Synthesis of PLA-based thermoplastic elastomer and study on preparation and properties of PLA-based shape memory polymers

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Abstract

As a new functional polymer material, shape memory polymer (SMP) has many advantages, and can be widely used in medical devices, textiles, aerospace and other fields. For thermal response SMPs, temporary deformation can be stored under external force above Tg with a rapid cooling down to below Tg or Tm, and when heated again to the critical temperature point, they return to their original shape. In this paper, shape memory poly(lactic acid) (PLA) block copolymers were prepared from a chain extension reaction of PLA with poly(ε-caprolactone) diol (PCL-OH). Using hexamethylene disocyanate (HDI) as a chain extender, the molecular weight of the prepolymer could be greatly increased by melt chain extension. Polylactic acid thermoplastic elastomer (PLAE) synthesized by chain extension reaction is soft and tough, similar to thermoplastic polyurethane (TPU). Polylactic acid-based shape memory polymers with good shape memory properties can be obtained by blending PLAE with PLA. The shape memory property test showed that the polylactic acid-based shape memory polymer was successfully prepared, and the recovery rate of the polylactic acid-based shape memory polymer could reach to approximately 80%. Besides, we also did thermal and microstructural analysis of the blend material. Due to their good biocompatibility and biodegradability, PLAE and PLA/PLAE will have potential applications in biomedical implant materials, engineering plastics, and textiles.

1. Introduction

Shape memory polymer (SMP) is a kind of polymer with initial shape which can be restored to its original shape after deformation and fixation under certain external conditions (heat, light, electricity, magnetism, solvent, etc) [1]. Since the first discovery of shape memory polymer, namely cross-linked polyethylene, by Ota [2] in the 1980s, shape memory polymers have been extensively studied. At present, polyurethane [3–6], shape memory epoxy resin [7–9], polystyrene-based shape memory polymer [10], shape memory polynorbornene [11], shape memory cyanate ester and so on have been reported.

Shape memory properties of these polymers are due to their two-phase structure composed of a stationary phase and a reversible phase. Stationary phase mainly contains cross-linked polymers, the winding structure of ultra-high molecular chain as well as the partial crystalline structure for remembering the initial shape, while the reversible phase such as the partial crystalline phase and the glassy polymer can be used for reversible transformation between softening and curing under the change of external conditions [12].

The shape memory effect (SME) of various SMPs has been well documented over the past few decades, with thermally activated SMPs being studied the most [13]. To date, the glass transition temperature (Tg) and melting temperature (Tm) are the two critical parameters for the shape change of the thermal response SMP. They were firstly heated above Tg or Tm to undergo temporary deformation under the action of external forces, and then...
rapidly cooled below \( T_g \) or \( T_m \) to maintain temporary deformation under the action of maintaining external forces [14]. After being heated to the critical temperature again, they will return to their initial shape [15].

The shape memory properties of polymer blends are achieved by the ‘interpenetrating polymer network’ (IPN) formed by the intertwining of molecular segments [16, 17]. The blending units for PLA-based shape memory polymers are usually thermoplastic elastomer (TPU) [18, 19], polyethylene glycol (PEG) [20] and other inorganic fillers. Besides traditional thermoplastic TPU, Zheng et al [21] found that thermoset shape-memory polyurethane can also be enabled with intrinsic plasticity by transcarbamoylation which induced a topological network rearrangement so that a classical thermoset shape-memory polyurethane is readily capable of permanent reshaping (plasticity). This method should be taken into consideration in designing SMP. The triblock copolymers of PLA-PEG-PLA were prepared by Kuitikov et al [22] and blended with hydroxyapatite (HA). It was found that the tensile strength and storage modulus of the copolymers increased with the addition of HA. The shape fixation rate is more than 99%, and the shape recovery rate is slightly reduced. When HA content is 20 wt%, the recovery rate is reduced to 90.6%. Zheng and Zhou [23–25] investigated the effects of biodegradable poly-D, L-lactic acid and inorganic materials on shape memory behavior. When PLA and \( \beta \)-tricalcium phosphate were compounded, shape memory materials with shape recovery rate of more than 95% were obtained.

