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Shape memory effects of poly(L-lactide) and its copolymer with poly(ε-caprolactone)

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Summary

The thermal properties, crystalline structure and shape memory effects of poly(L-lactide) (PLLA) and its copolymer with poly(ε-caprolactone) (PCL) are systematically investigated by differential scanning calorimetry (DSC), X-ray diffraction (XRD) and tensile tests. The influences of composition and intrinsic viscosity on structure and shape memory effects are also revealed. It is found that the PLLA homopolymer and poly(L-lactide-co-ε-caprolactone) (PCLA) copolymers exhibit good shape memory effects. The existence of PLLA crystal and amorphous phase play very important roles for shape memory effects. The intrinsic viscosity obviously affects the crystallinity of polymers and further affects the shape memory effects. The shape recovery rate decreases with increasing deformation strain, which is relate to the deformation of PLLA crystal. The recovery stress increase with the increase of the ε-CL content and maximum recovery stress is 3.54MPa obtained in the PCLA804 (20wt% ε-CL content, M_w=304,400). With the increase of cyclic testing number, the shape recovery rates decrease and the shape retention rates increase at the beginning and then approach to a steady value.

Introduction

Biodegradable polymers have been widely studied for various pharmaceutical and medical applications such as surgical sutures, tissue engineering and controlled drug delivery systems.[1-3] In order to expand the medical application fields, it is very important to give these materials the novel functional properties.

Shape memory effects have already been widely used in the clinical field, for example, the well known TiNi shape memory alloys (SMAs).[4] However, the unbiodegradable properties of SMAs mean that they remain in the body permanently and lead to foreign rejection by the human body. The disadvantages of SMAs make biodegradable shape memory polymer possibly ideal substitutes in minimal invasive surgery applications, such as stents.[5] In recent years, several kinds of biodegradable shape memory polymers have been reported.[6,7] Lendlein[8] studied the shape memory properties of multiblock copolymers based on oligo(ε-caprolactone) and oligo(p-dioxanone) segments. Nagata coworkers have synthesized photocurable biodegradable multiblock copolymers showing shape memory effects.[9] Min et al investigated the shape memory effects of polylactide-co-poly(glycolide-co-caprolactone) multiblock copolymer.[10] But it is known that the synthesis and post treatment methods of the polymer mentioned above need multi-step reaction. In contrast to the work mentioned above, our research work focuses on developing biodegradable shape memory polymers with easy synthsis method and high recovery stress. PLLA is one of the most intensively studied biodegradable polymers because of its good mechanical properties and its copolymers with PCL may expand its applications because the ε-CL appears to be a suitable comonomer for the preparation of copolymers with mechanical properties ranging from rigid to elastomeric. During the past years, many research works are concentrated on the synthesis, biodegradability and mechanical properties of these polymers.[11-13] However, to our knowledge, there have very few reports on shape memory effects of PLLA and PCLA copolymers especially on the recovery stress. In previous publications, we have first reported that the PLLA shows shape memory effects and the original shape can be recovered at 70°C.[14] In this study, we further investigate the shape memory effect of PLLA and PCLA copolymers and the dependency of the shape memory effects upon the compositions, intrinsic viscosity and shape memory process is also discussed.

Experimental

Materials

L-Lactide (L-LA) was synthesized according to the literature,[15] and purified by re-crystallization using ethyl acetate as solvent. ε-CL (Aldrich) was dried over molecular sieve 4Å and purified by distillation under reduced pressure. Stannous octoate (Sigma, A. R.) was used as received. Chloroform and methanol were used as received.

Polymerization

PLLA homopolymers were prepared by ring opening polymerization of L-lactide using stannous octaoate as catalyst. The reaction product was dissolved in chloroform and then precipitated in methanol and dried under vacuum.

PCLA random copolymers were prepared by simultaneous addition of two monomers (L-LA and ε-CL) into a flask with stannous octoate as initiator. After degassing, the flask was sealed under vacuum and then in an oil bath at 130°C for 48h. The resulting copolymers was first dissolved in chloroform and then precipitated by using methanol. Finally, the products were vacuum-dried at 40°C for 2 days.

