Effect of In Vitro Degradation of Poly(D,L-lactide)/β-tricalcium Composite on Its Shape-Memory Properties

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Received 27 June 2007; revised 10 September 2007; accepted 1 October 2007
Published online 27 December 2007 in Wiley InterScience (www.interscience.wiley.com). DOI: 10.1002/jbm.b.31003

Abstract: The in vitro degradation characteristic and shape-memory properties of poly(D,L-lactide) (PDLLA)/β-tricalcium phosphate (β-TCP) composites were investigated because of their wide application in biomedical fields. In this article, PDLLA and crystalline β-TCP were compounded and interesting shape-memory behaviors of the composite were first investigated. Then, in vitro degradation of the PDLLA/β-TCP composites with weight ratios of 1:1, 2:1, and 3:1 was performed in phosphate buffer saline solution (PBS) (154 mM, pH 7.4) at 37°C. The effect of in vitro degradation time for PDLLA/β-TCP composites on shape-memory properties was studied by scanning electron microscopy, differential scanning calorimetry, gel permeation chromatography, X-ray diffraction (XRD), and Fourier transform infrared spectroscopy (FTIR). The changes of structural morphology, glass transition temperature (Tg), molecular weight, and weight loss of composites matrix and pH change of degradation medium indicated that shape-memory effects at different degradation time were nonlinearly influenced because of the breaking down of polymer chain and the formation of degradation products. Furthermore, the results from XRD and FTIR implied that the degradation products, for example, hydroxyapatite (HA), calcium hydrogen phosphate (CaHPO4), and calcium pyrophosphate (Ca2P2O7) phases also had some effects on shape-memory properties during the degradation.

Keywords: β-tricalcium phosphate; poly(D,L-lactide); composite; degradation; shape-memory properties

INTRODUCTION

Shape-memory materials used in biomedical area that may greatly simplify the use of biomaterials in surgical procedures followed by device implantation have obtained increasing attention and development.1–3 Shape-memory polymers (SMPs) can be deformed and fixed into a temporary shape, and recover their predefined original shape when exposed to an external stimulus such as heat, light, magnetism, electricity, etc.4–7 In this decade, SMPs were widely applied in specific medical instruments as high recoverable and conventional materials for minimally invasive surgery;8 delivery system;9 vascular surgery;10 implant devices;11 and intracranial aneurysm surgery.12 Biodegradable, nontoxic, cheap, and easy manufactured SMPs represent potential for biomedical application.13 Thus, thermally induced polyurethane,14,15 poly(e-caprolactone),16,17 and polylactide18,19 have become outstanding shape-memory biomaterials.

Comparing to shape-memory metals and ceramics, SMPs possess their advantages, for example, low density, high recoverable strain. However, a main drawback of SMPs is its lower stiffness.20,21 On the other hand, shape-memory mechanism of polymers is very different with metals and ceramics, modulus of polymers exhibit a reduction with rising temperature, which limits the recoverable stress levels under constraint.22 So, it is necessary that some fibers and particles are added into polymer matrix in order to reinforce stiffness and other properties of SMPs. For example, magnetite filled SMPs in order to an appropriate heat was generated by power losses in applications with magnetic particles;23 carbon nanopowder filled SMPs that showed better mechanical and thermal properties,24 and had a typical jump-like growth of the electrical resistance;25 SiC particles filled thermo plastic resin in order to reinforce stiffness of shape-memory composite26; epoxy composition was filled by thermoexpanded graphite with low bulk density and good compactibility.27 However, so far the papers mentioned shape-memory composites including biodegradable polymer and bioactive ceramic are only
PDLLA/HA composites displaying well shape-memory effects.\textsuperscript{28–30} According to above discussion, the study on biodegradation, bioactive, and shape-memory composites is very potential in biomedical application.

