

# Shape memory properties of poly(D,L-lactide)/hydroxyapatite composites

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Received 23 January 2006; accepted 8 March 2006

## Abstract

Poly(D,L-lactide) (PDLLA) and Hydroxyapatite (HA) are compounded, which possess biodegradation, biocompatibility and shape memory properties. In the paper, we prepared serial imposing shape memory composites with different shapes, composite ratios and sample thicknesses. Scanning electron microscopy (SEM), differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) were carried out to examine surface morphology, glass transition temperature ( $T_g$ ), dynamic mechanical properties, and shape memory effect of PDLLA/HA composites, respectively. Moreover, some interesting shape memory behaviors were investigated. The results show that the better disperse morphology of HA grains using the experiment methods, and PDLLA/HA composites at a definite range of compound ratio have much better shape memory effect than pure PDLLA polymer. It indicates that HA particles can improve shape memory effect and PDLLA/HA composites are potential for biomedical applications.

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**Keywords:** Shape memory polymer; Poly(D,L-lactide); Hydroxyapatite; Composite; Biodegradation

## 1. Introduction

Shape memory materials are stimuli-responsive materials and have received increasing attention due to their interesting properties and potential applications in recent years. Metallic alloys with shape memory properties like NiTi alloys are already used in different areas, especially for biomedical applications [1]. However, their mechanical properties can be adjusted only within a limited range, and these are not biodegradable. Shape memory polymers (SMPs) comprise a new type of ‘intelligent’ polymers. SMPs can respond to changes in the external conditions such as temperature, ionic strength, pH, electromagnetism, solvent compositions, etc [2–6]. An elastomer will exhibit a shape memory functionality if the material can be stabilized in the deformed state in a temperature range that is relevant for the particular application. A change in

shape induced by a change in temperature is called a thermally induced shape memory effect. Thermally induced SMPs are outstanding in all kinds of SMPs. Its mechanism can be described: the polymer can retain temporary shape after deformation at the temperature above its  $T_{trans}$  (switching transition temperature), followed by cooling to laboratory temperature, and stress removing; after repeating heating above  $T_{trans}$ , the material returns to its original shape again [3]. The  $T_{trans}$  can be either a glass transition temperature ( $T_g$ ) or a melting temperature of polymer.

After Charlesby discovered that polyethylene had memory characteristic in 1950s [7], SMPs were rapidly developed in many fields due to their advantages, e.g., their easy availability and wide range of mechanical and physical properties [8–11]. A promising field in which SMPs could be an enabling technology for future applications is minimally invasive surgery [4,12–14]. The other benefit of using SMPs is that if the medical device is not intended to be permanent, it is possible to include biodegradability in the polymer [15,16]. Scaffolding devices for assisting in bone and tissue repair might be one application of such a biodegradable

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SMP. The medical possibilities of the SMP were recently demonstrated in the form of a self-tightening knot [4].

Here, we reported poly(D,L-lactide) (PDLLA)/hydroxyapatite (HA) composites showing shape memory properties. In recent years, biodegradable polymers, such as polylactide (PLA), polyglycolide (PGA), and their copolymer polylactide-co-glycolide (PLGA) find increasing applications in the pharmaceutical industry as matrices for drug delivery systems [17,18] and in medicine as material for bone implants and bone fixation devices [19–23], surgical sutures [24–25], and anastomotic devices [26] owing to their excellent biodegradation and biocompatibility. Except above advantages for PDLLA, it is also a sort of thermally induced SMP [27]. In hard tissue engineering, calcium phosphate ceramics, such as HA ( $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ ), have also attracted much attention due to their excellent biocompatibility and osteoconductivity [28–30]. However, their poor mechanical properties, such as low strength and fracture toughness, limited wide applications in hard tissue implantations [31]. As biomaterials, recently, many polymers were designed to be either biodegradable [18,22,23,25] or shape memory [13]. In recent research on biodegradable and SMPs, only oligo [(L-lactide-ran-glycolide)] dimethacrylates [32] and oligo ( $\epsilon$ -caprolactone) dimethacrylates [14,16] were reported. Moreover, recently reported shape memory composites were not biodegradable materials [6,11]. To the best of our knowledge, now the study on shape memory effect of PDLLA/HA composites was only simply mentioned by Shikinami [33]. However, relative work analyzing the relationship of shape memory effect and DMA of PDLLA/HA composites in the literature has hardly been addressed.

In this paper, we prepared PDLLA/HA composites in order to colligate their advantages and overcome their own shortcomings, and dispersed morphology of HA particles was examined by SEM. Subsequently, the shape memory effect and  $T_g$  of PDLLA/HA composites were analyzed by DMA and DSC. Moreover, we studied interesting shape memory behaviors of the composites.