Characterization

^{1}HNMR spectroscopy was carried out with a Bruker DMX 300 spectrometer. Chloroform was used as the solvent for the NMR measurements. The mole fraction of PCL in the copolymers was determined from the area of the peak at δ=4.05 ppm divided by the sum of the area of the peak at δ=4.05 ppm and the area of the peak at δ=5.15ppm corresponding to methane hydrogen in $-[OCH(CH_3)]$.

The molecular weight and the distribution of the polymers were measured by gel permeation chromatography (GPC; Agilent 1100). Tetrahydrofuran (THF) was used as the mobile phase at a flow rate of 1.0mL/min. Calibration was performed with polystyrene standards to determine the absolute weight-average and number-average molecular weights (Mw and Mn).The results were listed in Table 1. The intrinsic viscosity (η) of polymers is measured using chloroform as solvent with an Ubbelodhe viscometer at 25°C. The results are listed in Table 1.

Table 1 Sample code and characterization of PLLA and PCLA copolymers

Sample code	Monomer composition[a]	Copolymer composition[b]	M(n):M(I)/ mol:mol	[η]/(dl/g)	M_w[c]	M_w/M_n[c]
PLA1	100:0	100:0	2000:1	1.17	25,500	1.37
PLA2	100:0	100:0	4000:1	2.14	58,500	1.45
PLA3	100:0	100:0	6000:1	4.58	205,900	1.56
PLA4	100:0	100:0	8000:1	5.19	282,000	1.74
PCLA901	90:10	92:8	5000:1	1.34	119,200	1.64
PCLA902	90:10	92:8	4000:1	2.57	212,300	1.39
PCLA903	90:10	92:8	1000:1	3.92	300,900	1.89
PCLA904	90:10	92:8	2000:1	5.39	413,800	1.71
PCLA801	80:20	81:19	5000:1	2.12	177,900	1.52
PCLA802	80:20	81:19	4000:1	2.86	248,300	1.87
PCLA803	80:20	81:19	1000:1	3.64	260,400	1.64
PCLA804	80:20	81:19	2000:1	4.06	304,400	1.68

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

The glass transition temperature (T_g), melting temperature (T_m) and heat of fusion (ΔH_m) were measured on a Perkin-Elmer Diamond DSC at heating and cooling rate of 10°C/min. The crystallinity was calculated from the measured heat of melting, using the value of heat of melting of the crystallinity regions of PLLA ΔH_m=93.1J/g taken from the reference.[16]

The X-ray diffraction (XRD) method was employed for studying the crystalline structure by using a Rigaku D/max-rb rotating anode X-ray diffractiometer at 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 50mm/min. The tensile test specimens had dimensions of 40mm in length, 5mm in width and 0.4mm 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 50mm/min at T_k, (2) cooling the sample to T_l with the same ε_m, (3) maintaining the sample at T_l for 5min after removal the load, and (4) raising the temperature from T_l to T_k then maintain at the latter for 5min. Under these conditions, shape retention rate (R_f) and shape recovery rate (R_r) are defined as follows:[17]

$$\text{Shape retention rate (\%)} = \varepsilon_u \times 100 / \varepsilon_m \qquad (\mathbf{1})$$

$$\text{Shape recovery rate (\%)} = (\varepsilon_m - \varepsilon_p) \times 100 / \varepsilon_m \qquad (\mathbf{2})$$

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

For measurement of the recovery stress, the test procedure was similar to the mentioned above (1)~(3), the difference was the last step, (4) the specimen was clamped with its length fixed and then was heated until T_k, and the tensile stress was recorded as the recovery stress.

Results and discussion

Characterization

Figure 1 shows the GPC curves of PLLA and PCLA copolymers. There are only one peak on the GPC curves, which indicates the successful copolymerization of L-LA and ε-CL.