It is well known that poly(lactide) (PLA) exists three stereoisomers: poly(\(\varepsilon\)-lactide) (PDLLA), poly(\(\delta\)-lactide) (PLLA), and poly(\(\alpha\)-l-lactide) (PDLLA) because of lactic acid is a chiral molecule. PDLLA possessing well biodegradation and biocompatibility was widely investigated for safe use in long history in drug delivery systems,\textsuperscript{31} orthopedic or dental surgery,\textsuperscript{32} and bone implants.\textsuperscript{33} \(\beta\)-TCP (\(\beta\)-Ca\(_3\)(PO\(_4\))\(_2\)) is another promising candidate for medical application as bio-ceramic for bone substitution, dental repair, and orthopedic surgery,\textsuperscript{34} which represents good osteoconductivity, biodegradability, and bioresorbability.\textsuperscript{35} Moreover, the compounding of PDLLA and \(\beta\)-TCP particles can colligate their own advantages and overcome their shortcomings. The composites are most promising and desirable biomaterials applied in tissue engineering,\textsuperscript{36} and have been used clinically in various forms.\textsuperscript{37,38}

Currently the studies on biodegradation of PDLLA/\(\beta\)-TCP composites mainly focus on tissue or cell responses to materials \textit{in vitro} or \textit{vivo} and pH-stability of composites \textit{in vitro} degradation.\textsuperscript{39,40} However, the interaction mechanism between polymer matrix and inorganic particles during \textit{in vitro} degradation of composites was not systematically cared. In addition, to the best our knowledge, few literatures reported the shape-memory behaviors of PDLLA/\(\beta\)-TCP composite, especially the effect of \textit{in vitro} degradation time on shape-memory properties of the composite matrix. Therefore, in the paper, PDLLA/\(\beta\)-TCP composites with different weight ratios were prepared and their shape-memory behaviors were mainly investigated under different degradation time. During \textit{in vitro} degradation, the dispersed morphology, \(T_g\), and molecular weight of composites were examined by SEM, DSC, and GPC, respectively. Furthermore, the new crystalline phases formed during \textit{in vitro} degradation and their effects on shape-recovery properties of composites were analyzed and discussed by XRD and FTIR.

**Preparation of PDLLA/\(\beta\)-TCP and Pure PDLLA Samples**

The premolded press PDLLA/\(\beta\)-TCP composites were prepared at weight ratios of 1:1, 2:1, and 3:1 as our previous report.\textsuperscript{29} In the final step, these completely dried composites were press-molded at 85°C for 10 min in a mold which was designed to a film shape, and the press was performed in the range 10–15 MPa. As a result, we could obtain specimens with a film shape at weight ratios of 1:1, 2:1, and 3:1. Similarly, pure PDLLA was firstly dissolved in CHCl\(_2\) under stirring. Then, the completely dried polymers under vacuum were press-molded at 65°C for 5 min and in the pressing range of 10–15 MPa.

**In Vitro Degradation of Pure PDLLA and PDLLA/\(\beta\)-TCP Composites**

Pre-weighed pure PDLLA and PDLLA/\(\beta\)-TCP composites with dimensions of \(8 \times 4 \times 1\) mm\(^3\) \((l \times w \times t)\) at a weight range of 0.15–0.16 g were placed in individual test tubes containing 15.0 mL of phosphate buffer saline solution (PBS, pH = 7.4). These tubes were kept in a thermostated shaking water-bath that was maintained at 37°C and 100 cycles/min. At predetermined intervals, the specimens were removed from degradation medium and rinsed with distilled water to remove residual buffer salts, finally dried in vacuum.