## 2. Materials and methods

### 2.1. Materials

PDLLA (Mw:144KDa) was synthesized by ring-opening polymerization of cyclic lactide monomer as described previously [34]. The molecular weight distribution was 2.05 determined by Waters2695/2414 Gel Permeation Chromatography (GPC, Waters, America). Analysis was performed using tetrahydrofuran (THF) as solvent at a flow rate of 1.0 ml/min. HA with particle average size of 2.0  $\mu\text{m}$  determined by laser diffraction particle size analyzer (Malven, Mastersizer2000, UK) and with the molar ratio of Ca/P = 1.65 determined by chemical analysis was prepared by a hydrothermal method [35]. All other chemicals and solvents were of reagent grade or better.

### 2.2. Preparation of PDLLA/HA

PDLLA and HA composites were prepared at weight ratios of 1:1, 2:1, 7:3, 3:1. First, pre-weighted PDLLA was dissolved in  $\text{CHCl}_2$  under

stirring. Second, HA was dispersed in ethanol by a high-speed homogenizer for 10 min. Subsequently, the solution including HA and ethanol was slowly dropped into another stirring polymer solution by a pipette. During the process, a white emulsion was obtained because of some polymers precipitating in ethanol. The emulsion was stirred for at least 4 h in airproof continuously so that PDLLA could further be mixed with HA uniformly. Then, during the stirring in air, after solvent evaporated slowly from the emulsion, some floccules came into being gradually at the bottom of beaker, which were mainly PDLLA/HA composites. Finally, these floccules were kept in aerator overnight and dried at 30 °C under vacuum. Later, these completely dried composites were press-molded at 105 °C for 5 min in a mould, which was designed to a shape. The pressing was performed in the pressure range 10–15 MPa. Thus we could obtain specimens with some shape, which could be used to investigate shape memory properties as follows.

### 2.3. Characterization

The surface morphology of specimens was observed using a Quanta200 Scanning Electron Microscope (SEM, FEI, America). Pieces of the specimens were mounted and then coated with gold. The accelerating voltage and magnification was 10 keV and 10,000 $\times$ , respectively.

The  $T_g$  was detected by STA 449C Differential Scanning Calorimetry (DSC, NETZSCH, Germany). The specimens were heated from 15 to 100 °C at a rate of 5 °C/min in flowing nitrogen gas. Weights of all samples were from 4 to 6 mg.

DMA was carried out on a DMA983 analyzer (Du Pont, America), using a tensile resonant mode at a heating rate of 3 °C/min from 10 to 100 °C and at a frequency of 1 Hz. The storage modulus  $E'$  and loss factor  $\tan \delta$  for specimen size 10  $\times$  12  $\times$  2 mm (length  $\times$  width  $\times$  thickness) were tested.

### 2.4. Investigation of shape memory properties on PDLLA/HA composites

These interesting shape recovery behaviors of PDLLA/HA composites at different composite ratios were investigated. In this paper, we presented a typical example with very interesting shape recovery behavior. PDLLA/HA composites at a weight ratio of 7:3 were made of seven alphabets with dimensions of 25  $\times$  3  $\times$  2 mm ( $l \times w \times t$ ), as “s”, “c”, “i”, “e”, “n”, “c”, “e” by the method described in Section 2.2. These samples were heated to 68 °C over the  $T_g$  of PDLLA. After 3 min, these letters were all pulled into straight shape, and moved to a refrigerator for freezing stress and fixing deformed shape for 5 min. Then all the samples were placed in an oven at 70 °C, and the phenomena that these recovered to the original shapes could be observed clearly (shown in Fig. 4).

As described above, PDLLA/HA composites with weight ratios of 1:1, 1.5:1, 1.8:1, 2:1, 2.5:1, 3:1, 3.5:1, 4:1 were made of a series of samples with dimensions of 5  $\times$  15 mm, and thickness 0.5, 1, 2, and 3 mm, respectively. All these samples were deformed at 68 °C, and recovered at 70 °C; the effects of the composite ratios, sample thickness, and recovery temperature on shape memory recovery ratio and recovery time were investigated.

## 3. Results and discussion

### 3.1. Characteristic analysis

Fig. 1 shows SEM images of the microstructure of PDLLA/HA composites at a weight ratio of 1:1, 2:1, 7:3, 3:1, 4:1. It was evident that these u-HA particles were uniformly distributed in the PDLLA matrix. From Figs. 1b–e, we can see that some HA particles existed in the polymer matrix. The phenomenon suggests that the interface of PDLLA and HA phase has a close contact.

