C, and no melting peak can be observed in PCLA60 curve which means that PCLA60 is amorphous. ε-CL units increase the chain flexibility and mobility and cause a considerable decrease in the T_g and T_m. It can also be seen from Table I that the crystallinity decreases obviously with the increase of ε-CL concentration. The decrease of crystallinity is because of the increase of chain flexibility and chain disorder with the increasing addition of ε-CL.
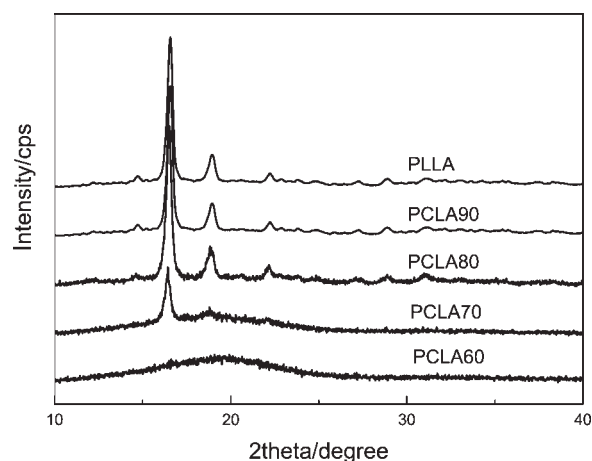
The X-ray diffraction pattern is shown in Figure 2. It is seen that there are two main peaks at $2\theta = 16.7°$ and $19.1°$ which characterize the crystalline of PLLA; the peak positions coincide with those reported by other authors.[18] With increasing the content of ε-CL in the copolymers, the peak intensities decrease and disappear. However, the typical diffraction peaks of crystalline PCL reported[18] at $2\theta = 21.4°$ can not be observed in the patterns of the copolymers, which indicates that PCL is in amorphous phase in the copolymer. The width of the diffraction peak seems to be independent of the amount of ε-CL. This observation suggests that the crystal size of PLLA is not largely influenced by the presence of ε-CL.

Mechanical properties of PCLA copolymers

Figure 3 shows the stress–strain curves of the materials at room temperature. All the curves demonstrate the elastic properties of the materials and none of these copolymers show a yield point. The correlation
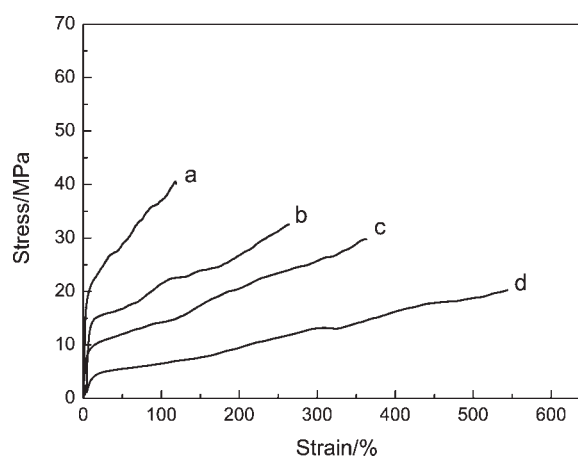

Figure 3 Stress–strain curves of: (a) PCLA90; (b) PCLA80; (c) PCLA70; and (d) PCLA60 obtained at room temperature.
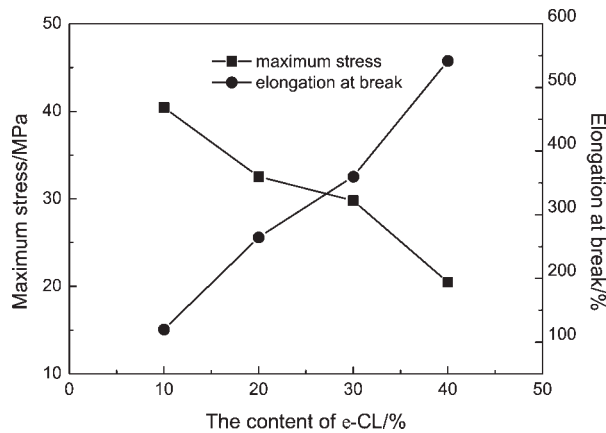
Figure 4 Tensile properties of materials as a function of the content of ε-CL at room temperature.

