Research Article

Epoxy Resin Composite Bilayers with Triple-Shape Memory Effect

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Triple-shape memory epoxy composites with bilayer structures of well-separated glass transition temperatures have been successfully prepared. The different glass transition temperatures of the epoxy composites were obtained by physically incorporating various amounts of nanosilica particles, which were introduced into the epoxy by utilizing polyethylene glycol. A scanning electron microscope and a transmission electron microscope were used to analyze the dispersibility of the nanosilica particles. The effects of nanosilica particles on the mechanical properties as well as on the dual-shape memory effects (DSME) and triple-shape memory effects (TSME) of the nanocomposites were studied. The nanosilica particles were homogeneously dispersed in the matrix and well incorporated into the epoxy matrix. The resulting nanocomposites exhibited excellent TSME, and their shape fixity properties were significantly improved by nanosilica particles.

1. Introduction

Shape memory polymers (SMPs) are smart materials that can fix their deformed temporary shapes and recover their permanent shapes in a defined way upon external stimuli [1–3]. SMPs have attracted considerable attention because of their promising applications in textiles [4–6], adhesives [4, 5], smart coatings [4–9], biomedical devices [4–6, 10], and aerospace structures [6, 10].

In recent years, triple-SMPs (TSMPs) have received even greater attention because shape changes are no longer limited to being unidirectional but could now potentially offer unique opportunities in many applications, including morphing aircrafts, fasteners, and medical devices [1, 11]. Unlike conventional dual-SMPs, which can recover from a temporary shape to a permanent shape, TSMPs can fix two temporary shapes and recover sequentially from one temporary shape to the other and eventually to the permanent shape [12]. TSMPs have either more than one switching thermal transition [1] or a single switching transition with a broad thermal transition range [13]. Triple-shape memory effects

(TSME) can be achieved through many ways, including polymers blends, grafting and blocking copolymers, SMP hybrids, and polymer laminates [14]. Bellin et al. [15] first reported a SMP with a two-step TSME by copolymerizing poly(ethylene glycol) monomethyl ether monomethacrylate with poly(caprolactone) dimethacrylate. The grafting and blocking copolymers of different soft segments result in more than one well-separated multiple phase in a single SMP. Bae et al. prepared SMPU bilayer films of different molecular weights with nanosilica particles acting as multifunctional cross-links and reinforcing fillers [16]. Xie et al. prepared TSMP bilayer epoxy by curing the high T_g epoxy layer on top of the low T_g epoxy layer [1].

Herein, novel triple-shape memory epoxy nanocomposites with two different glass transition temperatures have been prepared through casting nanosilica/epoxy nanocomposites layer by layer. By varying the amounts of polyethylene glycol (PEG) and nanosilica in the epoxy system, we achieved a series of composite layers with different glass transition temperatures. The dispersibility of the nanosilica particles was evaluated via field emission scanning electron microscopy

TABLE 1: Raw material ratios of pure EP and A₁₀, A₀₀, A₀₁, and A₀₂.

	E-51 (g)	PA (g)	Nanosilica (g)	PEG (g)
EP	50	39	0	0
A ₁₀	50	39	0	20
A ₀₀	50	39	0	10
A ₀₁	50	39	1	10
A ₀₂	50	39	2	10

(FE-SEM) and transmission electron microscopy (TEM). The effects of the nanosilica particles on the mechanical and shape memory properties of the composites were analyzed and discussed.

2. Experiment

2.1. Materials. Epoxy resin E-51 (WSR618) and the curing agent (PA) were procured from Jinhong Resin Factory, Hangzhou, China. Nanosilica (15 ± 5 nm) was obtained from Aladdin Chemical Reagents Co., Ltd., Shanghai, China. Polyethylene glycol 200 (PEG200) was purchased from Shanghai Putong Gaonan Chemical Plants, China.

2.2. Preparation of SiO₂/Epoxy Resin Nanocomposites. SiO₂/epoxy nanocomposites were prepared according to our previous report with a slight modification [17]. Typical procedure was as follows: a known amount of SiO₂ was dispersed in PEG by mechanical stirring for 3 h. Then epoxy resin and curing agent were dissolved in the SiO₂ dispersion under mechanical stirring for another 0.5 h. Subsequently, the mixture solution was degassed placed in a vacuum oven. And then, the mixture solution was poured into a Teflon mold, cured at 60°C for 4 h. Changing the mass ratio of the SiO₂ and PEG in the mixture and according to the above method, the SiO₂/epoxy nanocomposites were obtained with different mass ratio of 1 wt% and 2 wt%, respectively. Meanwhile, the pure epoxy and the PEG mixed epoxy composites were also prepared in the absence of nanosilica particles via the method described above. The stoichiometric amounts of every material used to prepare the SiO₂/epoxy nanocomposites have been listed in Table 1.