TPU is a block copolymer with carbamate group, which can be divided into polyether type and polyester type according to the type of macromolecule glycol used. TPU is mainly composed of three chemical components: diisocyanate, diisocyanate and chain extender diol [26]. Therefore, the block polyurethane composed of macromolecule glycol, diisocyanate and chain extension sequence can be divided into ‘soft’ phase and ‘hard’ phase. Hard segments tend to aggregate into an ordered ‘hard’ phase, while soft segments form soft phases due to chain flexibility. The ‘hard’ phase is equivalent to the physical crosslinking between vulcanized rubber and chemical crosslinking. This structure gives TPU a variety of mechanical properties. ‘Soft’ phase is equivalent to flexible molecular chains in rubber with high flexibility and resilience, giving TPU high elasticity [27]. Therefore, the versatility of TPU can be achieved by changing the ratio of hard and soft segments, molecular chains and chemical types.

PLA molecules are used as hard segments in TPU, and flexible segments with low \( T_g \) are introduced into the chain. Thermoplastic elastomers based on PLA, mainly triblock copolymers or multiblock copolymers, can be prepared. The prepolymerus reported as flexible segments include polyethylene glycol (PEG) [28–30], polycaprolactone (PCL) [31, 32], poly (3-hydroxybutyrate) (PHB) [33–35], polyethylene oxide (PEO) [36–39], poly (1,3-trimethylene carbonate) (PTMC) [40], polydimethylsiloxane (PDMS) [41, 42] and so on. In low-molecular weight block copolymers, the addition of chain extender or coupling agent can further improve their molecular weight, resulting in multi-block TPU.

This paper reports the preparation of PLA-based thermoplastic elastomers and PLA-based shape memory composites. Polylactic acid-polycaprolactone-polylactic acid triblock copolymers were prepared by melt polycondensation using degradable polymers PLA and PCL. Then, hexamethylene diisocyanate (HDI) and 1,4-butanediol (BDO) were used to extend the chain of PLA-polycaprolactone triblock copolymers to obtain environmentally friendly polylactic acid-based thermoplastic elastomers, and their properties were studied. Polylactic acid-based thermoplastic elastomer was blended with polylactic acid, and the blend was hot-pressed by hot-pressing plate method. Polylactic acid-based shape memory polymer and test splines were prepared. The structure, morphology, thermal properties, thermal stability and shape memory properties of the material were characterized, and its properties were analyzed. The results showed that the biodegradable polylactic acid-based shape memory polymers with good shape memory properties were prepared. Compared with literatures, polylactic acid-based thermoplastic elastomers which made PLA more toughened were prepared by condensation and melt chain extension. Polyurethane structure was introduced into the polylactic acid chain segment. The present study is an alternative approach to the previously reported works on the polylactic acid-block- polycarbonate diol-based and polylactide-block-poly(butylene adipate) diol-based thermoplastic elastomers. Using this approach, various high-performance polylactic acid-based materials could be prepared. At the same time, polylactic acid-based shape memory polymer was prepared by blending method, and both the PCL segments in elastomer as well as PLA matrix are biodegradable and compatible, so that the shape memory polymer not only had good shape memory performance but also had a good performance of biodegradability and compatibility which could be utilized in medical and textile fields.
2. Experiments

2.1. Materials
Poly(lactic acid) (PLA, 4600D, pellet form) was obtained from NatureWorks Inc. Before any processing, the pellets were dried in an oven at 40 °C for at least 12 h. Poly(caprolactone) diol (PCL-OH, Mn = 2000) was supplied by Jining Huakai resin Co., Ltd. Lactic acid (88%) was obtained from Holland Purac Company.

2.2. Synthesis of PLA–PCL–PLA prepolymer (PLAG)
The synthesis of prepolymer was divided into two steps. The oligomer of l-lactic acid was firstly prepared via self-condensation reaction. Specifically, 500 g l-lactic acid containing 12 wt% water was added into the reaction flask and heated to 80 °C under the pressure of 1000 Pa with mechanical stirring (rotational speed 140 r min⁻¹). Then the reaction temperature was well controlled and increased at the speed of 10 °C h⁻¹. After the catalyst (0.1 wt% SnCl₂ in toluene) was added at 110 °C, the reaction system was further heated to 165 °C with the same heating speed to perform the self-condensation for 12 h. Secondly, the oligomer of l-lactic acid and PCL was put into the reactor at a certain proportion. Under mechanical stirring condition (rotate speed 160 r min⁻¹), vacuum degree was further improved and kept at around 60 kPa. After reaction at 165 °C for 6 h, the PLAG was obtained.