Figure 5 Cyclic tensile behavior of the PCLA70 at a maximum strain of 100%.

of tensile properties between the content of ε-CL are illustrated in Figure 4. The composition of the copolymers has great effects on the tensile properties of PCLA copolymers. The maximum stress decreases almost linearly, but the elongation at break gradually increase with the increase of ε-CL content. In PCLA copolymers, the crystalline PLLA is expected to serve as physical crosslinked points, which are the main contributor to mechanical strength, thus, the higher crystallinity results in the higher tensile strength. Otherwise, various interactions can occur among copolymers, such as hydrogen-bonding and dipole–dipole interactions. Such interactions among the PLLA segments and the PCL segments can influence the mechanical properties to some extent. Therefore, the increase of the amount of ε-CL may result in a reduction of interactions, along with a low-tensile strength and a high elongation at break. In general, it can be concluded that these PCLA copolymers combine high flexibility, high strength, and superior extendibility.

Shape-memory behaviors of PCLA copolymers

The cyclic tensile tests are used to characterize the shape-memory behaviors of these samples. The sample is first elongated at $T_g + 15°C$ to ε_m of 100%, at a constant elongation rate of 50 mm/min. Then the sample is cooled to $T_g - 15°C$ with the strain keeping at ε_m, after that the sample is unloaded. Upon removing the constraint, a small recovery of the strain to ε_u occurs. The sample is subsequently heated to $T_g + 15°C$ over a period of 10 min, and then keep at this temperature for a further 5 min, so allowing the strain to recover. This complete one thermomechanical cycle ($N = 1$), leaving a residual strain, ε_p, at which the next cycle ($N = 2$) starts. A typical stress–strain diagram for a thermocyclic test is shown in Figure 5. The experiment allows the
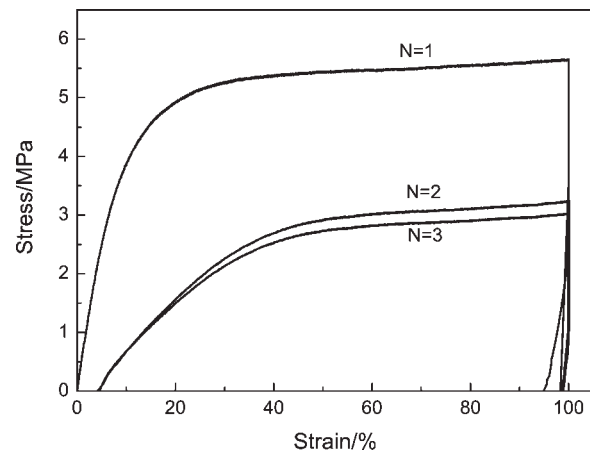
determination of the shape-retention rate as well as the shape-recovery rate, and the results of copolymers with different composition are shown in Figure 6. It is found that the shape-recovery rate increases with the increase of the content of ε-CL. However, the shape-retention rate keeps a monotonously decrease with the increase of the content of ε-CL, and all of the copolymers show more than 90% of shape-retention rate.

Generally, shape-memory polymers consist of two phases, a thermally reversible phase for maintaining transient shape and a fixed phase for memorizing original shape. Crystal, glassy state, entanglement, or crosslinking can be used as a fixed phase.[19] When they are deformed at the rubbery plateau above the glass transition temperature (T_g) and subsequently cooled down below T_g under constant strain, the deformed shape is fixed because molecular mobilities are frozen. As they are reheated above T_g, the original shape is recovered by the elastic force generated during the deformation. As discussed earlier,
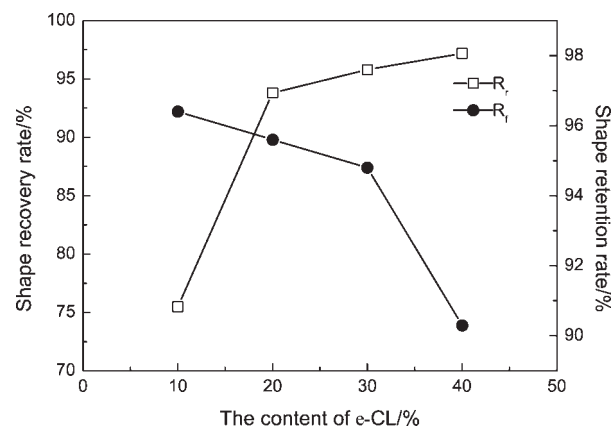

