Shape memory effect of poly(D,L-lactide)/Fe₃O₄ nanocomposites by inductive heating of magnetite particles

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1. Introduction

Shape memory materials have received increasing attention for biomedical applications in recent years due to their interesting stimuli-responsive properties [1–3]. Moreover, in this decade, biodegradable, non-toxic, cheap, and easily manufactured shape memory polymers (SMPs) represent additional potential for biomedical devices such as minimally invasive surgery [4], drug delivery systems [5], vascular surgery [6,7], implant devices [8], intracranial aneurysm surgery [9], etc. However, SMPs have disadvantages such as reduced stiffness compared to shape-memory alloys (SMAs) [10]. Therefore, it is necessary to add fibers or particles to the polymer matrix to improve the stiffness and other properties of SMPs. For example, carbon nano-powder has been used to increase Young’s modulus and functional properties [11–13], and thermo-expanded graphite to increase the bulk density and compactability of an epoxy matrix [14]. However, most shape memory composites are thermo-induced materials. Studies of the shape memory effect by inductive heating of magnetic nanoparticles was reported by Mohr et al. [15], and it was shown by Razzaq et al. [16] that heat was generated by power loss in composites with magnetic particles. However, questions remain. For example, the shape memory effect applied in an alternating magnetic field usually requires a high frequency (f = 258 kHz) or more recovery time in clinical application.

Here, we report PDLLA/Fe₃O₄ nanocomposites showing a good shape memory effect in an alternating magnetic field with a frequency of 20 kHz. In recent years, biodegradable PLA polymer has been widely used in the pharmaceutical industry in drug delivery systems [17]. Furthermore, it was also reported that PLA is a thermally induced shape memory material [18,19]. Recently, many researches have been focused on iron oxides due to their potential uses such as in pigments, magnetic drug targeting, magnetic resonance imaging for clinical diagnosis, recording materials catalysts, etc. [20–22]. However, to the best of our knowledge, the shape memory effect of PDLLA/Fe₃O₄ nanocomposites by inductive heating of magnetic nanoparticles has rarely been addressed.

In this study, Fe₃O₄ nanoparticles were synthesized by the convenient and cheap chemical co-precipitation method, which has the potential to produce well-dispersed Fe₃O₄ nanoparticles with well controlled size by appropriate use of surfactants [23,24]. We prepared Fe₃O₄ nanoparticles by a co-precipitation synthesis of modified divalent/trivalent iron salts and by adjustment with aqueous ammonium hydroxide (NH₄OH). PDLLA/Fe₃O₄ nanocomposites with maximized advantages and minimized disadvantages were prepared. The micro-structural morphology and other properties of PDLLA/Fe₃O₄ nanocomposites were investigated. The shape mem-
ory behavior of the nanocomposites in an ultrasonic alternating magnetic field were also explored.

2. Materials and methods

2.1. Materials

PDLLA (Mw: 152 kDa) was synthesized by ring-opening polymerization of cyclic lactide monomer as described previously [25]. The molecular weight distribution (PDI) was 1.57 determined by gel permeation chromatography (Waters 2695/2414 GPC). Analysis was performed using tetrahydrofuran (THF) as solvent at a flow rate of 1.0 ml/min. Polyethylene glycol (PEG, Mw: 10,000 kDa), and the precursor materials of Fe3O4 nanoparticles, i.e. divalent (FeCl2·4H2O), trivalent (FeCl3·6H2O) iron salts and aqueous NH4OH (25–28%, w/w) were purchased from Kelong Chemical Reagent Company (Chengdu, China). All other chemicals and solvents were of reagent grade or better.

2.2. Preparation of Fe3O4 nanoparticles

Conventionally, the preparation of Fe3O4 nanoparticles is a chemical co-precipitation of an aqueous mixture of Fe2+ and Fe3+ chloride at a molar ratio of 1:2. The overall chemical reaction is as follows [26,23]:

\[
\text{Fe}^{2+} + 2\text{Fe}^{3+} + 8\text{OH}^- \rightarrow \text{Fe}_3\text{O}_4 + 4\text{H}_2\text{O}
\]

Fe3O4 nanoparticles were prepared according to our previous report [27], except that PEG was selected as the surfactant. The Fe3O4 nanoparticles were collected by centrifuge (AvantiTM J-30I, BECKMAN COULTER, USA) at 16,000 rpm. The resultant nanoparticles were rinsed with distilled water and centrifuged five times. Finally, the washed Fe3O4 nanoparticles were dispersed and stored in ethanol solution. The average size of the Fe3O4 nanoparticles was 20 nm as determined by transmission electron microscopy (TEM).