2.3. Synthesis of PLA-based thermoplastic elastomer (PLAE)
HDI and BDO (molar ratio = 3: 2, total 16.7 wt% of PLAG) were dropwise added to the obtained PLA–PCL–PLA prepolymer under the protection of argon gas. After 30 min, the PLA-based thermoplastic elastomer was synthesized. The purified products were dried to constant weight in a vacuum oven at room temperature for further experiments. The reaction scheme is shown in scheme 1.

2.4. Preparation of PLA/PLAE blends
PLA and PLAE were dried in a vacuum oven overnight before using. After that, the PLA and PLAE were dissolved in the anhydrous CH₂Cl₂, and completely mixed through magnetic stir for 8 h. The solvent was evaporated at room temperature overnight and then was kept in a vacuum oven for about 2 days to eliminate the solvent entirely. Finally, the obtained films were hot compression molded at 165°C to get the finial PLA/PLAE blends. The samples are denoted by the weight% content of PLAE which is shown in table 1.

2.5. Polymer characterization
Fourier transform infrared spectroscopy (FTIR) was determined in the 400–4000 cm⁻¹ range with an EQUINOSS/HYPERION2000 spectrometer (Bruker, Germany). The molecular structure and copolymerization ratio of PLA were obtained by ¹H NMR spectroscopy (Bruker DMX 500 NMR spectrometer), and all the spectra were measured at room temperature from 15% (v/v) CDCl₃ solutions. The chemical shifts were calibrated using tetramethylsilane. Gel permeation chromatography was used to test the polymer molecular weight and dispersity. GPC analysis was carried out by the Japanese HLC-8320 (Tosoh) analysis system. The two channels were TSK gel super AWM-H x 2, R9009 + R00 900, THF and 10 mM lithium bromide were used as eluent and the flow rate was 0.6 ml min⁻¹. PS calibration kit was used as calibration standard.

2.6. Crystallization behavior
X-ray diffraction was used to evaluate the dispersion state of the PLAE. X-ray diffraction (XRD) was carried out on Bruker GADDS x-ray diffractometer with an area detector. In addition, the crystallization behavior was tested by Lycra DFC320 polarized microscope. Samples were heated to 170 °C and then cooled at different cooling rates. The crystallization process of the samples was observed and the crystallization pictures were taken.

2.7. Shape memory properties
The shape memory properties were obtained from the dynamic mechanical analyzer (DMA, Q800, TA Instrument) by utilizing a dual cantilever setup under a temperature sweep setting. Before testing, the film samples (18 mm × 4 mm × 0.01 mm) were first equilibrated at 30 °C for 5 min, and then a 3 °C min heating rate was applied until the temperature reached 100 °C. During the temperature ramping, a 15-mm, 1-Hz frequency oscillation was applied. In addition, the DMA was employed to characterize the shape memory performance of the samples under custom testing procedures by utilizing a tensile testing setup. First, the samples were stretched to 100% strain at 40 °C. After stretching, the deformed samples were equilibrated at 75 °C and a continuous measurement of recovery strain was recorded.
2.8. Thermal analysis properties

Thermogravimetric analysis (TGA) was carried out with a TA instruments Q500. In the differential scanning calorimetry (DSC) (DSC 2010 from TA instruments) analysis testing, the samples were sealed in Al-crucible pans, and the procedure was performed under nitrogen atmosphere. In the first heating cycle, the samples were heated to 180 °C at a rate of 10 °C min⁻¹ and annealed at 180 °C for 10 min in order to remove the prior thermal history. Next, in the cooling cycle, the samples were cooled to room temperature using scan rate of 10 °C min⁻¹. After that, the samples were reheated to 180 °C at a rate of 10 °C min⁻¹ in the second heating cycle.