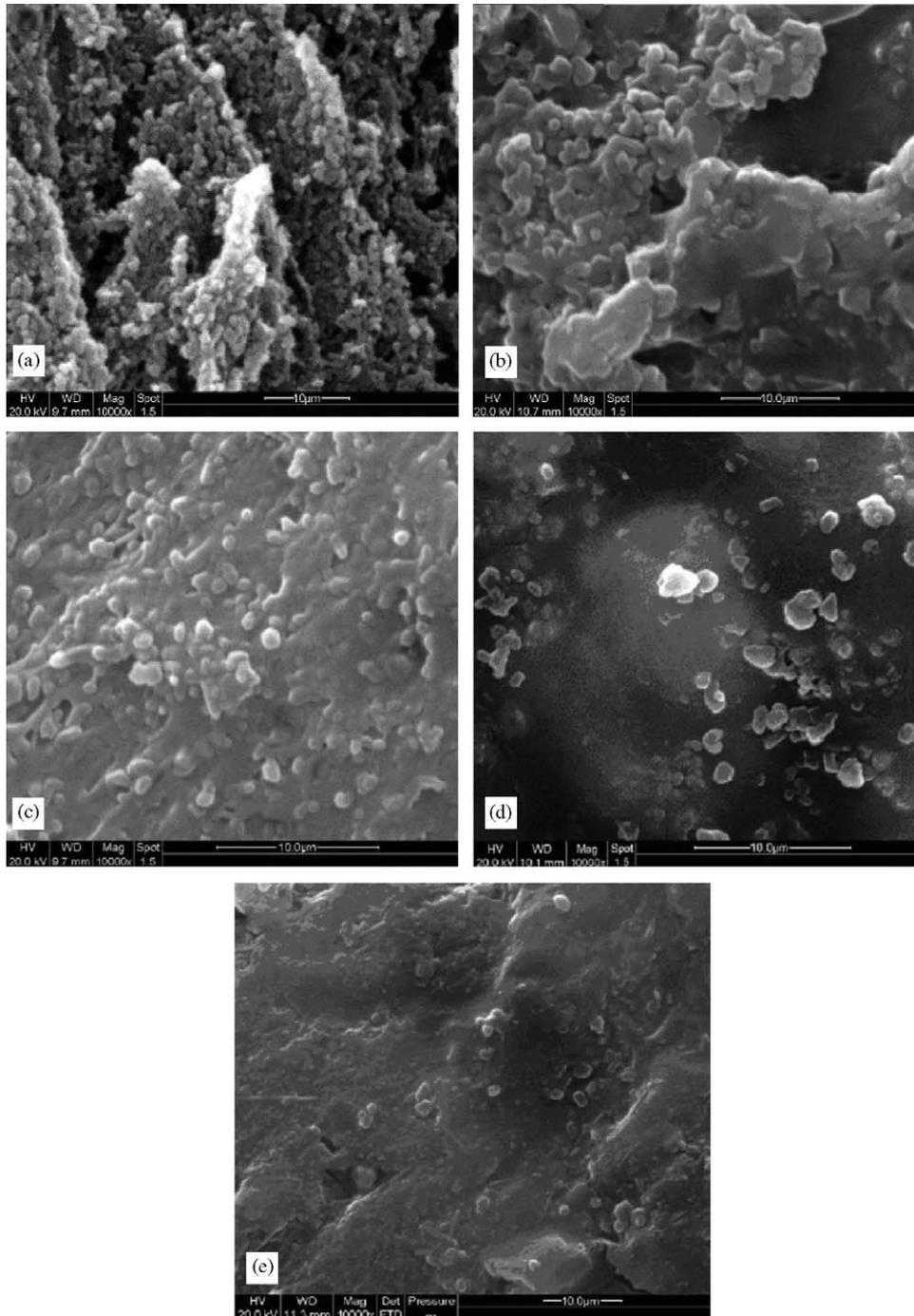


Fig. 1. SEM micrographs for PDLLA/HA composites at a (a) 1:1, (b) 2:1, (c) 7:3, (d) 3:1, (e) 4:1 weight ratio.

The interface also contributes to formation of two phases of SMPs [36]. These SEM photos indicate that the selected solvent and synthetic technique should be an effective approach to prepare PDLLA/HA composites, which may be applied for biomedical engineering.

The DSC thermogram curves of pure PDLLA and PDLLA/HA composites are shown in Fig. 2.  $T_g$  of pure PDLLA and PDLLA/HA composites at a weight ratio of 3:1, 7:3, 2:1, 1:1 were 53.7, 55.6, 56.8, 57.2, 59.0 °C, respectively.  $T_g$  peaks is mainly influenced by the endothermic energy for phase transition of amorphous

PDLLA, because the HA phase in the testing temperature range is stable. Transition peak temperature slightly increased with the addition of HA. The reason may be two facts as follows; on the one hand, there existed interfacial interaction of PDLLA and HA as shown in Fig. 1. On the other hand, the micro-Brownian thermal motions of molecular chain segments of PDLLA were constrained by HA particles. Evidently Fig. 1a shows that surfaces of PDLLA microstructure were completely covered by HA particles. In conclusion, HA particles play a very important role in these changes of  $T_g$  [37,38].