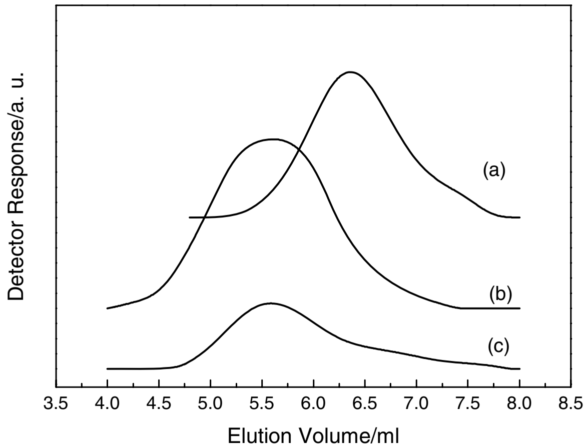

Figure 1 GPC curves of (a) PLLA2 (b) PCLA903 (c) PCLA804 polymers

Thermal properties

Figure 2 shows the DSC curves of first heating and cooling for PLLA and PCLA copolymers. An endothermic peak can be observed on the DSC heating curves of each sample, which corresponds to the melting of PLLA crystal. Only the PLLA shows a clear exothermal peak at about 110°C due to the cold crystallization. The glass transition temperature, the melting temperature and the heat of fusion are summarized in Table 2. It can be seen that copolymerization with ε-CL has a dramatic impact on thermal properties and both the glass transition temperature and the melting temperature decrease with the increase of the amount of ε-CL. The introduction of ε-CL units which have five methylene groups increases the chain flexibility and mobility and results in a considerable decrease in the T_g and T_m.

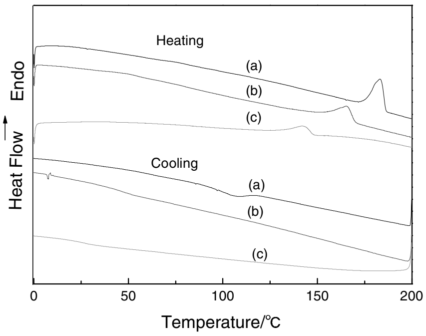

Figure 2 DSC curves of first heating and cooling for (a) PLLA3 (b) PCLA904 (c) PCLA804 polymers

Table 2 Thermal properties of PLLA and PCLA copolymers

Sample	T_g (°C)	T_m (°C)	ΔH_m (J/g)
PLA1	62.1	175.4	46.1
PLA2	61.6	173.8	34.8
PLA3	65.3	173.7	14.4
PLA4	64.1	173.9	25.6
PCLA901	51.7	154.7	34.9
PCLA902	53.5	158.4	26.7
PCLA903	54.3	155.6	25.1
PCLA904	55.6	153.3	22.0
PCLA801	35.3	142.1	23.7
PCLA802	39.7	143.7	10.4
PCLA803	41.7	143.3	11.4
PCLA804	42.5	146.0	12.8

Figure 3 shows the crystallinity of PLLA and PCLA copolymers as a function of intrinsic viscosity. It can be seen that the crystallinity decreases obviously with the ε-CL addition. The decrease of crystallinity is due to the increase of chain flexibility and chain disorder with the addition of ε-CL. Moreover, with the increase of intrinsic viscosity, the crystallinity of PLLA and PCLA copolymers decreases sharply at the beginning and then changes slightly after the intrinsic viscosity of samples reaches a certain value.

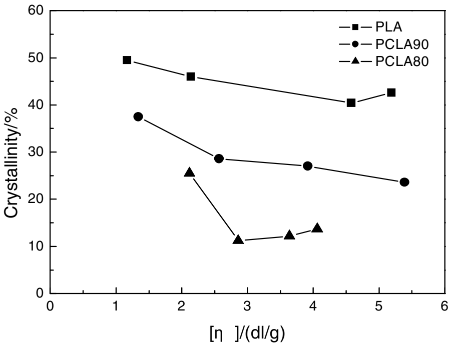

Figure 3 The crystallinity of PLLA and PCLA copolymers as a function of intrinsic viscosity

Crystalline structure

Figure 4 shows the X-ray diffraction patterns of PLLA and PCLA copolymers. It is seen that there are two peaks at 2θ=17°and 19°which characterize the crystalline of PLLA. However, the typical diffraction peaks of crystalline PCL reported at 2θ=21.4°[13] can not be observed in the patterns of the copolymers, which indicates that PCL is fully 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.