Table 1. Labels of samples.

| Samples | PLA content/wt% | PLA-E content/wt% |
|---------|-----------------|-------------------|
| PLA90   | 90              | 10                |
| PLA80   | 80              | 20                |
| PLA70   | 70              | 30                |
| PLA60   | 60              | 40                |
| PLA50   | 50              | 50                |
| PLA40   | 40              | 60                |
| PLA30   | 30              | 70                |
| PLA20   | 20              | 80                |
| PLA10   | 10              | 90                |
2.9. Blend morphology characterization
To investigate the fractured surface morphology of the PLA/PLAE blends, all samples were gold coated prior to investigation. And the fractured surface morphology was observed by scanning electron microscopy (SEM) using a FEI QUANTA250FEG. The SEM images were collected at an accelerating voltage of 10 kV. The samples were fractured at low temperature in liquid nitrogen environment and observed sections.

3. Results and discussion

3.1. Synthesis of the PLAG and PLAE
The chemical structure of PLAG elastomers was characterized by $^1$H NMR spectroscopy. Figures 1 and 3 showed the $^1$H NMR spectra of extracted PLAG and PLAE in CDCl$_3$ respectively.

It could be seen from the figure 1 that $b$ (4.35 ppm) and $a$ (5.16 ppm) correspond to proton peaks on -CH in lactic acid molecules, and the former was the proton peak in the terminal group of lactic acid. $g$ and $f$ were the proton peaks on the -CH$_3$ of the lactic acid molecule. It is found that the peak area ratio of -CH and -CH$_3$ is 1:3, corresponding to the molecular structure of PLA. The $d$ peak at 4.10 ppm was associated with the proton peak linked to the ester group of polycaprolactone glycol.

Therefore, the approximate molecular weight of PLAG could be calculated by the sum of the area of $a$ and $b$ two peak and the area ratio of $d$ peak, which would be explained below. According to the $^1$H NMR spectra, we calculated that the molecular weight of the polymer was about 7000 g mol$^{-1}$. And this result was consistent with the GPC test results (as shown in figure 2).

The results of GPC analysis showed that the molecular weight of PLA-PCL-PLA triblock prepolymer is 8000, which agrees well with the results calculated by $^1$H NMR In addition, the molecular weight distribution PDI = 1.04 is determined from GPC test results. The above test results showed that the synthesis of triblock copolymers was successful.

After the chain extension reaction, as shown in figure 3, the $b$ peak of PLAG at 4.35 ppm disappeared, which indicated that the terminal hydroxyl group of PLAG has completely reacted with isocyanate. In addition, a new peak $k$ peak appeared at 3.16 ppm, which was the group peak of the -CH$_2$ on the linear segment of the HDI. The change of $^1$H NMR indicated that the prepolymer had an effective chain extension reaction with HDI. A new characteristic peak(1) was also found at 5.02 ppm, which was related to the -NH structure in the urethane bond.

The FTIR spectra of PLAG and PLAE were shown in figure 4. The absorption peak of PLA-PCL-PLA prepolymer appears at 3509 cm$^{-1}$, which was the absorption peak of hydroxyl stretching vibration of hydroxyl terminated poly (lactic acid). There was no absorption peak in 3300 cm$^{-1}$ – 3150 cm$^{-1}$, indicating that there was no -COOH group in the polymer. The polymer had a strong –C=O expansion vibration absorption peak at 1756 cm$^{-1}$ and a C-O-C telescopic vibration absorption peak at 1087 cm$^{-1}$ and 1182 cm$^{-1}$. It indicated that there are -COO groups in the product, which means, the polymer contains the ester group. We could see that the characteristic absorption peak of the urethane bond appeared near 1520 cm$^{-1}$ after chain expansion, indicating

![Figure 1. $^1$H NMR spectra of PLAG in CDCl$_3$.](image)
Figure 2. PLAG gel chromatogram.

Figure 3. $^1$H NMR spectra of PLAE in CDCl$_3$.

Figure 4. FTIR absorption spectra of PLAG and PLAE.
the success of the chain extension reaction. The vibrational absorption peak of -NCO was invisible near 2200 cm$^{-1}$, indicating that HDI has completely reacted with PLAG.