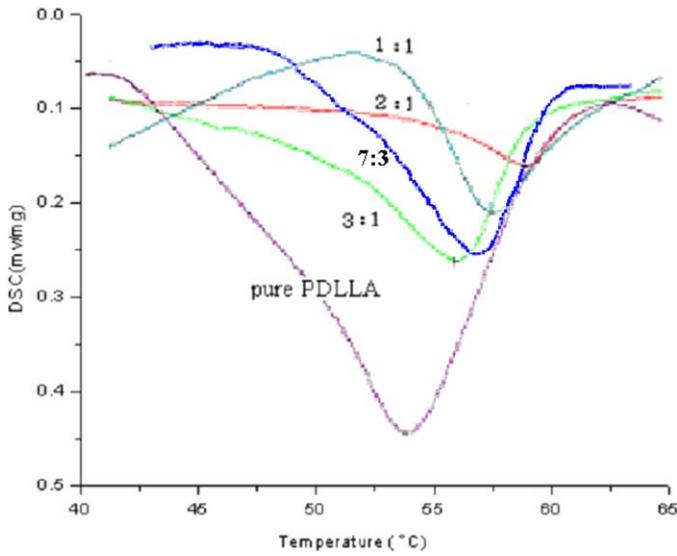


Fig. 2. DSC thermograms of pure PDLA and PDLA/HA composites at a weight ratio of 1:1, 2:1, 7:3, and 3:1.

Fig. 3 shows the changes of storage modulus ( $E'$ ) and loss factors ( $\tan \delta$ ) in pure PDLA and PDLA/HA composites on heating from the DMA testing. All the specimens had a transition temperature range where  $E'$  suddenly decreased and  $\tan \delta$  sharply changed with the increasing temperature. Either the peak of modulus curve or the peak of the  $\tan \delta$  curve is often employed to define the  $T_g$  [39,40]. Here the peak of the  $\tan \delta$  vs. temperature curve is defined as  $T_g$ . Fig. 3b shows that the  $T_g$  of pure PDLA and PDLA/HA composites at a weight ratio of 3:1, 7:3, 2:1, 1:1 were 52.8, 55.2, 56.7, 57, 59.3 °C, respectively. The result of  $T_g$  increasing with addition of HA particles accorded with that of DSC testing.

Fig. 3a shows that the storage modulus of the specimens is almost constant at a temperature of the glassy state and rubbery state. For example, the  $T_g$  for the PDLA/HA composite at a weight ratio of 3:1 is 52.8 °C. The storage modulus is almost constant below 22.8 °C ( $T_g - 30$  °C) and above 82.8 °C ( $T_g + 30$  °C). Moreover, the storage modulus at 22.8 °C ( $E' = 3220$  MPa) is about two orders of magnitude larger than that at 82.8 °C ( $E' = 29.6$  MPa). In the same way, PDLA/HA composite at a weight ratio of 7:3, 2:1, 1:1 can also be deduced with the similar result in Fig. 3a. In addition, a large glassy state modulus would lead to large shape fixity upon cooling, and a large rubbery state modulus would lead to large shape recovery upon heating. Hence, the above-mentioned properties are highly desirable for shape memory materials [40,41]. Consequently, Fig. 3 suggests that the PDLA/HA composites have shape memory effects.

### 3.2. Shape memory properties

From the above discussion, in the paper, the temperature 68.0 °C as shape memory deformed temperature and 70.0 °C as recovered temperature were chosen based on

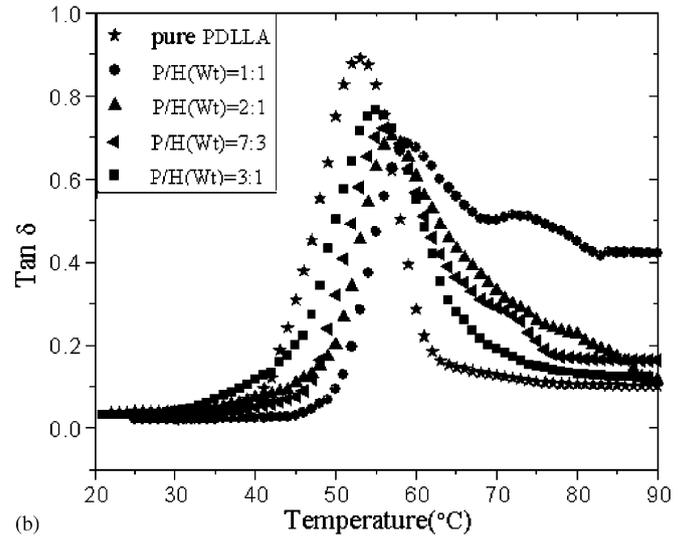
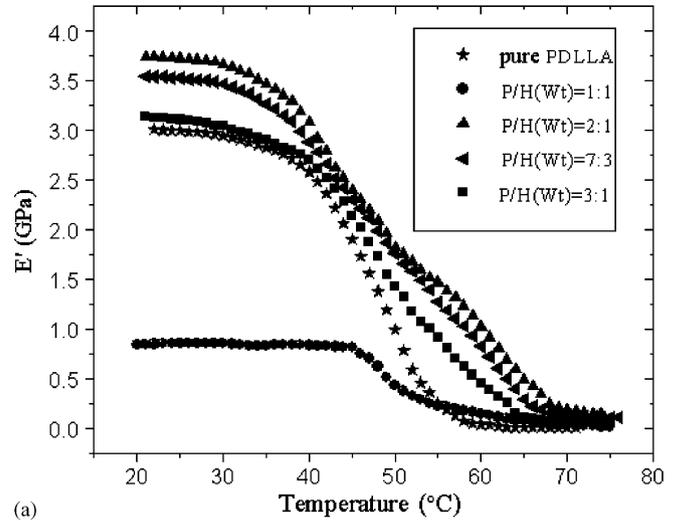


