A dual-functional polymeric system combining shape memory with self-healing properties

Hongqiu Wei [a], Yongtao Yao [a], Yanju Liu [b], Jinsong Leng [a, *]

[a] Center for Composite Materials and Structures, Harbin Institute of Technology (HIT), Harbin 150080, People's Republic of China
[b] Department of Astronautical Science and Mechanics, Harbin Institute of Technology (HIT), Harbin 150080, People's Republic of China

A B S T R A C T

With the aim of seeking a convenient way for integrating functional materials, a polymeric system, presenting both self-healing property and shape memory behavior, was proposed and constructed based on epoxy based shape memory polymer (ESMP) and poly (ε-caprolactone) (PCL). The synthesis principle of PCL–ESMP composite was based on phase separation phenomenon between the two ingredients. Such phase separated PCL–ESMP composite reserved melting transition of PCL and glassy transition of ESMP, respectively, which was the crucial mechanism for achieving self-healing performance and shape memory behavior. A bending-recovery experiment demonstrated that PCL–ESMP composite possessed excellent thermal-induced dual-shape memory effect. Meanwhile, single edge notched bend testing revealed that such composite exhibited desirable self-healing performance as well. This article introduced a simple contrivable concept and exhibited some experimental results of the PCL–ESMP dual-functional composite system. The promising applications are expected to more widely, such as functional composite matrix and intelligent structures.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

Stimulus-responsive materials based on polymer networks have been witnessed significant growth in the past decades, especially for the two branches, shape memory polymers (SMPs) and self-healing polymers (SHPs) [1]. SMPs are characterized for the shape memory effect (SME), which present the performance to revert the original shape from the provisional shape when they are triggered by external stimulus, such as heat [2–4], ultraviolet irradiation [5], electricity [6–8], water or moisture [9], and magnetic field [10], appropriately. Based on the unique capabilities, SMPs possess a broad applied range that changes from deployable structures and actuators to biomedical devices as well as sensors [11–15]. The other one, SHPs, inspired by the self-healing of organism, are known for the capability to self-repair from a physical crack or damage under certain external stimulus [16–18]. Self-healing performance not only reduces the cost of maintenance, but also endows high security and long service lifetime to the materials [19,20].

Both shape memory and self-healing are intelligent and promising characteristics. It has attracted increasingly interests of

researchers to construct materials with both self-healing and shape memory properties [21–23]. Sodano presented polyurethanes based on Diels–Alder (DA) reaction exhibiting shape memory behavior and healed capabilities [21]. Wang also constructed a polymer network possessing both shape recovery and self-healing properties upon utilizing the cross-linking reaction between poly(vinyl butyral) (PVB) and hexamethylene diisocyanate (HDI) [22]. Both of them demonstrated that traditional materials exhibited smart behavior at the presence of SME. Moreover, self-healing performance could realize without the need of external forces. Such dual-functional polymeric systems present potential to broaden and enrich the developments of smart materials and structures.

Epoxy resin as a class of traditional engineering materials possesses a plenty of advantages, especially for the superior mechanical properties, chemical stabilities, excellent thermal and thermomechanical behaviors, etc. [24–26]. Recently, researches have concentrated on developing intelligent properties of epoxy resins to widen their applications as engineering smart materials and structures. Both epoxy based shape memory polymers (ESMP) [27–30] and self-healing epoxy systems [31–35] have been prepared successfully, however, it is more important to fabricate epoxy based polymer presenting both the two properties for smart systems. Mather et al. developed shape memory assisted self-healing

* Corresponding author. Tel./fax: +86 451 86402328.
  E-mail address: lengjs@hit.edu.cn (J. Leng).

(SMASH) systems recently [36,37]. They reported a SMASH coating achieving via spin-coating ESMP on electrospinning poly(ε-caprolactone) (PCL) membrane [36]. In this composite, once cracks or damages generated, PCL fibers could melt and flow to heal the damages with the assistance of SME to close the cracks by heating. Even through the study only focused on a coating, the method they mentioned paved the way for the developments of smart epoxy-based materials.

Inspired by the researches above, a thermoset—thermoplastic polymeric system, consisting of ESMP and PCL, was utilized to fabricate a kind of materials with thermally-induced dual-shape memory and self-healing properties in this study. ESMP and PCL constructed a phase separated composite, so that the two ingredients could reserve their original performance, which guaranteed the achievement of shape memory and self-healing. The chemical and morphology structure were investigated with Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscopy (SEM). Thermo-mechanical performances of the materials were presented by Dynamic Mechanical Analysis (DMA). In what follows, the smart capabilities, self-healing capacity and shape memory behavior, were evaluated by Single Edge Notched Bend (SENB) and Bending-recovery test in detail.

2. Experimental details

2.1. Materials

The polymer matrix was ESMP, which was fabricated as presented in our previous report [28]. The thermoplastic poly (ε-caprolactone) (PCL) pellets purchased from Perstorp Chemical Trading Co., Ltd. (CaPa 6500, $Mn = 40,000-50,000$; density: 1.146 g/mL) were chosen as healing agent. All materials were used as received without further treatment.