2.3. Preparation of PDLLA/Fe3O4 nanocomposites

PDLLA/Fe3O4 nanocomposites were prepared at weight ratios of 1:1, 2:1, 3:1. It is noted that the concentration of the magnetic material is given as weight ratio instead of volume ratio, because the density of PDLLA differs depending on the synthesis method. However, to compare published experimental data because the density of PDLLA differs depending on the synthesis method. To determine the volume fraction of filler material is necessary. Thus, the typical values for the densities of PDLLA and magnetite are given in this paper, namely 1.3 g/cm3 for PDLLA and 5.1 g/cm3 for magnetite, which could give the reader the possibility to calculate the volume ratio. Firstly, pre-weighed PDLLA was dissolved in CHCl3 under stirring. Secondly, Fe3O4 was dispersed in ethanol by a high-speed homogenizer for 30 min. Subsequently, this dispersion was added dropwise to the polymer solution (under stirring) using a pipette. During the process, a black emulsion was obtained due to the precipitation of some of the polymer in ethanol. The emulsion was stirred for 4 h in air so that the PDLLA could be mixed uniformly with the Fe3O4 nanoparticles. The solvent was then evaporated slowly from the emulsion under stirring, and floccules consisting mainly of PDLLA/Fe3O4 nanocomposites formed gradually. Finally, these floccules were kept in an aerator overnight and dried under vacuum at 30 °C and a pressure of 0.1 atm. The completely dried composites were press-molded to a designed shape (10 min, 65 °C, 15 MPa). Specimens with shapes suitable to investigate shape memory properties were thus obtained.

2.4. Characterization

The glass transition temperature (Tg) of the PDLLA/Fe3O4 nanocomposites was determined by differential scanning calorimetry (STA 449C DSC, NETZSCH, Germany). The specimens were heated from 10 to 90 °C at a rate of 5 °C/min in flowing nitrogen gas. Measurements were performed in a closed alumina pan. Weights of all samples were from 5 to 10 mg.

The surface morphology of specimens was observed using a Quanta 200 Scanning Electron Microscope (SEM, FEI, America). Samples were mounted and then coated with gold. The accelerating voltage and magnification were 20 kV and 60,000×, respectively.

Fourier transform infrared spectroscopy (Nicolet 5700 FTIR, Thermo Electron, USA) was performed to identify changes in functional groups in PDLLA/Fe3O4 nanocomposites compared with pure PDLLA and Fe3O4. All specimens were in particle from 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.

Tensile strength and ultimate elongation of the nanocomposites were measured using an Instron 5567 testing machine (INSTRON, USA). The testing standard of the specimens was obtained from the tensile tests under the guidance of ASTM. The mechanical data were determined from the average of three specimens tested at a tensile speed of 5 mm/min.

2.5. Investigation of shape memory properties of PDLLA/Fe3O4 nanocomposites

The magnetic field-induced shape recovery behavior of PDLLA/Fe3O4 nanocomposites of different composition was investigated. Inductive heating was accomplished in an alternating magnetic field at a frequency of f = 20 kHz and a magnetic field strength of H = 6.8 kA m−1. The magnetic system consisted of a supersonic frequency induction heating machine (Duolin Company, Chengdu, China), a copper-induced magnetic coil with a diameter of 40 mm with five loops, a water-cooled system, and a thermosensor device for monitoring the temperature of specimens. We prepared PDLLA/Fe3O4 nanocomposites at weight ratios of 3:1, 2:1 and 1:1 with dimensions of 40 mm × 20 mm × 1 mm (length × width × thickness). The specimens were folded at a deformation temperature above the Tg of PDLLA polymer. After freezing the stress, the folded nanocomposites were placed in the alternating magnetic field. When the temperature reached about 62 °C after magnetic field-induced heating, recovery of the specimens to their original shapes could be observed clearly. Parameters including magnetic field response time, recovery time and shape memory recovery ratio were also investigated.

3. Results and discussion

3.1. Characteristic analysis of PDLLA/Fe3O4 nanocomposites

Fig. 1 shows SEM images of the microstructure of the PDLLA/Fe3O4 nanocomposites at weight ratios of 1:1, 2:1, 3:1. It is evident that these Fe3O4 nanoparticles are uniformly distributed in the PDLLA matrix, visible as bright points in the SEM pictures. Moreover, from Fig. 1 we can see that some nanoparticles are embedded in the polymeric matrix, suggesting that few inorganic nanoparticles agglomerate due to the favorable interface between the PDLLA and Fe3O4 phases. It can also be seen from Fig. 1(a) that some holes occurred in the polymeric matrix due to discontinuous molecular chains of polymer. An advantage of the interface is that it also contributes to formation of a stationary phase and a reversible phase of SMPS [28]. These SEM images indicate that the selected solvent
and synthesis technique provide an effective approach to prepare PDLLA/Fe₃O₄ nanocomposites for applications in biomedical engineering.