Fig. 3. Storage modulus  $E'$  and loss factor  $\tan \delta$  vs. temperature of pure PDLA and PDLA/HA composites measured by DMA.

the  $T_g$  of PLA during studying shape memory effect of the composites [33,42]. As a result, these PDLA/HA composites at different composite ratios showed desirable shape recovery effect; their recovery ratios were all above 95.0%. We illustrated a typical PDLA/HA composite at a weight ratio of 7:3 with very interesting shape recovery behavior. As shown in Fig. 4, the initial shape came from the seven letters of “science” word were made of PDLA/HA composites. The photos for the full process of shape memory recovery were taken at different times. When the deformed poles were heated at 70.0 °C again, these started to recover shape immediately. The deformed samples looked like their original shape at 60th second, and recovered basically to “science” word at 100th second. The results indicated that PDLA/HA composite had well shape memory effect. The reason is that when amorphous PDLA polymer and crystalline calcium phosphate particles were compounded, the stationary phase and reversible phase would come into being [36], which were

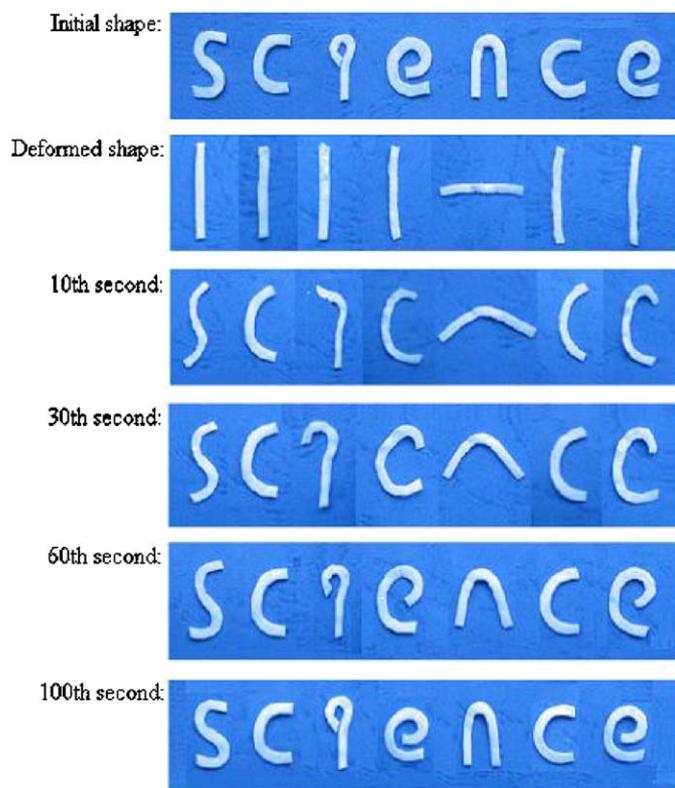


Fig. 4. The photos showing the process of shape memory recovery of “science” word made of PDLLA /HA composite taken with digital camera.

a necessary condition to form shape memory effect. Fig. 1 also strongly supported the theory.

The results of shape memory effects shown in Fig. 4 are in good agreement with the suggestion that PDLLA/HA composites have shape memory effects shown in Fig. 3.

In the paper, shape recovery ratios of the composites were tested and calculated according to a previous report [41] in order to further compare PDLLA/HA composites and PDLLA polymer. The shape recovery ratios of all the above composites are more than 95%, whereas PDLLA polymer has a low shape recovery ratio of 80.6%. Thus, shape memory effect of the biodegradable PLA can be improved by compounding with HA particles. At the same time, the biodegradable PLA polymer can also be prepared into all kinds of shapes based on our need. The desirable shape recovery effect of composites indicates that these are potential for applications of biomaterials.