**Shape-Memory Effects on PDLLA/\(\beta\)-TCP Composites**

According to previous reports, PDLLA/calcium phosphate composites had good shape-memory effects.\textsuperscript{28–30} Therefore, it is necessary that the interesting shape-recovery behaviors of PDLLA/\(\beta\)-TCP composites after \textit{in vitro} degradation are evaluated. In this article, at predefined degradation time, the remnant pure PDLLA and PDLLA/\(\beta\)-TCP composites with weight ratios of 1:1, 2:1, and 3:1 at days of 0, 3, 21, and 56 were fold-deformed after the samples became soft at 60°C. Then they were moved to a refrigerator for freezing stress and fixing deformed shape for 5 min, and reheated at 62°C. The fold-deformed samples would recover to the original shapes, as fold-deformed test of the previous report.\textsuperscript{29} The shape-recovery ratios \((R)\) of the samples with about dimensions of \(7.8–8 \times 4 \times 1\) mm\(^3\) \((l \times w \times t)\) at predetermined degradation intervals were investigated. The final shape-recovery ratio \((R)\) of every sample was calculated by the following formula:

\[
R = \frac{180° - \text{final angle}}{180°} \times 100%.
\]

**Estimation of In Vitro Degradation**

pH value of PBS (initial pH 7.4), in which the \textit{in vitro} degradation was performed, was carried out with a model PHS-3B pH meter (Shanghai Scientific Instrument, China) equipped with a combined glass electrode. Mass loss was
determined gravimetrically by comparing the dry weight remaining at a specific time with the initial weight. Quantitative calculation was according to the following equation:

\[ \text{Percentage weight loss (\%) } = \frac{(W_o - W_t)}{W_o} \times 100 \, , \]

where \( W_o \) and \( W_t \) are weights of samples before and after degradation, respectively.

\textbf{Analytical Methods}

Waters2695/2414 Gel Permeation Chromatography (GPC, Waters, America) was used to examine the molecular weight of polymers in composites. GPC analysis of the samples was carried out at a flow rate of 1 mL/min and at 25°C using tetrahydrofuran (THF) as the eluting solvent. Monodisperse polystyrene standards were selected for calibration. Concentrations of all samples dissolved in THF were ~0.5% mg/mL.

The surface morphology of dried remnants was observed using a Quanta200 scanning electron microscope (SEM, FEI, America). Pieces of the specimens were cut in two parts, and then insides of samples were mounted and coated with gold. The accelerating voltage and magnification was 20 keV and \( \times 6000 \), respectively.

The \( T_g \) of pure PDLLA and PDLLA/\( \beta \)-TCP composites at predetermined degradation time was examined by STA 449C differential scanning calorimetry (DSC, NETZSCH, Germany). The specimens were heated from 5 to 90°C at a rate of 5°C/min in flowing nitrogen gas. Weights of all samples were from 5 to 10 mg.

Crystalline phases of composites before and after degradation were identified and compared by XL-30 X-ray diffraction (XRD, Philips X’ Pert Pro, Netherlands). The diffractometer with Cu Kα radiation (\( \lambda = 1.5406 \) Å) from the copper anode source was employed at 40 kV and 40 mA at diffraction angles (2θ) between 5 and 80° performing a step size of 0.03° 2θ/s.

Nicolet 5700 Fourier transform infrared spectroscopy (FTIR, Thermo Electron, America) was performed to analyze the new emerged functional groups in PDLLA/\( \beta \)-TCP composites after \textit{in vitro} degradation comparing with spectra before degradation. All specimens were made into little powders and mixed with KBr grains at a weight ratio of 0.5–1%. Pure KBr was used as IR spectral reference and each sample was recorded from 4000 to 400 cm\(^{-1}\) by 64 scans.