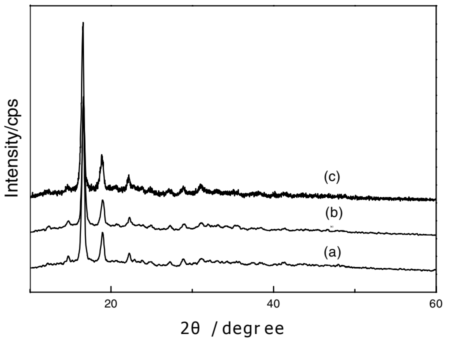

Figure 4 The X-ray diffraction patterns (a) PLA3 (b) PCLA904 (c) PCLA804

Mechanical property

Figure 5 shows the stress-strain curves of polymers at room temperature. All the curves demonstrate the elastic properties except the PLLA3 shows a yield point at room temperature. The composition of the polymers has great effects on the tensile properties and the maximum stress decreases almost linearly, but the elongation at break gradually increases with the increase of ε-CL content. According to the result of DSC, the crystalline PLLA is expected to serve as physical cross-linked 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.

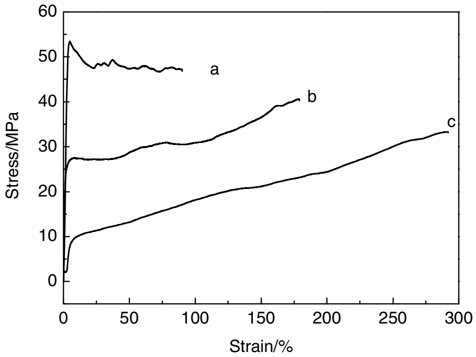

Figure 5 Stress-strain curves of the polymers (a) PLLA3 (b) PCLA904 (c) PCLA804

Shape memory effect

The shape recovery rate (R_r) and the shape retention rate (R_f) are the two important parameters to identify the shape memory effects of shape memory polymer. Figure 6 shows the effect of intrinsic viscosity on the shape memory properties of PLLA homopolymer and PCLA copolymers (deformation strain 50%). Figure 6(a) shows that the R_f of PLLA increases with the increase of intrinsic viscosity, but the R_r first increase with the increase of intrinsic viscosity and then decrease with further increase of intrinsic viscosity. A maximum R_r can be obtained at 4.58 of intrinsic viscosity value. Figure 6(b) shows that both the R_f and R_r of PCLA90 increase with the intrinsic viscosity increasing. The evolvement of R_r and R_f of PCLA80 with the intrinsic viscosity is almost similar to that of PCLA90, as shown in Figure 6(c). Thus, from the above results, it can be concluded that 85-100% of shape recovery rate is obtained at an appropriate intrinsic viscosity for PLLA and PCLA copolymers, but PLLA homopolymers exhibit slightly lower shape recovery rate than the PCLA copolymers, and all of the polymers 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.[18] Crystals, glassy states, entanglements, or crosslinkings can be used as a fixed phase memorizing the original shape.[19] As discussed above, the PLLA and PCLA copolymers have the crystalline phase of PLLA and the attainable crystallinity of PLLA is low. It is considered that the crystal of PLLA refers to as the physical crosslink points and the amorphous state acts as the reversible phase for PLLA and PCLA copolymers. Reversible phase transformation of amorphous state is reported to be responsible for the shape memory effect. As mentioned above, the crystallinity of polymers varies with the intrinsic viscosity, that is to say, the content of amorphous state first increases with the increase of intrinsic viscosity and then decreases slightly with further increase of intrinsic viscosity, which is in accordance with the evolution of R_r. The R_f is relate to strength of polymers at glass state and the polymers with high intrinsic viscosity has higher strength to fix the permanent shape of the material. So the increase of intrinsic viscosity of the polymers can improve the R_f.