The DSC thermogram curves of pure PDLLA and PDLLA/Fe₃O₄ nanocomposites are shown in Fig. 2. The glass transition temperatures ($T_g$) of pure PDLLA and nanocomposites at weight ratios of 3:1, 2:1, 1:1 were 53.0 ± 0.2, 51.1 ± 0.2, 50.1 ± 0.2, 48.2 ± 0.2 °C, respectively. $T_g$ is mainly influenced by the endothermic energy for the phase transition of amorphous PDLLA in the composites, because the Fe₃O₄ phase in the temperature range of testing is stable. However, $T_g$ of the nanocomposites decreased slightly with the addition of Fe₃O₄. The reason may be that the micro-Brownian thermal motions of molecular chain segments of PDLLA are enhanced by well-distributed Fe₃O₄ particles during the endothermic process, and these magnetic particles may transfer heat during the glass transition of the polymer so that $T_g$ of the composites decreased with the addition of the inorganic particles. Thus, the Fe₃O₄ nanoparticles play a very important role in the decrease of $T_g$ due to their plasticization effect [29].

FTIR spectra of the nanocomposites were used to analyze the relationship between the inorganic phase and the polymeric matrix. The IR spectra of pure PDLLA, Fe₃O₄ nanoparticles and PDLLA/Fe₃O₄ nanocomposites at weight ratios of 3:1, 2:1, and 1:1 are exhibited in Fig. 3. From Fig. 3(a), it can be seen that there is a strong absorption band at 1756.2 cm⁻¹ corresponding to the carbonyl group (C=O). The bands in the range of 2995.0–2847.0 cm⁻¹ were assigned to the C–H stretching vibrations of CH₃ groups in the side chains and the –CH– groups in the main chains of PDLLA. The band at 3502.8 cm⁻¹ is assigned to terminal hydroxyl groups (–OH) of PDLLA [30]. In addition, the peak at 3437.7 cm⁻¹ in Fig. 3(a) is assigned to the stretching vibrations of Fe–OH groups absorbed on the surface of Fe₃O₄ nanoparticles. The bands at 893.5 and 794.0 cm⁻¹ are attributed to iron oxide lattice deformations and the surface OH groups of the nanoparticles [31]. Moreover, the absorption bands corresponding to the Fe–O group of bulk magnetite are split into two peaks at 630.7 and 581.9 cm⁻¹. This indicates that some polymeric molecules are bound to the surface of the magnetite nanoparticles by chemical bonds [32]. Thus, the surface of Fe₃O₄ may be linked with hydroxyl groups from PEG polymer used as a surfactant in this work.

FTIR spectra of PDLLA/Fe₃O₄ nanocomposites at weight ratios of 3:1, 2:1, and 1:1 are shown in Fig. 3(b). It is obvious that some changes took place in several absorption bands. For example, the strong absorption bands corresponding to the C=O groups of PDLLA in the nanocomposites shifted to 1755.0, 1753.4 and 1751.1 cm⁻¹, for weight ratios of 3:1, 2:1, and 1:1, respectively. Moreover, the peak at 3437.7 cm⁻¹ assigned to the stretching vibrations of Fe–OH groups of Fe₃O₄, shifted to 3435.8, 3433.6 and 3420.4 cm⁻¹ in the
Fig. 3. FT-IR spectra of pure PDLLA, nano-Fe$_3$O$_4$ particles (a) and PDLLA/Fe$_3$O$_4$ nanocomposites at weight ratios of 3:1, 2:1, and 1:1 (b).

composites at weight ratios of 3:1, 2:1, and 1:1, respectively. However, there was no obvious shift in the absorption bands at about 893.5–794.0 cm$^{-1}$ corresponding to the surface OH groups and the Fe–O groups of bulk magnetite. Thus, it may be deduced from the IR data that hydrogen bonding occurred between the surface Fe–OH group of nano-Fe$_3$O$_4$ and the CO of PDLLA in the composite, i.e., Fe–OH···O–C were present in the PDLLA/Fe$_3$O$_4$ nanocomposites at weight ratios of 3:1, 2:1 and 1:1. However, interfacial interactions among the nanocomposites was apparently very weak based on the slight change of wave number values of Fe–OH and C=O bands, which increased with the addition of Fe$_3$O$_4$ nanoparticles.

Fig. 4 shows the tensile strength and percentage elongation of pure PDLLA and PDLLA/Fe$_3$O$_4$ nanocomposites at weight ratios of 3:1, 2:1, and 1:1 at a temperature of 25 °C. The average values of tensile strength are 31, 42.3, 44.0 and 48.2 MPa, respectively. It is evident that the tensile properties of PDLLA/Fe$_3$O$_4$ composites are improved compared with amorphous PDLLA polymer, presumably attributable to the interfacial interactions of two phases in the composites. However, as seen from Fig. 4, the percentage elongation of PDLLA/Fe$_3$O$_4$ nanocomposites was very low compared with pure PDLLA. This suggests that the mechanical properties of the composites were influenced by the Fe$_3$O$_4$ nanoparticles resulting in the enhancement of tensile strength and a decrease of the percentage elongation.