\textbf{RESULTS}

\textbf{Shape-Memory Behaviors Before and After Degradation}

For investigating shape-memory properties of pure PDLLA and PDLLA/\( \beta \)-TCP composites before and after degradation, we tested shape-recovery behaviors of composites with same shapes and different compounded ratios by fold-deformed methods. Figure 1 shows the process of shape recovery of pure PDLLA and PDLLA/\( \beta \)-TCP composite with a weight ratio of 1:1, 2:1, and 3:1 at days of 0, 3, 21, and 56. As a consequence, pure PDLLA and PDLLA/\( \beta \)-TCP composites displayed very different shape-memory effects at different degradation time. It can be seen from the set of recovery photos that the deformed shapes of samples were performed by an exterior pulling stress at 60°C, and the new temporary shapes were cooled at a low temperature. When the samples were reheated in the above deformed state, the temporary shapes would recover to a constant final shapes approaching approximately to original shapes, as seen in Figure 1. Moreover, it can be noted that the shape-recovery effects of pure PDLLA was not as good as that of PDLLA/\( \beta \)-TCP composites after same degradation time. Figure 1(a) shows the shape-recovery behaviors of pure PDLLA and PDLLA/\( \beta \)-TCP composites before degradation, and they displayed desirable shape-memory effects comparing with the samples after degradation. The recovery behaviors of the samples became undesirable with increase of degradation time, as seen in Figure 1(b–d).

\textbf{Quantitative Evaluation to the Shape-Memory Effect of the Composites}

Both PDLLA and \( \beta \)-TCP are widely investigated as bio-degradable and bioresorbable materials for medical application.\textsuperscript{33,34} Moreover, PDLLA/\( \beta \)-TCP composites possess the special properties, that is, the shape-memory effects. Therefore, the study on the \( R_s \) of composites during degradation in PBS was interesting and vital for clinical application. To quantitatively evaluate the shape memory effect of the materials after degradation, the result of \( R_s \) of pure PDLLA and the three composites at days of 0, 1, 3, 5, 7, 10, 14, 21, 28, 42, and 56 was showed in Figure 2. At the last degradation time, \( R_s \) of PDLLA/\( \beta \)-TCP composites with weight ratios of 1:1, 2:1, and 3:1 are from original 97.8%, 98.3%, and 96.9% to final 56.3%, 66.7%, and 63%, respectively. Moreover, \( R_s \) of pure PDLLA decreases from 77% to only 36.2%. The calculated results show that \( R_s \) of pure PDLLA and PDLLA/\( \beta \)-TCP composites decrease with the increase of \textit{in vitro} degradation time in PBS, namely the shape-memory properties of pure PDLLA and PDLLA/\( \beta \)-TCP composites become undesirable with the increase of \textit{in vitro} degradation time. Furthermore, the \( R_s \) of composites are always higher than that of pure PDLLA at the same degradation time, and shape-recovery ratios of the composites decreased slowly with addition the \( \beta \)-TCP particles. The reason that PDLLA/\( \beta \)-TCP composites have better shape-memory properties than pure PDLLA can be explained that the shape fixity of amorphous PDLLA polymer depends on a random winding of molecular chains due to no adequate two separated phases, namely stationary phase and reversible phase.\textsuperscript{28} Which were necessary for desirable shape-memory properties of materials. And shape-memory effect of the pure PDLLA can be improved by compounding with calcium phosphate particles, because the
inorganic particles dispersed in polymer matrix constrained the irreversible motion of molecular chains of PDLLA polymer, thus the more stationary phase came into being. In addition, it should be noticed that \( R_s \) of all composites at 21st day of degradation slightly increase when comparing with the last \( R_s \). The reason may be relevant to destroy of the molecular chains of polymer and change of the crystal phases of inorganic particles in PDLLA/\( \beta \)-TCP composites during degradation process.

**Weight Loss and pH Change**

The above result showed that the degradation time had a great effect on shape-memory properties of the composites. So it was necessary that the degradation behavior was investigated by measuring the mass loss of the composites and pH change of the medium in PBS at 37°C. Figure 3 shows the rate of weight loss and pH change of PBS medium of pure PDLLA and PDLLA/\( \beta \)-TCP composites with weight ratios of 1:1, 2:1, and 3:1 for in vitro degradation over 56 days. The percentage weight loss of materials was calculated by the formula as mentioned above and shown in Figure 3(a). It can be seen that weight loss of all specimens increases slowly with increase of in vitro degradation time. The rate of weight loss of all samples is slight at a range of 14–21 days. Weight loss of pure PDLLA and PDLLA/\( \beta \)-TCP composites with weight ratios of 1:1, 2:1, and 3:1 at 56th day is 7.82%, 5.48%, 6.03%, and 6.41%, respectively. The reason may be attributed to the diffusion of the degradation products resulted from PDLLA and the gradual dissolution of the part \( \beta \)-TCP particles into PBS medium.43