In order to further evaluate shape memory behaviors of the composites, we investigate the effects of composite ratios and sample thickness on shape memory recovery ratio. Fig. 5 shows the changes of the shape recovery ratios of PDLLA/HA composites with different weight ratios and different shape thicknesses. These original samples are all bars with dimensions of 10 (length) × 4 mm (width) and different thicknesses, and deformed shape is folded to 180° shape. The final shape recovery ratio ( $R$ ) was calculated by the following formula:

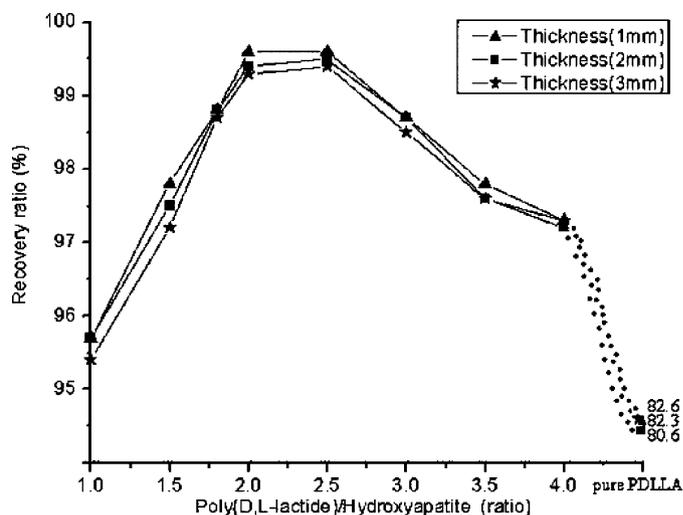


Fig. 5. The effect of composite ratios and samples thickness of PDLLA/HA composites on shape recovery ratios.

$$R = \frac{180^\circ - \text{final angle}}{180^\circ} \times 100\%.$$

The shape recovery ratios for all composites are over 95%, whereas pure PDLLA samples with thicknesses of 1, 2, and 3 mm have recovery ratios of around 80%. From Fig. 5, effect of composites ratios on shape recovery ratios of PDLLA/HA composites can be discussed through the same thickness samples. For example, at the thickness of 2 mm, the recovery ratio increases from 95.7% to 99.4% with the increase of composite ratio from 1:1 to 2:1, whereas the recovery ratio decreases from 99.5% to 97.2% with the increase of composite ratio from 2.5:1 to 4:1. PDLLA/HA composite at thicknesses of 1 and 3 mm also has the same regularity. An interesting phenomenon is shown that the shape recovery ratios of all composites reach a peak value of 99.6% when the composites ratios increase from 2.0 to 2.5. Once the composite ratios exceed 2.5, all recovery ratios decrease with the increase of composite ratios. The thickness of these samples has a little effect on shape recovery ratio. The smaller the thickness of the samples with same composite ratios, the bigger the shape recovery ratio.

Fig. 3b shows that the  $\tan \delta$  decreased with addition of HA particles, because HA particles as stationary phase constrained random motions of molecular chain segments of amorphous PDLLA. The lower the  $\tan \delta$  of composites, the better the shape memory effect. However, the  $E'$  of PDLLA/HA composite at a weight ratio of 1:1 is lower than of those at other weight ratios. So the composite is less desirable for shape memory effect [41]. As a result, the shape recovery ratios of composites at a weight ratio from 2.0 to 2.5 are higher than those of above 2.5 and below 2.0. The  $E'$  of amorphous PDLLA polymer in rubbery state is very low, shown in Fig. 3a. Thus pure PDLLA polymer is also not a desirable shape memory material.

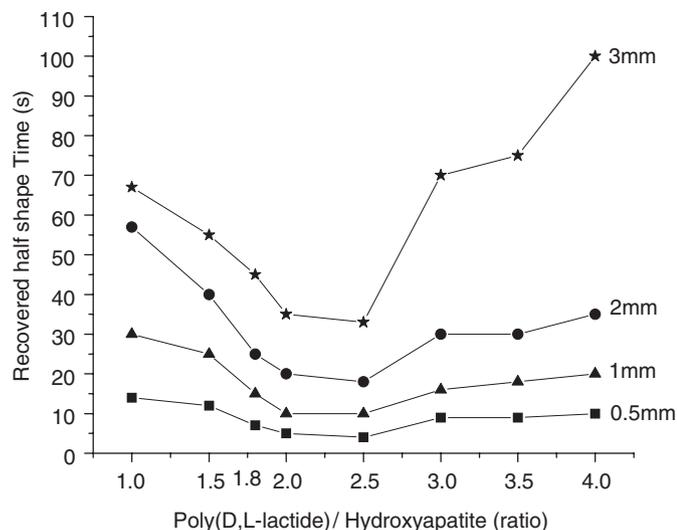


Fig. 6. The effect of composite ratios and samples thickness of PDLLA/HA on half shape recovery time.