3.2. Thermal properties, miscibility and crystallinity of PLA/PLAE blends

Differential scanning calorimetry (DSC) was used to characterize the thermal properties, miscibility and crystallinity of the PLA/PLAE blends. The second heating DSC curves of blends with various constituent compositions were shown in figure 5. DSC analysis showed that the glass transition temperature ($T_g$), crystallization temperature ($T_c$) and melting temperature ($T_m$) of PLA/PCL blends increased with the increase of PLA content.

DSC is usually used to determine the compatibility and non-compatibility of polymer blends. If only one glass transition temperature ($T_g$) appears in the DSC curve, the polymer system is compatible, and the two glass transition temperatures ($T_g$) indicated that the polymer system was incompatible or partially compatible. The degree of crystallization and phase separation of soft and hard segments could be eliminated by thermal transformation, such as glass transition temperature, melting point temperature and crystallization temperature. The results of DSC second heating scanning showed that PLA had good compatibility with PLAE. The glass transition temperature of PLAE was low, and the $T_g$ of PLA was reduced after blending with PLAE, indicating that there was some compatibility between the two [43]. In addition, the crystallization temperature of the blends decreased after PLAE was added. The crystallization peak of pure PLA was very weak, and $T_c$ was about 100 °C, indicating that it is difficult to form crystals during the heating process. With the addition of PCL, $T_c$ gradually decreases and the enthalpy of crystallization increases.

It could also be seen that the $T_c$ of the blends decreased with the increase of PLAE content, indicating that PCL promoted the crystallization of PLA segments in PLAE, and the crystallization of the blends was improved compared with that of pure PLA, as shown in the table 2. It has been reported that the increase of $\Delta H_m$ and $\Delta H_c$ is due to the decrease of the content of urethane bond.

The results of the thermal degradation analysis were shown in figure 6, with initial degradation temperature ($T_i$) and maximum weight loss slope ($T_{\text{max}}$) data summarized in table 3. As could be seen in the diagram, PLAG thermal decomposition occurred at 180–200 °C, and there was no obvious platform, but a continuous weightlessness process. The thermal degradation curve of pure PLA showed obvious thermal degradation platform. The decomposition temperature of pure PLA is at about 320 °C was obvious and it was fully degraded at 380 °C while the PLAE portion within the composites continued degrading after 400 °C.

Since pure PLA exhibited the highest degradation temperature (324 °C) while pure PLAE exhibited the lowest degradation temperature (200 °C) and the presence of PLAE could be seen through the slow-down in degradation rate after 380 °C, we could conclude that the higher the PLA content is, the more obvious the thermal degradation platform is; the higher the initial degradation temperature is; The thermal degradation curve of PLA with lower PLA content approached that of PLAE, and the thermal degradation platform gradually disappeared and the thermal degradation process gradually prolonged.

3.3. SEM and morphologies

In order to study the microstructure of PLA and PLAE blends, SEM images of brittle fracture specimens were analyzed. Figures 7(a)–(d), (E) are the SEM images of blending ratio PLA10/PLAE90, PLA30/PLAE70, PLA50/PLAE50, PLA70/PLAE30, PLA90/PLAE10, respectively. Figure 7(a) showed that when the PLA content is 10%,
there was a very obvious fibrous structure in the blends, which is PLAE structure. When the content of PLA in the blend was 30%, there was obvious island structure. At this time, the two interfaces of PLA and PLAE are clear, as shown in figure 7(b). Figure 7(c) was a SEM diagram of the blends at PLA: PLAE = 1:1. It could be seen from the diagram that the two-phase interfaces are vague and it looks close to stable continuous phase structure, but we still could see some ‘island and hole’ structures. When the PLA content was 70%, the two-phase interface appears, but it could be seen that the dispersion of PLAE was homogeneous, which was shown in figure 7(d). Figure 7(E) showed the SEM image of the blends when the content of PLA was 90%. It could be seen from the figure that the island structure was obvious, and the PLAE was evenly dispersed in the PLA matrix.