2.2. Fabrication of PCL—ESMP composites

Different weight ratios of epoxy based resin and PCL pellets were added in a 500 mL flask and stirred constantly at 80 °C. Two hours later, curing agent was added and stirred continuously for another 30 min to obtain a homogeneous PCL—ESMP mixture. In order to remove bubbles, the above mixture was degassed at a vacuum oven for 15 min at 80 °C, then, inserted into the preheated glass molds. The curing condition was set as follows: 80 °C for 3 h, 100 °C for 3 h and 150 °C for 5 h. The fully cured materials were cooled down to room temperature at a rate of 20 °C/min. Finally, the PCL—ESMP composites were obtained. The nomenclature and content of each component were shown in Table 1. The fabricated PCL—ESMP composite was defined as Px, which meant the mass ratio of PCL/ESMP was x/100, and the PCL content was treated as x wt%.

2.3. Characterizations

A Fourier Transform Infrared Spectroscopy (FTIR) (Spectrum One, Perkin Elmer) was employed to analysis the reaction between PCL and ESMP during the curing process. The sample was powder

Table 1
Compositions of the PCL—ESMP composites.

Samples	Epoxy based resin (g)	Curing agent (g)	PCL (g)	PCL/ESMP (wt%)
ESMP	100	83.6	0	0
P6.1	90	75.24	10	6.1
P13.6	80	66.88	20	13.6
P23.3	70	58.52	30	23.3

and prepared by KBr pellets. The test condition was used a spectral range of 4000—370 cm^{-1} and a resolution of 4 cm^{-1}.

Scanning Electron Microscopy (SEM) (Quanta 200FEG) was used to discuss the morphologies of (I) the cracks of the samples before after healing (II) the fractured surfaces of the samples. In order to investigate morphology of phase separation, completely cured specimens were quickly fractured in liquid nitrogen and then immersed in chloroform for 30 min to eliminate PCL ingredient. All the SEM samples were sputter-coated with gold before testing.

Dynamic Thermo-mechanical Analyzer (DMA/SDTA861e, Mettler—Toledo) was conducted by tension mode at a frequency of 1 Hz and 0.05% strain. The test temperature ranged from 25 °C to 250 °C with a heating rate of 5 °C/min.

Single Edge Notched Bend (SENB) testing was conducted by ASTM D5045 to evaluate self-healing ability. The test was under a three-point mode with a span of 40 mm and a cross-head speed of 1 mm/min (Zwick/Roell instrument). The specimen ($50 \times 10 \times 5$ mm^3) with a 3 mm notch in center was obtained by laser cutting machine, after that razor blade was used to generate a 2 mm deep pre-crack. Such pre-crack sample was loaded until the point which was 90% loss of the peak load, then, it was healed for 30 min at a certain temperature, 84 °C, 104 °C, 124 °C, or 144 °C, respectively, in an oven. Such healed sample was cooled to room temperature at a rate of 20 °C/min. In order to characterize the healing efficiency of PCL—ESMP, the sample was re-loaded to failure according to the procedure described above. The original and post healing maximum loads were required to calculate the healing efficiency. The equation was as follows [18,31]:

$$\text{Healing efficiency}(\%) = \frac{\text{Max. Load}_{\text{healed}}}{\text{Max. Load}_{\text{original}}} \times 100\% \qquad (1)$$

Shape memory behavior of PCL—ESMP was investigated by a bending-recovery test. A strip with dimension of $50 \times 5 \times 1$ mm^3 was performed as original shape. It was bended into a "U" shape as its temporary shape at $T_g + 20$ °C. The "U" shape sample was fixed by cooling down the sample to room temperature at a rate of 20 °C/min. When deformed sample was re-heated above $T_g + 20$ °C, it could recovery to the original shape. Shape recovery ratio (Rr) and shape recover speed (Rs) were employed for characterizing the shape memory behavior of PCL—ESMP. Rr was defined as $Rr = \theta r / 180°$, where θr was obtained by measuring the released angle after the recover process. Rs was determined by the recovery time.

3. Results and discussions

3.1. Structural characterization

FTIR spectrum ranging from 4000 to 370 cm^{-1} was employed to analyze the interaction between PCL and ESMP. From Fig. 1, it is clear that PCL—ESMP composites have same characteristic absorption peaks, indicating those materials have same functional groups. The absorption peaks at 2946 cm^{-1} and 2870 cm^{-1} are corresponding to $-CH_2-$. A sharp absorption peak appears at 1733 cm^{-1} belongs to $-C{=}O-$ groups. The absorption peak at 1455 cm^{-1} is assigned to the stretch vibration of C—H bonds. The absorption peak at 1182 cm^{-1} is pertained to the C—O bonds, and the absorption peak at 1363 cm^{-1} demonstrates that the C—O bonds are attached to cyclic anhydride [28]. All these characteristic absorption peaks belong to either ESMP or PCL. It reveals that no new characteristic absorption peaks emerge between ESMP and PCL. So there is only physical reaction between them during the curing process. It is the basis for phase separation phenomenon.

To reveal the phase separated morphology of polymers, some microscopy techniques have already been presented [38]. In this