Fig. 6 shows the effect of composite ratios and samples thickness of PDLLA/HA on half shape recovery time. The original shapes are films with dimensions of 10 (length)  $\times$  4 mm (width) and different thicknesses, and deformed shape is folded. The time that the folded shape requires to recover from the angle 180° to 90° is defined as recovery half shape time. As seen from Fig. 6, the smaller the thickness of the samples with same composite ratios, the shorter the recovery half shape time. With increase of composite ratios in the initial stage, the recovery half shape time takes a downtrend. For example, at the thickness of 1 mm, the recovery time decreases from 30 to 10 s with the increase of composite ratio from 1:1 to 2:1, whereas the recovery time increases from 10 to 20 s with the increase of composite ratio from 2.5:1 to 4:1. PDLLA/HA composite at a thickness of 2 and 3 mm has the same regularity too. When the composite ratios are in range between 2.0 and 2.5, the time is the shortest. Once the composite ratios are below 2.0 and above 2.5, the time takes an uptrend again.

Fig. 7 shows the effect of composite ratios and samples thickness of PDLLA/HA on final shape recovery time. The original shapes are also films with dimensions of 10 (length)  $\times$  4 mm (width) and different thicknesses, and deformed shape is folded. The whole shape recovery time is the time that the deformed shape requires to recover to the final shape, i.e. from the angle 180° to final angle approaching 0°. The result shown in Fig. 7 corresponds to Fig. 6. It can be seen that the final recovery time of composite at a composite ratio of 2.0 or 2.5 is shorter than that of composite at other composite ratios.

From the foregoing statement, we know that DMA testing can demonstrate the PDLLA/HA composites have desirable shape memory effect. In addition, the theory reasons that the PDLLA/HA composite has shape recovery behaviors may also be found from viscosity–elasticity dynamics [16,43]. If a material has shape memory property, it must include reversible phase and stationary phase. In our

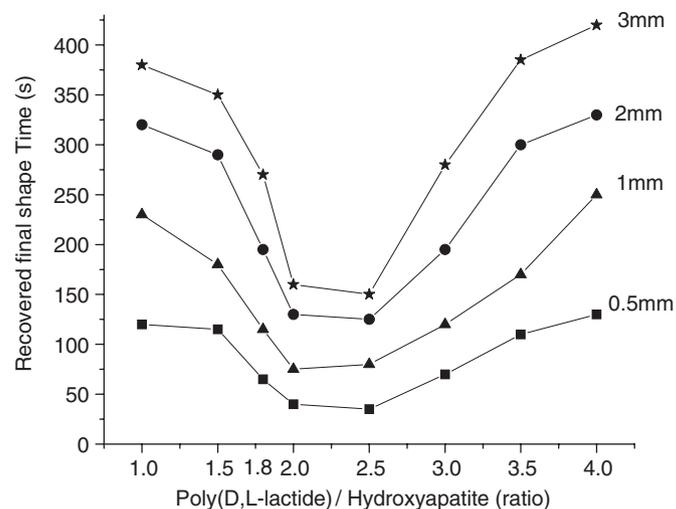


Fig. 7. The effect of composite ratios and samples thickness of PDLLA/HA on final shape recovery time.

experiment, the amorphous PDLLA polymer in the composite material was selected as reversible phase and crystal HA particles were selected as stationary phase. At a definite temperature above  $T_g$  of polymer, the reversible phase brings deformation in stress, but the stationary phase fixes the strain in order not to bring irreversible changes. Polymer brings strain ( $\epsilon_t$ ) in exerted stress at high temperature, which is divided into several parts, including the elastic deformation ( $\epsilon_1$ ) in glassy state, the high elastic deformation ( $\epsilon_2$ ) in the rubbery state, the viscoelastic deformation ( $\epsilon_3$ ) in viscous flow state.  $\epsilon_t (= \epsilon_1 + \epsilon_2 + \epsilon_3)$  is frozen after the material is cooled. When the material is heated again over  $T_g$ , it should recover completely, but in practice it recovers the original shape mostly because  $\epsilon_3$  is irreversible strain for amorphous polymer. So it needs stationary phase to prevent deformation from bringing  $\epsilon_3$ .

We can also analyze the result from molecular mechanism of polymer according to a previous report [44]. The flexibility of the chain segments of polymer should be a function of the temperature. The thermal transition ( $T_{trans}$ ) of the chains is in the temperature range of interest for the particular application. At temperatures above  $T_{trans}$ , the chain segments are flexible, whereas the flexibility of the chains below this thermal transition is at least partly limited. In the case of a transition from the rubber-elastic or viscous state to the glassy state, the flexibility of the entire segment is limited.

Therefore, the results of Figs. 6 and 7 are that the shape recovery requires more time because of few HA particles as stationary phase in composites and it also requires more time due to too many HA particles resulting in a resistance for movement of polymer chain. When HA particles are too few, amorphous PDLLA polymer brings more irreversible strain ( $\epsilon_3$ ). If HA particles are too many, the movements of chain segments of amorphous PDLLA polymer are greatly restricted during shape recovery.