3.2. Shape memory properties

Because the reported results on the shape memory effect of magnetic particles have some disadvantages such as too high frequency or too long recovery time, a heating magnetic field by supersonic frequency induction at a frequency of $f=20$ kHz and a magnetic field strength of $H=6.8$ kA m$^{-1}$ was used in our study. Typical interesting shape recovery behavior of PDLLA/Fe$_3$O$_4$ nanocomposite at a weight ratio of 2:1 in the magnetic field was found, as shown in Fig. 5. The fold-deformed specimen (temporary shape) was placed in a copper-induced magnetic coil. Due to the Brownian and Néel relaxation losses of the Fe$_3$O$_4$ nanoparticles in the alternating magnetic field, the temperature would reach a recovery temperature above $T_g$ of the PDLLA polymer[16]. Namely after a magnetic field response time of 35 s the specimen began recovering to the original plane shape (permanent shape), as shown clearly in Fig. 5. A as a result, the final shape recovery ratio ($R$) of the composite reached 98.3%. Moreover, the PDLLA/Fe$_3$O$_4$ nanocomposites at other weight ratios also displayed good shape memory effects.

It is important to further evaluate the effects of composite ratios on the magnetic field response time, recovery time and shape recovery ratio. Magnetic field response time refers to the time from sample induction by the alternating magnetic field to the beginning of shape recovery. Similarly, recovery time is defined as the time from beginning to end of shape recovery. The results are shown in Table 1. The original samples with dimensions of 40 mm $\times$ 20 mm $\times$ 1 mm ($l \times w \times t$) were folded at a deformation temperature above $T_g$ of PDLLA polymer. The final $R$ was calculated using the following formula:

$$R(\%) = \frac{180° - \text{final angle}}{180°} \times 100.$$ 

The results illustrate an interesting phenomenon: magnetic field response time, recovery time and $R$-value of PDLLA/Fe$_3$O$_4$ nanocomposites all showed a downturn trend with addition of magnetite particles. The amount of Fe$_3$O$_4$ nanoparticles is an important factor for heating of composites in an alternating magnetic field. Heat transfer from nanoparticles to polymeric matrix is controlled by the thermal diffusivity of the polymer and is therefore dependent on the distances between particles [33,16]. Thus, magnetic field response time and recovery time of the PDLLA/Fe$_3$O$_4$ composite at a weight ratio of 1:1 are shorter than for the other composites. In
addition, although the shape memory capability of PDLLA polymer may depend on the physical entanglements of molecular chains for fixation of the permanent shape, the effect of entanglements is low during the glass transition due to physical interactions. As a result, the shape memory effect of PDLLA polymer is obviously less than other composites [19]. Moreover, pure PDLLA polymer does not present any shape memory property in a magnetic field since there is no inductive heating of magnetite particles. It could be also shown that PDLLA/Fe3O4 nanocomposite had a shape memory effect by thermally induced heating, as shown in Table 1. It is seen in Table 1 that the R-value of PDLLA/Fe3O4 nanocomposite at a weight ratio of 1:1 is lower than that of the other composites. The reason is that Fe3O4 particles as a filler in nanocomposites may be excessive, so that the thermo-motions of chain segments of amorphous PDLLA polymer are greatly restricted during shape recovery [19].

4. Conclusions

Fe3O4 nanoparticles with a diameter of 20 nm were successfully synthesized by co-precipitation of divalent and trivalent iron salts using PEG-10000 as a dispersing surfactant. PDLLA/Fe3O4 composites were prepared by a hot press-molding method. Nanoparticles were uniformly dispersed in the PDLLA matrix and played a plasticization role among polymer molecules as shown by SEM and DSC. IR spectra further indicated that weak hydrogen bonding, namely Fe–OH···O=C, between the surface Fe–OH group of nano-Fe3O4 and C=O of PDLLA existed in the composites. Interfacial interactions had a positive effect for the improvement of the tensile properties and shape memory ratios of the PDLLA/Fe3O4 nanocomposites. The magnetic field-induced shape memory effect of the composites was determined in an alternating magnetic field with a frequency of f=20kHz and a magnetic field strength of H=6.8 kA m \(^{-1}\). The nanocomposites displayed an excellent shape memory effect. In general, these biocompatible and shape memory nanocomposites show potential for application as magnetically controlled smart implants in the biomedical field.

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References