Bilayer SiO₂/epoxy nanocomposite was prepared as follows: the mixture solution A₀₂ was poured into a Teflon mold, cured at 60°C for 0.5 h. And then the mixture solution A₁₀ was poured on top of the A₀₂, cured at 60°C for 3.5 h. Finally, the bilayer SiO₂/epoxy nanocomposite was obtained with the weight ratio of A₀₂ to A₁₀, that is, 2 : 1, and the sample was designated as B₂₁.

2.3. Characterization. The dispersibility of nanosilica particles dispersed in PEG and the fracture surfaces of some samples were characterized by field emission scanning electron microscope (ZEISS ULTRA55) and transmission electron microscope (TEM, JSM-2100).

Tensile properties of the composites were measured by using a universal testing machine (UTM) (Instron 3367R4415, Canton, MA, USA) at a crosshead of 5 mm/min.

FIGURE 1: Schematic of a temperature (T)-loading stress (M)-length (L) plot showing the eight-step thermomechanical cycle for attaining triple-shape memory effect.

The dimensions of the rectangular film were 50 mm × 5 mm × 2 mm, and the length gripped the sample was 30 mm.

Dynamic mechanical analysis (DMA) was performed with the use of DMA Q800 (TA Instruments, New Castle, USA) in a uniaxial tension mode at 1 Hz and a heating rate of 3°C/min. The dimensions of the rectangular film were 10 mm × 5 mm × 2 mm.

A thermomechanical cycle test was conducted with a UTM with a temperature controlling chamber. To investigate the dual-shape memory effect (DSME), the sample was stretched to the maximum strain (ϵ_m) of 10% at T_{d1} ($T_{d1} > T_g$, where T_g is the glass transition temperature), followed by cooling the sample to T_{d2} ($T_{d2} < T_g$) and maintaining the load for several minutes. And then, the sample was unloaded at T_{d2} with an unloading strain (ϵ_u). The permanent strain (ϵ_p) was reached during the reheating of the sample from T_{d2} to T_{d1} . This completes a thermomechanical cycle and four circles were conducted to examine the shape recovery capacity of the composites. Shape fixity (R_f) and shape recovery (R_r) ratios for the cycle are defined as follows [16, 18]:

$$\text{Shape fixity ratio, } R_f = \frac{\epsilon_u}{\epsilon_m} \times 100\%,$$

$$\text{Shape recovery ratio, } R_r = \frac{\epsilon_r}{\epsilon_m} \times 100\%, \quad (1)$$

where $\epsilon_r = \epsilon_m - \epsilon_p$. T_{d1} and T_{d2} were 42°C and 15°C for A₁₀ and A₀₀ and 72°C and 42°C for A₀₂ and A₀₁, respectively.

The triple-shape memory was performed through eight thermomechanical loading steps using a DMA Q800 in a uniaxial tension mode, as shown in Figure 1 [19]. The analysis was conducted under strain controlled programming and the heating and cooling rates were 3°C/min. At step 1 (F_1), the sample was stretched from L_0 to L_1 at T_h ($T_h > T_{\text{trans1}} > T_{\text{trans2}}$, where T_{trans1} and T_{trans2} are two thermal transition temperatures); the corresponding strain was recorded as ϵ_{mB} .

FIGURE 2: (a) TEM and (b) FE-SEM images of nanosilica dispersed in PEG.

FIGURE 3: Cross section morphology of silica/epoxy nanocomposites: (a) A₀₁ and (b) A₀₂.

At step 2 (F_2), the sample was cooled to T_m ($T_{\text{trans1}} > T_m > T_{\text{trans2}}$) and the load was maintained, where A₁₀ and A₀₂ were glassy and rubbery states, respectively. At step 3 (F_3), the external load was removed, and the sample was fixed at the first temporary shape B, with the strain of ϵ_{uB} :

$$R_{fB} = \frac{\epsilon_{uB}}{\epsilon_{mB}} \times 100\%, \quad (2)$$

where ϵ_{mB} and ϵ_{uB} are the maximum and the loading strains, respectively.