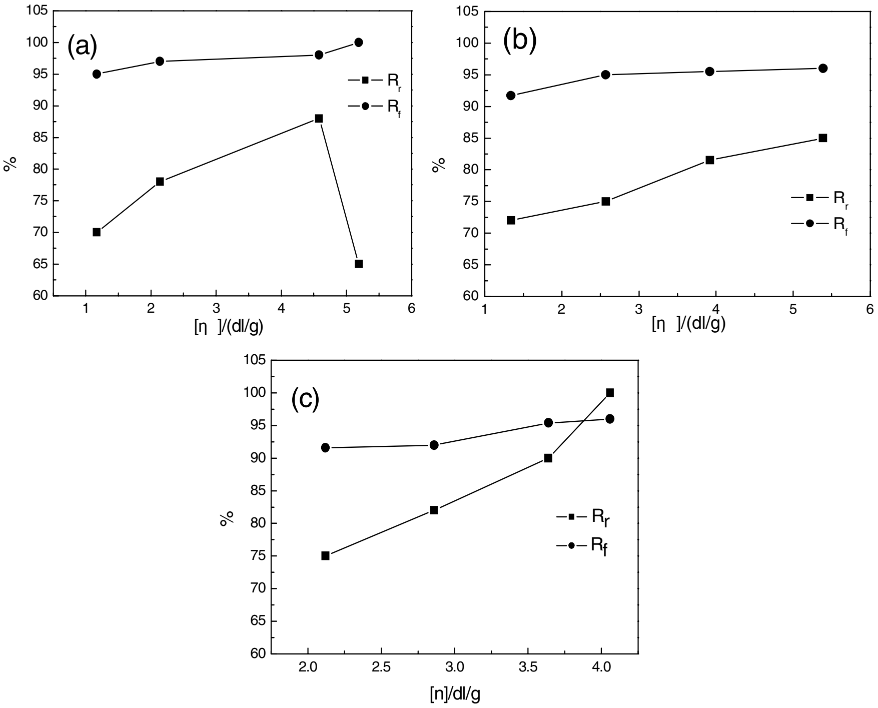

Figure 6 The influences of intrinsic viscosity on the shape memory effects under 50% deformation strain (a) PLLA (b) PCLA90 (c) PCLA80

Figure 7 shows the influences of deformation strain on the shape recovery rate for PLLA and PCLA copolymers. It can be seen that the R_r of the samples decreases rapidly with an increase of deformation strain and the decrease value of R_r decreases with the content of ε-CL increasing. In general, when the deformation is applied to the samples, the amorphous phase having low modulus will be extended in the first stage of deformation, and as the deformation strain increases, stress will be transferred to the crystalline domain.[20] When the stress transferred to the crystalline domain is increased, the plastic deformation of crystalline domain will occur. With the increase of the deformation strain, the irreversible deformation formed by the deformation of PLLA crystal increases, as a result, the R_r decreases with an increase of deformation strain. Moreover, the change of the decrease value of R_r is in accord with the variety of crystallinity of polymers.

The recovery stress is measured by tensile test while a pre-stretched specimen is heated to a certain temperature with the specimen length fixed. As shown in Figure 8, the recovery stress increases with the content of ε-CL and the maximum recovery stress is 3.54MPa obtained in PCLA804. 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 pre-deformation 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. It is apparent from these data, PCLA90 and PCLA80 display recovery stress superior to those exhibited by other biodegradable shape memory polymers recently developed. For example, Leindlein reported that the recovery stress of PDC multiblock copolymer was in the range between 1 and 3 MPa. [7]

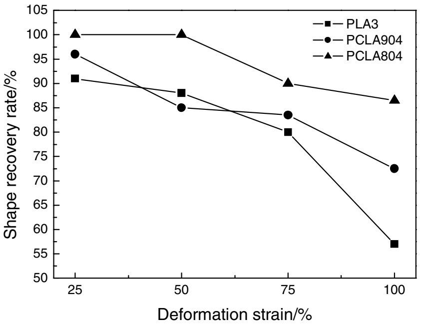

Figure 7 The influences of deformation strain on shape recovery rate for PLLA homopolymer and PCLA copolymers