The changes of pH values of PBS medium for all samples are shown in Figure 3(b). The result almost corresponds with Figure 2. It shows that all pH values almost reduce with the increase of degradation time. It can be seen clearly that the rates of pH reduction for composites are lower than that of pure PDLLA. The rate of pH reduction increases with the decrease of \( \beta \)-TCP particles in polymer matrix. However, there is an obvious difference in pH values of PBS medium between pure PDLLA and composites. The pH values for all composites had a sudden rise within original 1 day, and especially the pH value for PDLLA/\( \beta \)-TCP composite with the weight ratio of 1:1 reached 7.55. It can be considered that \( \beta \)-TCP is alkaline, and the alkaline material diffuses into PBS medium resulting in the rise of pH.44,40 In the following period, the acid product from PDLLA degradation can be neutralized by the alkaline material from \( \beta \)-TCP, which can make the pH of PBS be effectively compensated,45 and further depress the degradation of polymer. On the other hand, it is also important for the stabilization of pH in the physiological range due to the existence of enough ceramic material.43

**GPC Analysis**

The \( M_w \) of the remaining polymer was examined by GPC method, which can be used to further characterize polymer degradation. Figure 4 shows that \( M_w \) in the pure PDLLA...
and PDLLA/β-TCP composites was from original 100K Da to 30–40K Da at beginning in vitro degradation because of the decomposition of PDLLA during the thermo mold-press process. With increase of degradation time, all $M_w$ of the remaining PDLLA decreased, especially $M_w$ in pure PDLLA reduced most quickly from 30.5K Da at beginning to 9.2K Da after 56 days degradation. Moreover, reduction of $M_w$ in PDLLA/β-TCP composite at a weight ratio of 3:1 was fastest among all composites at the same in vitro degradation time.

**Morphology of PDLLA/β-TCP Composites**

Figure 5 shows SEM images of PDLLA/β-TCP composites with weight ratios of 1:1, 2:1, and 3:1 upon high magnification of ×6000. As shown in Figure 5(a–c), it can be observed that although there are a few agglomerations of crystal phases on the surface of PDLLA matrix, the most β-TCP particles are uniformly dispersed in the polymer matrix. Furthermore, we can find that many crystalline particles were exposed from embedded polymer matrix with increasing degradation time because of the molecular chains of polymer were broke down in PBS medium. Figure 5(a1–3, b1–3, and c1–3) evidently suggest that those bigger β-TCP particles in the polymer matrix with three compound ratios gradually disappeared with increase of degradation time. At the same time, size distribution of the remnant crystalline particles became narrow and the agglomerations before degradation also disappeared. As a consequence, Figure 5(a3, b3, and c3) shows that the average size and size distribution of β-TCP particles after 56 days are 450 nm and in the range of 150–1000 nm, respectively.

**$T_g$ of PDLLA/β-TCP Composites**

The DSC heating curves of pure PDLLA and PDLLA/β-TCP composites with weight ratios of 1:1, 2:1, and 3:1 before and after degradation are exhibited in Figure 6. The endothermic peaks of remnant composites after in vitro degradation attribute to the amorphous PDLLA. As seen from Figure 6, it is evident that $T_g$ of the pure PDLLA and composites decreased with the increasing degradation time. For example, after 56 d $T_g$ of the pure PDLLA and composites with the weight ratios of 1:1, 2:1, 3:1 are 38.2°C, 41.2°C, 42.2°C, 42.9°C, respectively. Moreover, the $T_g$ of composites decreased with the addition of β-TCP concentration in matrix at the same degradation time.