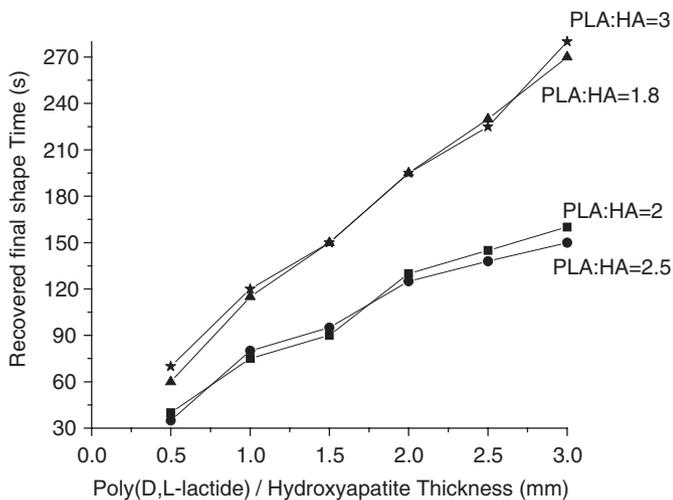


Fig. 8. The effect of samples thickness of PDLA/HA on recovery final shape time.

Fig. 8 shows that final shape recovery time is almost linear increase relation with increase of thickness of composites. The reason was also that the movements of polymer chains influenced shape recovery time of materials directly. The frozen strain can be released only when strong molecular interaction has disappeared after subsequent heating to a high temperature. The driving force for the strain release is micro-Brownian thermal motion, which becomes increasingly important at higher temperature [45]. Based on the thermodynamic concepts of molecular internal energy, the thicker the sample, the more the energy required to get rid of molecular interactions. Thus the thicker composites require more time.

It can be seen that the shape recovery time was influenced by thickness of composites shown in Figs. 6–8. In practice, an optimum composite ought to consider not only time parameter but also other factors. For example, a shape memory bone pin made of u-HA/PDLA composite was used in a rabbit thigh bone [33]. The diameter and composite weight ratio of u-HA/PDLA composite was 2.0 mm and 1:1, respectively. However, Fig. 7 shows that the final recovery time of composite at a thickness of 2.0 mm and a weight ratio of 1:1 was beyond 60 s. According to Fig. 7, such composite is not desirable, considering the recovery time. The example [33] considered not only recovery time of material but also the effect of amount of biocompatible and osteoconductive HA in bone. On the other hand, the size (thickness, length, and width) of medical device required in clinical use was determined by size of wound. Of course, in practical application, an optimum composite obtained may consider many complicated factors. In this paper, the results from Figs. 6–8 can give a valuable reference on composite ratio and thickness parameters for study on their medical application.

Fig. 9 shows the effect of recovery temperature on the recovery time of PDLA/HA composites. Compared with

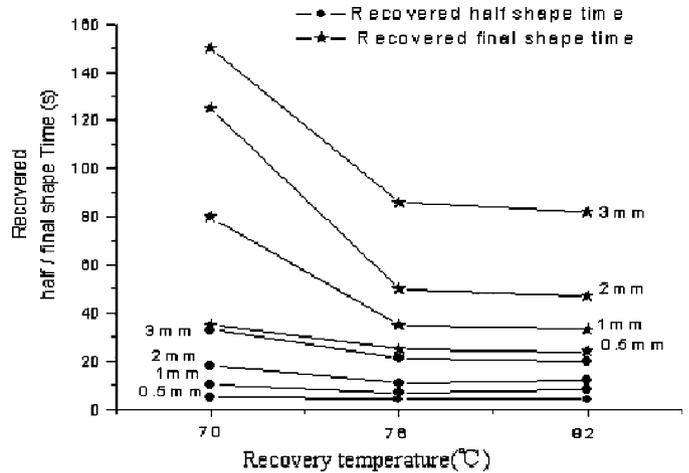


Fig. 9. Recovery time of different recovery temperatures of poly(D,L-lactide)/hydroxyapatite composites. Weight ratio: 2.5; thickness: 0.5, 1, 2, 3 mm.

Fig. 3a, we found that when recovery temperature ranged from 70 to 76 °C, the  $E'$  of PDLA/HA composite still changed and tended to a stable value. From the onset of 76 °C on recovery temperature, the recovery time little decreased. The reason may be that the  $E'$  of composites is almost constant in rubbery state from the onset of a definite temperature. Thus the shape memory forces upon heating are constrained by rubbery state modulus.

#### 4. Conclusions

In the paper, we successfully prepared several shape samples with PDLA/HA composites by a simple method. PDLA/HA composites had desirable shape memory effects and amount of HA particles in composites played an important role during the shape memory recovery. The shape recovery ratios of the PDLA/HA composites are the biggest and shape recovery time is the fastest at a composite ratio between 2.0 and 2.5. The composites have these advantages, e.g. excellent shape memory effect, the biodegradation, biocompatibility, easier availability of PDLA, and osteoconductivity of HA, which are potential for application in minimally invasive surgery and bone and tissue repair.

#### Acknowledgements

This work was supported by Project 50303018 supported by National Natural Science Foundation of China and the Cultivation Fund of the Key Scientific and Technical Innovation Project, Ministry of Education of China.

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