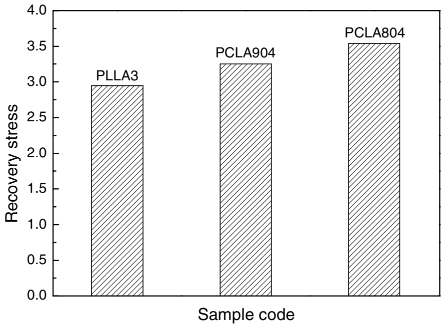

Figure 8 Recovery stress of PLLA and PCLA copolymers under 100% deformation strain

The stability of shape memory effect is of great significance in practical applications. The curves of shape memory effects as a function of the cyclic testing number for PLLA and PCLA copolymers are shown in Figure 9 (deformation strain 50%). It can be seen from Figure 9(a), the shape recovery rates dramatically decrease with an increase of cycle number at the beginning, and then approach to a steady value. This could be ascribed to the orientation of PLLA crystal by the extension during the early cycle results in the increase of irrecoverable deformation. In Figure 9(b), the shape retention rates increase with the increase of cycle number. It is considered that cyclic hardening is induced by the orientations of hard segments during extension, thus, the strength of polymers can be enhanced by cyclic testing, which is responsible for the increase of R_f. Moreover, the resistance to deformation increases with cycling, that is to say, the further deformation of PLLA crystal is difficult, thus the R_r and R_f tend to a steady value after several tests.

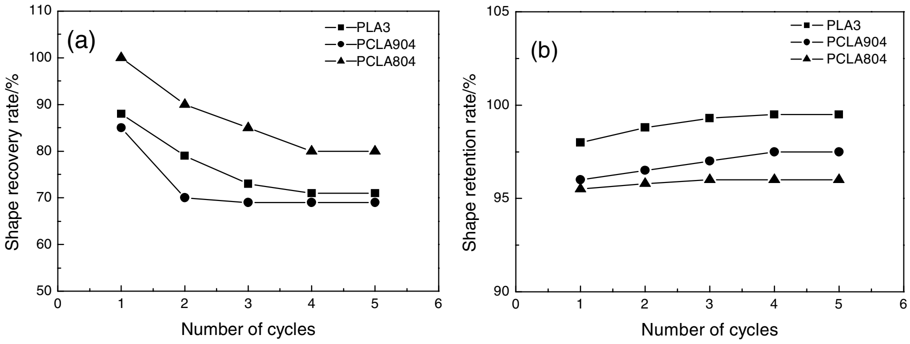

Figure 9 (a) shape recovery rate (b) shape retention rate as a function of cycle number for PLLA homopolymer and PCLA copolymers

Conclusion

The shape memory effects of PLLA homopolymers and PCLA copolymers are systematically investigated. The following conclusions can be drawn from the experimental results.

PLLA homopolymers and PCLA copolymers exhibit good shape memory effects and the PLLA crystal and the mobility of amorphous phase are responsible for the shape memory effects.

The intrinsic viscosity has obviously influence on the shape memory effects. The PLLA homopolymer exhibits a maximum shape recovery rate with the increase of the intrinsic viscosity, and show high shape retention rate of more than 95%. The shape memory effects of PCLA copolymers have been improved by the increase of the intrinsic viscosity.

The recovery stress increases with the content of ε-CL and the maximum recovery stress is 3.54MPa obtained in PCLA804, which is superior to those exhibited by other biodegradable shape memory polymers recently developed.

The shape recovery rates decrease with the increase of deformation strain due to the deformation of PLLA crystal. With the increase of cyclic testing number, the shape recover rates decrease and shape retention rates increase initially and then approach to a steady value, which is ascribed to the deformation and orientation of PLLA crystal during the tests.

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