### 3.4. Polarized microscopy

The pure polyactic acid melt forms spherulites when it is cooled. The spherulites are spherical, small to several microns and large to several millimeters. The main factors affecting PLA crystallization include structure factors (relative molecular weight, molecular chain symmetry, molecular chain softness, conformation regularity, optical purity), forming conditions (temperature, cooling rate, forming time, orientation operation), crystallization nucleating agent, etc.

Zeiss polarizing microscope (POM) with digital camera was used to test the crystallization of PLA/PLAE blends. Firstly, the blends were melted at 180 °C for 5 min to eliminate the thermal history. Then the blends were cooled at 20 °C min⁻¹ and the crystallization was observed. The crystallization behavior of PLA70/PLAE30, PLA50/PLAE50 and PLA30/PLAE50 blends was observed at 130, 120, 100 and 60 °C respectively (as shown in figure 8). The final crystallization diagram was shown in figure 9.

From figure 8, it can be observed that during the cooling process, a small amount of crystallization appeared in the blends with 70% PLA content, while no crystallization has occurred in the blends with 50% and 30% PLA content, indicating that the former has a higher crystallization temperature. When the temperature decreased to

### Table 2. The thermal test data of PLA/PLAE blends.

| Samples | T_a (°C) | T_c (°C) | ΔH_c (J g⁻¹) | T_m (°C) | ΔH_m (J g⁻¹) |
|---------|----------|----------|--------------|----------|--------------|
| PLA10   | 42.91    | 111.5    | 3.792        | 164.19   | 2.755        |
| PLA20   | 41.1     | 106.73   | 14.24        | 164.04   | 11.04        |
| PLA30   | 41.65    | 109.33   | 15.13        | 164.32   | 11.54        |
| PLA40   | 45.94    | 103.51   | 21.3         | 165.83   | 24.77        |
| PLA50   | 47.23    | 102.55   | 25.95        | 165.52   | 28.24        |
| PLA60   | 47.51    | 111.88   | 28.17        | 166.13   | 27.94        |
| PLA70   | 48.87    | 117.86   | 29.01        | 167.04   | 32.94        |
| PLA80   | 54.1     | 112.08   | 29.19        | 167.4    | 35.72        |
| PLA90   | 50.33    | 118.18   | 27.39        | 167.22   | 30.06        |
| PLA     | 59.98    |          |              | 167.17   | 3.935        |

![Figure 6. TGA results of PLA/PLAE blends.](image-url)
120 °C, the blends with 70% PLA and 50% PLA content have shown some obvious crystallization behaviors, while the blends with 30% PLA content also began to show a small amount of crystallization. When the temperature continued to drop to 100 °C, the blends with 70% and 50% PLA content began to crystallize in large quantities, and the blends with 30% PLA content also showed obvious crystallization. This indicated that the crystallization rate of PLA blends with 70% and 50% PLA content were very fast in the range of 100–80 °C, and a large number of crystals were formed. From the above phenomena, it could be seen that the crystallization temperature of the blends with less PLA content was lower, which was consistent with the DSC test results. The crystallization temperatures of blends with 70% PLA, 50% PLA and 30% PLA were 117.86 °C, 110.55 °C and 106.33 °C, respectively.

We further amplified the two fully crystallized prepolymer s to 400 times and observed their crystal structure, as shown in figure 9. As could be seen from the figure, the crystal type was irregular spherulite, which had a clear trend of outward growth. In addition, the crystal size increased with the increase of PLA content. The reason for this phenomenon may be that when the crystallization temperature was low, it was conducive to nucleation, so
there were many nuclei, many small spherulites. When the crystallization temperature increased, it was not conducive to nucleation, and the temperature was more conducive to the growth of nuclei, so larger spherulites would be formed and grow quickly. When the temperature was too high, the crystal growth would be hindered and the growth rate would be greatly slowed down. Some related studies also showed that the spherulite size of PLA melt was linear with the crystallization temperature when it was cooled and crystallized. The higher the crystallization temperature was, the larger the spherulite size was.