**XRD Analysis on Shape-Memory Effects**

In order to know what relationship between shape-memory effects and in vitro degradation, the XRD patterns for the change of crystalline phases in composites before and after degradation are presented in Figure 7. It is evident that the three intense peaks of crystalline β-TCP in PDLLA/β-TCP before and after degradation are exhibited in Figure 6. The endothermic peaks of remnant composites after in vitro degradation attribute to the amorphous PDLLA. As seen from Figure 6, it is evident that $T_g$ of the pure PDLLA and composites decreased with the increasing degradation time. For example, after 56 d $T_g$ of the pure PDLLA and composites with the weight ratios of 1:1, 2:1, 3:1 are 38.2°C, 41.2°C, 42.2°C, 42.9°C, respectively. Moreover, the $T_g$ of composites decreased with the addition of β-TCP concentration in matrix at the same degradation time.

![Figure 3: (a) Weight loss and (b) pH change of PBS medium of pure PDLLA and PDLLA/β-TCP composites at weight ratios of 1:1, 2:1, and 3:1 incubated in PBS at 37°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

![Figure 4: $M_w$ change of pure PDLLA and PDLLA/β-TCP composites at weight ratios of 1:1, 2:1, and 3:1 incubated in PBS at 37°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]](image-url)
composites with weight ratios of 1:1, 2:1, 3:1 at days of 0, 3, 21, and 56 can be found at around 27.9°, 31.1°, and 34.4° 2θ, which are assigned to (214), (0210), and (220), respectively. It indicated that crystalline phase of β-TCP always existed in composites during in vitro degradation. However, it should be noted that after 3 days there were several new crystal peaks appeared at about 2θ = 26.6°, 27.8°, 28.7°, and 31.7° corresponding to the (200) of CaHPO₄, (012) and (022) of Ca₃P₂O₇, and (211) of HA phases, respectively.⁴⁶,⁴⁷ The result indicated that the crystalline phases of CaHPO₄, Ca₃P₂O₇, and HA should come into being during in vitro degradation, which may belong to phase transformation of degradable crystalline β-TCP in composites.

Figure 5. SEM micrographs for PDLLA/β-TCP composites at weight ratios of (a) 1:1, (b) 2:1, and (c) 3:1 incubated in PBS at 37°C.
Figure 6. DSC thermograms of (a) pure PDLLA and PDLLA/β-TCP composites at weight ratios of (b) 1:1, (c) 2:1, and (d) 3:1 incubated in PBS at 37°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figure 7. XRD patterns of PDLLA/β-TCP composites at weight ratios of (a) 1:1, (b) 2:1, and (c) 3:1 incubated in PBS at 37°C. (Note: (□), (●), (+), and (■) represents crystalline phases of β-TCP, HA, Ca₃P₂O₇, and CaHPO₄, respectively.) [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
**FTIR Analysis on Shape-Memory Effects**