Figure 6 Shape-memory properties as a function of ε-CL content at $\varepsilon_m = 100\%$.
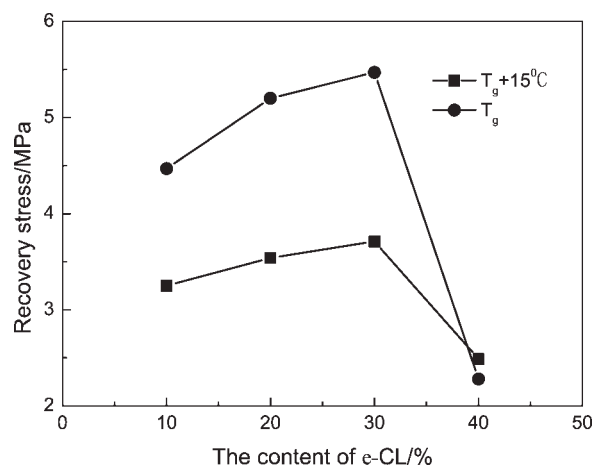
Figure 7 Recovery stress as a function of ε-CL content at $\varepsilon_m = 100\%$ obtained by tensile test (●) elongation at $T_g - 15°C$ and recovery at $T_g + 15°C$, (■) elongation at $T_g + 15°C$ and recovery at $T_g + 15°C$.

the structure of PCLA copolymers with the composition from 10 to 30 wt % ε-CL consists of crystalline hard domains of PLLA and amorphous soft phase. The crystalline PLLA domains are expected to serve as physical crosslinked points, while the flexibility of the amorphous phase provides the large elongation and the shape recovery. According to the analysis of DSC, the crystallinity of PCLA copolymers decreases with the increase of the ε-CL content, thus, the experimental results mentioned in Figure 6 can be explained as follows: on the one hand, the crystalline of PLLA served as the fixed phase can fix the deformation, which leads to the shape-retention rate of copolymers decreasing with the increase of the ε-CL content. On the other hand, the residual deformation can be caused by the plastic deformation or the orientation of the crystalline PLLA, therefore, the shape-recovery rate may increase with the increase of the ε-CL content. These results indicate that an appropriate ratio of LA/ε-CL is necessary for PCLA copolymers to exhibit excellent shape-memory effects. However, PCLA60 is amorphous and the entanglements of molecular chain serve as the physical crosslinks. In addition, hydrogen-bonding interactions also contribute to the physical crosslinks in PCLA copolymers. Thus, the shape-recovery rate is high under the present test condition and shape-retention rate is relatively low because of the lack of the PLLA crystalline that provides stronger crosslink comparing with the physical crosslinks formed by the entanglements of molecule chains.

To evaluate the driving force for shape recovery, the recovery stress is measured by tensile test while a prestretched specimen is heated to a certain temperature with the specimen length fixed. As shown in Figure 7, the recovery stress increases with the

content of ε-CL, reaches the maximum, and then decreases. Recovery stress relates to two aspects, namely, the applied maximum stress and the shape-recovery rate. Firstly, recovery stress is proportional to the applied maximum stress because the inner stress stored in the specimen during predeformation and fixed processes is the driving force for shape recovery. With the increase of the content of ε-CL, the applied maximum stress decreases as a result of the decrease of the recovery stress. Secondly, recovery stress is also proportional to the shape-recovery rate. As we know, the higher shape-recovery rate means the lower plastic deformation, which suggests that the higher proportion of applied stress can be stored in the specimen. Thus, the recovery stress increase as a result of the content of ε-CL increasing. The combination of the two aspects can explain the variation of recovery stress with the content of ε-CL. Moreover, it should be pointed out that the recovery stress is dependent on the stretching condition. When the specimen is stretched at T_g, a high-drawing force is needed and the inner stress stored in the specimen is high. When it is stretched at $T_g + 15°C$, much less drawing force is needed and, consequently, less inner stress is stored in the specimen, resulting in a relatively low-recovery stress. It is apparent from these data, that PCLA70 displays recovery stress markedly superior to those exhibited by other biodegradable shape-memory polymers recently developed. For example, Lendlein and Langer reported that the recovery stress of PDC multiblock copolymer was in the range between 1 and 3 MPa.[7] According to the Table I, it is worth noted that the recovery temperature of the PCLA70 copolymer is near to the body temperature, which is very significant for medical implantations.

Figure 8 shows the effects of deformation strain on the shape-recovery rate and recovery stress for the PCLA70 copolymer at different stretching conditions. It can be seen that, the variations of shape-recovery rate and recovery stress have a similar trend: with an increase of deformation strain, the R_r and recovery stress increase initially, and then decrease. It can be seen that there is correspondence between the two curves: the recovery stress maximum corresponds to the R_r maximum. These results are in accordance with the discussion mentioned earlier.