3.5. Shape memory characterization
In order to study the shape memory properties of the blends, 0.1 mm thick strip blend films were prepared. The shape memory properties of the blends were investigated by dynamic thermomechanical analysis (DMA) and the results are shown in figure 10.
Firstly, the film samples were stretched to 100% (curve 1) at 40 °C; After the release of stress, the material could be observed slightly spring back (curve 2); Subsequently, the temperature rose to 75 °C under stress-free conditions, and the obvious shape recovery can be observed from curve 3. In previous studies, conventional shape memory polymers generally required higher deformation temperatures than their shape recovery temperatures. For polymers with glass transition temperature as same as shape memory temperature, the deformation temperature was generally around $T_g + 15$ °C. In this experiment, we found that the blend could achieve about 40 °C tensile finalization, in the cyclic test could reach nearly 80% recovery.

The stress-strain curves of the blends showed obvious yield points, which were typical plastic tensile curves. As we can see from the figure 10, the yield stress of blends decreases with increase of PLAE content. The yield stress of PLA80/PLAE20 blends is $17.4 \pm 0.5$ MPa, and the yield stress of PLA70/PLAE30 blends is $14.5 \pm 0.5$ MPa. When the PLAE content comes to 40 wt%, the yield stress of blends decreases to $7.6 \pm 0.3$ MPa.

The composites’ shape memory behaviors were characterized by the parameters of shape recovery ratio ($R_r$) and shape fixing ratio ($R_f$). These parameters are determined using the equations (1) and (2): [1]

$$R_r = \frac{\varepsilon_u - \varepsilon_p}{\varepsilon_m}$$

$$R_f = \frac{\varepsilon_u}{\varepsilon_m}$$

where $\varepsilon_u$ is the strain after the unloading of the testing stress, $\varepsilon_p$ is the strain after shape recovery, and $\varepsilon_m$ is constant representing 100% strain. The results of the $R_r$ and $R_f$ are shown in figure 11.

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Figure 9. Final crystallization diagram of the blend (magnification 400 times).

Figure 10. Shape memory cycle for (A) PLA60/PLAE40, (B) PLA70/PLAE30, (C) PLA80/PLAE20.
molecular chains generate an instantaneous retraction force. In addition, the modulus of materials at low temperature. For materials with high modulus at low temperature, when external forces are revoked, a strong recovery stress will be generated. The combined effect of two factors makes it difficult for materials to attain the fixed rate of 100%. From figure 10, we found that the blends hardly recover at about 40 °C until being heated above Tg. The shape fixation rate and shape recovery rate of all blends were above 97% and 70%, which indicated that the blends had certain shape memory properties.

In figure 12, a picture sequences illustrate, as an example, the macroscopic observation of the shape memory performance of PLA70/PLAE30. The sample strip was wrapped on the glass rod for 3 min in 65 °C water, and then immediately cooled in 0 °C water for 10 seconds to obtain the temporary spiral shape of the material. Figures 12(A)–(F) showed the complete shape recovery process. The image was taken at different time at 60 °C.
It could be clearly seen from figure 12 that when the deformed strip was heated at 60 °C, the perpetual shape of the straight strip almost completely restored in a few seconds. In order to achieve thermally induced shape memory behavior, it is well known that the polymers should have two components at the molecular level: a fixing phase made from physical or chemical cross-links, which can provide dimensional stability for shape fixity, and a reversible phase, which can impart elastomeric properties in shape recovery [45].

4. Conclusion

In this study, polylactic acid based thermoplastic elastomer PLAE was prepared by lactic acid and PCL-OH as raw materials. Then, PLA was blended with thermoplastic elastomer PLAE to obtain the poly(lactic acid) shape memory polymer. The pure materials and the blends with different contents of PLA and PLAE were characterized in terms of thermal properties, microstructure and shape memory properties. The results of \(^1\text{H}\) NMR and FTIR showed that PLA based thermoplastic elastomers were successfully prepared in this experiment. The shape memory property test showed that the polylactic acid-based shape memory polymer was successfully prepared, and the recovery rate of the polylactic acid-based shape memory polymer could reach about 80%. Because of the good biocompatibility and biodegradability of polylactic acid polymers, PLAE and PLA based blends will have high potential applications as biomedical implant materials, engineering plastics, and textile.

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