From the above discussion, we can almost draw a conclusion that the degradation of PDLLA/β-TCP composites has a great effect on shape-memory effects because of the changes of polymer and crystalline phases in composites. Here, FTIR analysis was further used to investigate why shape-memory behaviors were influenced by the *in vitro* degradation. The IR spectra of PDLLA/β-TCP composites with weight ratios of 1:1, 2:1, and 3:1 at days of 0, 3, 21, and 56 in PBS are presented in Figure 8. From the curves of PDLLA/β-TCP composites at 0 day shown in Figure 8(a–c), it can be observed that the bands at 2997.6 and 2854.7 cm⁻¹ are assigned to the C–H stretching vibrations of CH₃ groups in the side chains and the —CH— groups in the stem chains of PDLLA, respectively. Meanwhile, there is a strong absorption band at 1756.2 cm⁻¹ corresponding to P=O stretching vibrations of PH₃ groups of HA. 30 The broad peaks at about 3494 cm⁻¹ are related to adsorbed H₂O in degradation medium. 49 In addition, the two bands located at about 868 and 706 cm⁻¹ are assigned to the presence of hydrogenophosphate ions (HPO₄²⁻) and pyrophosphates (P₂O₇³⁻), respectively. 50 The bands of crystal water of CaHPO₄·2H₂O also appear at about 1627 cm⁻¹. 51 The new groups indicated emerging at days of 3, 21, and 56. The band at 3651.6 cm⁻¹ is attributed to P—OH vibration bands in PO₄³⁻ groups of HA. 30 The broad peaks at about 3494 cm⁻¹ are related to adsorbed H₂O in degradation medium. 49 In addition, the two bands located at about 868 and 706 cm⁻¹ are assigned to the presence of hydrogenophosphate ions (HPO₄²⁻) and pyrophosphates (P₂O₇³⁻), respectively. 50 The bands of crystal water of CaHPO₄·2H₂O also appear at about 1627 cm⁻¹. 51 The new groups indicated emerging at days of 3, 21, and 56. The band at 3651.6 cm⁻¹ is attributed to P—OH vibration bands in PO₄³⁻ groups of HA. 30

It can be found from Figure 8 that some new absorption peaks emerged at days of 3, 21, and 56. The band at 3651.6 cm⁻¹ is attributed to P—OH vibration bands in PO₄³⁻ groups of HA. 30 The broad peaks at about 3494 cm⁻¹ are related to adsorbed H₂O in degradation medium. 49 In addition, the two bands located at about 868 and 706 cm⁻¹ are assigned to the presence of hydrogenophosphate ions (HPO₄²⁻) and pyrophosphates (P₂O₇³⁻), respectively. 50 The bands of crystal water of CaHPO₄·2H₂O also appear at about 1627 cm⁻¹. 51 The new groups indicated emerging at days of 3, 21, and 56. The band at 3651.6 cm⁻¹ is attributed to P—OH vibration bands in PO₄³⁻ groups of HA. 30

**D I S C U S S I O N**

**Effect of the Characterization Results on Shape-Memory Effects of PDLLA/β-TCP Composites**

**The Weight Loss and pH.** Thermodynamic mechanism of PDLLA/β-TCP composites displaying shape-memory behaviors can be explained that because of entropy elasticity, the deformed shapes cooled their strain are forced back to the pre-deformed permanent shapes in reheating condition. 13, 29 It can be indicated from Figure 1 that PDLLA/β-TCP composites before *in vitro* degradation exhibit desirable shape-memory effects.

The weight loss and pH reduction immediately reflected the structure change of β-TCP and polymer degradation, so that the shape-memory effects based on the random winding of molecular chains of polymer were not well preformed. 29

**The M_w and T_g During Degradation.** Shape-memory effect of the amorphous PDLLA polymer mainly attributes to the stationary phase resulting from the random physical winding of molecular chains. 30 As a consequence of the reduction of M_w of the remnant PDLLA, the pure PDLLA polymer and PDLLA/β-TCP composites would gradually lack the stationary phase resulting from the random physical winding of molecular chains and reversible phase resulting from the linear molecular chains in polymer matrix with increase of degradation time. Moreover, faster the reduction of M_w in the pure PDLLA during degradation, lower is the shape-recovery ratio.

One reason may be that the decrease of M_w of the remaining PDLLA was influenced by the break of molecular chains of polymer during *in vitro* degradation, and further resulted in the decrease of T_g of composites. 31 On the other hand, it can be explained that the molecular chains of polymer were plasticized by inorganic particles in composites, 24, 39 so that T_g of composites decreased quickly with the addition of β-TCP particle. It can also be proved from SEM images shown in Figure 5. In addition, it can be concluded that with the decrease of M_w of remnant polymer after degradation, the entanglement which acts as physical crosslink of the elastic polymer would bring relaxed response. Furthermore, entanglement density of PDLLA polymer in composites after degradation is too low to give the polymer sufficient elasticity, namely shape-memory effect. 31 It was in agreement with the results of GPC analysis shown in Figure 4.