In general, when the deformation is applied to the samples, the amorphous phase having low modulus will be extended in the first stage, and the number of extended amorphous chain would increase with increasing the deformation strain. However, at a high-deformation strain value, two factors unfavorable for recovery should be taken into consideration. One is the relaxation of the extended amorphous chain because of their dislocation from the PLLA crosslinks; another should be the plastic deformation
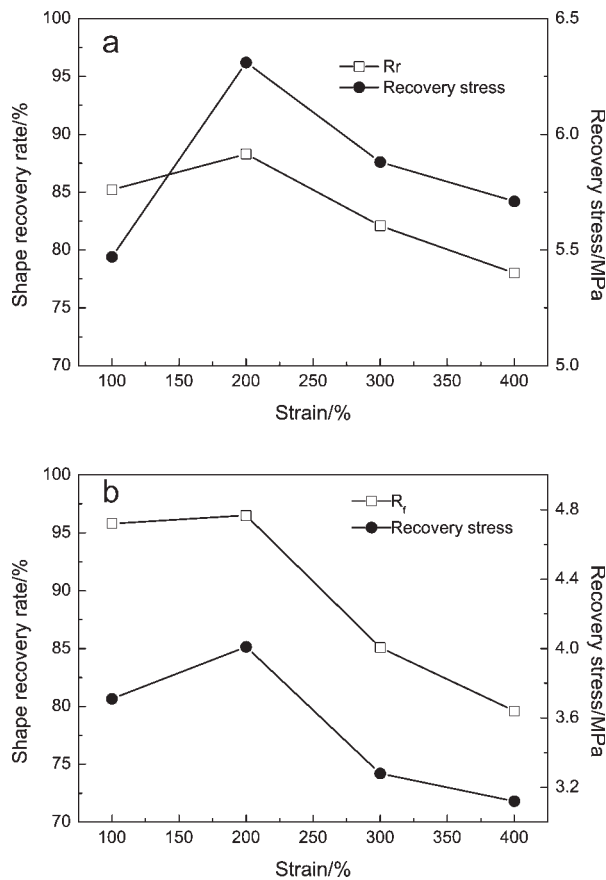
Figure 8 Effect of deformation strain on shape-memory properties of the PCLA70 copolymer (a) elongation at $T_g - 15°C$ and recovery at $T_g + 15°C$, (b) elongation at $T_g + 15°C$ and recovery at $T_g + 15°C$.

of crystalline domain because of stress transfer to the crystalline domain as the deformation strain increases further and with the increase of the deformation strain, the irreversible deformation formed by the deformation of PLLA crystal increases. In fact, the recovery process is provided by comparatively highly oriented amorphous chains, and the recovery stress comes from the relaxation of internal stress that is frozen in the sample after deformation (orientation). Therefore, there exists an optimal deformation strain value corresponding to the maximum shape-recovery rate and recovery stress.

Degradation process of PCLA copolymers

Mass loss of polymers during degradation time is shown in Figure 9. It can be seen that copolymers with higher ε-CL content have higher degradation rate. PCLA90 shows no apparent mass loss until 150 days, while PCLA80, PCLA70, and PCLA60 start losing mass rapidly after immersion in the PBS 90 days. Copolymers of higher ε-CL content possess poorer crystallinity when compared with those of lower ε-CL content and this make them of good per-

meability for water, hence of comparatively faster degradation rate. On the other hand, PLLA has more ester groups in the molecule structure, so the water absorption of copolymers with lower ε-CL content is comparatively higher than those of higher ε-CL content. The high water absorption accounts for the fast hydrolytic degradation. Considering the two reasons, it can be concluded that the crystallinity is the leading parameter of the biodegradability of these polymers, playing a more important role than the molecule structure.

Figure 10 demonstrates the tensile properties and shape-memory properties of PCLA copolymers after 30 days *in vitro* degradation. It is apparent that the tensile strength as well as the elongation at break of the PCLA copolymers drops rapidly. It can also be seen that the shape-recovery rates and recovery stress of all copolymers reduce significantly during the degradation process. As mentioned earlier, during the early stage of the degradation, the amorphous phase degrades initially, which results in the decrease of the amount of amorphous phase. Moreover, the chain scission occurs in the molecule chain during degradation process. The two reasons are responsible for the decrease of tensile properties and shape-memory properties. It is worth stressed, that most of the copolymers remain with relative good mechanical properties and shape-memory properties. After 30 days *in vitro* degradation, for example, PCLA70 copolymer displays a strength around 25 MPa, a shape-recovery rate of around 90%, and recovery stress of 3.5 MPa.