**The XRD of Composites.** In addition, it can be seen from Figure 5 that the polymer matrix of composites was divided into many parts with increasing degradation time. According to discussion above, it can indicate that the phase change of β-TCP particles in polymer matrix may bring an effect on shape-recovery ratios of composites during *in vitro* degradation.

The result of XRD patterns are also agreed with the results that T_g, structural morphology, weight loss, and pH change of composites are related to existence of these new transition particles, as shown in Figures 3–6. Moreover, the random winding of molecular chains of amorphous polymer as stationary phase on shape-memory properties would respond to the change of phases in composites.

**Effect of the New Phases of PDLLA/β-TCP Composites During Degradation on Shape-Memory Effects**

Based on above results and reported literatures, 52 it can be deduced that Ca₃P₂O₇, CaHPO₄, and HA phases were...
formed in PDLLA/β-TCP composites during in vitro degradation via the following reaction formulae:

\[
4\beta\text{-Ca}_3(\text{PO}_4)_2 + \text{H}_2\text{O} \rightarrow \text{Ca}_2\text{P}_2\text{O}_7 + \text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2;
\]

\[
\text{Ca}_2\text{P}_2\text{O}_7 + \text{H}_2\text{O} \rightarrow 2\text{CaHPO}_4.
\]

Thus the existence of several new phases in degradation process could be testified by the two reactions. The big crystalline particles preferred transformation in degradation medium, so the size distribution of β-TCP particles in composites slowly became narrow, as seen in Figure 5. At the same time, the new inorganic phases might play a role on the decrease of \(T_g\) of composites after degradation due to their plasticization on polymer molecules, despite decrease of \(T_g\) of PDLLA/β-TCP composites was mainly influenced by the decrease of \(M_w\) of the remaining PDLLA as described in Figures 4 and 6. As for the slight increase of the shape-recovery ratios of composites with different weight ratios at 21st day degradation as shown in Figure 2, it can be explained that the part degradation of PDLLA in composites increases the random winding of the molecular chains and micro-Brownian thermal motions of molecular chains of polymer were constrained because of the \(\text{Ca}_2\text{P}_2\text{O}_7, \text{CaHPO}_4, H\text{A particles filling in the spaces among polymer chain segments during shape-recovery process. As a consequence, the more stationary phase prevent reversible phase from bringing irreversible strain during inter-transition from glassy state to rubbery state.}\]

However, with the increase of degradation time the shape-recovery effects of the composites became undesirable because of the mass rupture of the molecular chains of PDLLA.
polymer and the dissolution degradation of the inorganic phases in PDLLA/β-TCP composites.

CONCLUSIONS

The shape-memory behaviors and the degradation characteristics of PDLLA/β-TCP composites were investigated. The composites possessed desirable shape-memory effects before degradation, but then shape-recovery ratios of composites reduced with the increasing degradation time. The GPC result suggested that the break of molecular chains of amorphous PDLLA polymer in remnant composites after degradation played an important role on the shape-recovery behaviors. The XRD and IR results showed that the Ca$_2$P$_2$O$_7$, CaHPO$_4$, and HA phases were existed in PDLLA/β-TCP composites. Moreover, the reaction formulae of crystalline phase transformation in vitro degradation were founded based on the above analytical results. The formulae could explain that the change of shape-memory properties of PDLLA/β-TCP composites may partly result from the new inorganic particles during in vitro degradation. It is potential for the investigation on shape-memory properties of biodegradation composites during implantation process. Certainly, it will be necessary to further clarify if the mechanism concerning shape-memory effect of polymeric/inorganic composites, especially during the degradation, there will exist some new components resulted from degradation of polymeric and inorganic compositions.

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