CONCLUSION

In this study, the PCLA biodegradable shape-memory polymers synthesized by ring-opening polymer-
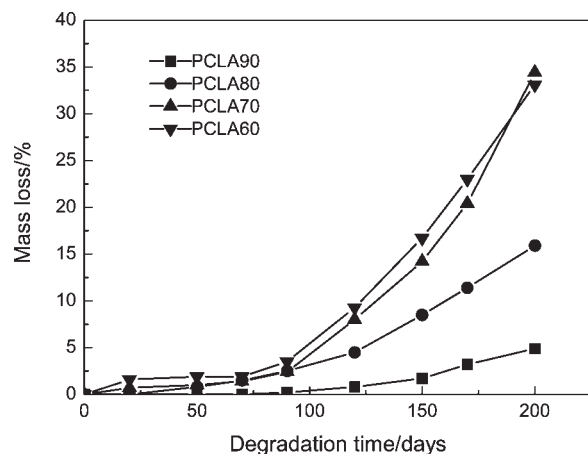

Figure 9 Dependence of mass loss of polymers on degradation time under pH 7.4 at 37°C.
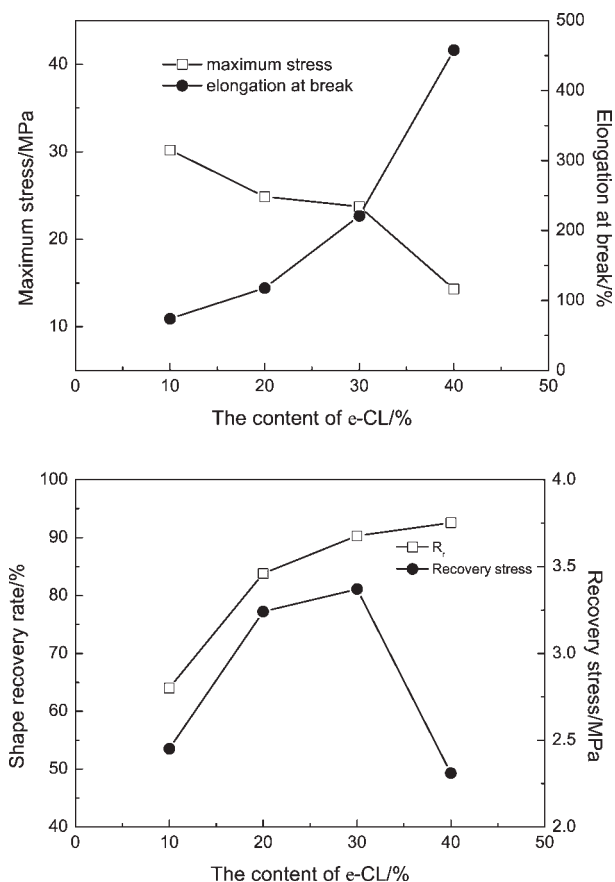
Figure 10 (a) Tensile properties (b) shape-memory properties of PCLA copolymers after 30 days *in vitro* degradation.

the amorphous phase performs as reversible phase. Most of the PCLA copolymers exhibit high-recovery stress and the values exceed 3 MPa, which is superior to the value reported in other biodegradable shape-memory polymers. The higher ε-CL content, the faster *in vitro* degradation of the polymers, and the shape-recovery rate and recovery stress of all copolymers obviously decrease during degradation process. On the whole, the experiment results reveal that the PCLA copolymers with high mechanical properties, superior shape-recovery rate, and recovery stress, recovery temperature near to the body temperature and a suitable degradation rate can be obtained by controlling the ratio between the LA and the ε-CL.

izization are developed. The structure, mechanical properties, and shape-memory behaviors are investigated and their dependence on composition is assessed. The structure of these polymers varies from the semicrystalline polymer to amorphous polymers. The tensile strength of these copolymers decrease from the 40 to 20 MPa and the shape-recovery rates increase from 75 to 97% when the content of ε-CL increase from 10 to 40%, and all the polymers show more than 90% of the shape-retention rate. The PLLA crystal or the entanglements of chains function as physical crosslink points, while

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