At step 4 (F_4), the sample was further stretched to the strain of ϵ_{mA} (L_2) at T_m . At step 5 (F_5), the sample was cooled to T_l while keeping the strain at ϵ_{mA} . At step 6 (F_6), the second temporary shape A with a strain of ϵ_{uA} was fixed at T_l after the removal of the external force:

$$R_{fA} = \frac{\epsilon_{uA} - \epsilon_{uB}}{\epsilon_{mA} - \epsilon_{uB}}, \quad (3)$$

where ϵ_{mA} and ϵ_{uA} are the maximum and unloading strains, respectively.

At step 7 (F_7), the sample was reheated to T_m , and it was recovered to the first temporary shape B, with the strain of ϵ_{pB} . At step 8 (F_8), the sample was recovered to shape C with

the strain of ϵ_{pC} by heating back to T_h . The recovery ratio of shape band shape C was obtained as follows:

$$\begin{aligned} R_{rB} &= \frac{\epsilon_{uA} - \epsilon_{pB}}{\epsilon_{uA} - \epsilon_{uB}}, \\ R_{rC} &= \frac{\epsilon_{pB} - \epsilon_{pC}}{\epsilon_{uB}}. \end{aligned} \quad (4)$$

T_l , T_m , and T_h are set to 15°C, 42°C, and 72°C, respectively; $\epsilon_{mB} = 2.5\%$ and $\epsilon_{mA} = 5\%$.

3. Results and Discussion

3.1. Morphology of Nanocomposites. Figure 2 shows the morphology evolution of nanosilica dispersed in PEG. Figure 2(a) and Figure 2(b) are the TEM and FE-SEM images of nanosilica dispersed in PEG, respectively. It confirms that the nanosilica particles are well distributed and no agglomerates present in the PEG. The cryofractured cross section of the silica/epoxy nanocomposites was observed by FE-SEM. In Figure 3, the samples A₀₁ (Figure 3(a)) and A₀₂ (Figure 3(b)) images reveal that the nanosilica particles are also well dispersed in the epoxy matrix. Through the typical process, it is noted that the obtained silica/epoxy nanocomposites

FIGURE 4: DMA curves for the samples.

TABLE 2: Glass transition temperature (T_g) of A₁₀, A₀₀, A₀₁, A₀₂, and B₂₁.

Sample	A ₁₀	A ₀₀	A ₀₁	A ₀₂	B ₂₁
T_g (°C)	36	38	48	65	30, 66

are fully composed of well dispersion of nanosilica particles within epoxy matrix, which may lead to excellent mechanical properties of composites [17].

3.2. Dynamic Mechanical Properties. The dynamic mechanical properties of samples from the DMA test are shown in Figure 4. The samples A₁₀, A₀₀, A₀₁, and A₀₂ prepared in this study possess glass transition temperatures (T_g s) of 36°C, 38°C, 48°C, and 65°C, respectively, based on their tan δ peaks in the DMA curves (as shown in Figure 4(a)), as shown in Table 2. It is also noted that the T_g of sample was increased with the increasing amount of nanosilica and decreased with the increasing amount of PEG, which was attributed to the segmental motion of polymer that was hindered by nanosilica particles and PEG acted as a plasticizer.

In view of the well phase mixing of nanocomposites, A₀₂ and A₀₁ show a relatively narrow switching transition, implying that sufficient chain movement is achieved within that short temperature regime. The tan δ peaks of all of samples are relatively high (higher than 0.6) indicating that the significant difference between viscous and elastic components of SMP in the T_{trans} regime, which is of great benefit to shape recovery ratio of sample [20–22]. Moreover, in Figure 4(a), two tan δ peaks can be clearly observed in the curve of B₂₁, and it is also found that the sample B₂₁ possessed the two well-separated glass transitions, which is

shown in Figure 4(b). This phenomenon could be attributed to the formation of the phase-separated bilayer structure and provided the conditions to achieve TSME.

3.3. Mechanical Properties of the Composites. Figure 5 shows the stress-strain behaviors of the composites at different temperatures. It can be seen from the results of Figures 5(a), 5(c), and 5(e) that the break strength and elongation of the silica/epoxy nanocomposites were improved by the addition of nanosilica particles, except for the sample A₀₀ that has better break elongation than the samples A₀₁ and A₀₂ at 15°C. It may be attributed to the reinforcing function and homogeneous dispersion of the nanosilica particles as observed in the FE-SEM images (Figure 3). Moreover, the samples A₀₁ and A₀₂ also show good strain energy storage capacity which can be obtained from the area under the stress-strain curve, implying that the silica/epoxy nanocomposites may have better shape recovery effect [16, 20]. Meanwhile, the break strength and the elongation of the composites decreased with the increasing amount of PEG, indicating that PEG serves as plasticizer.

The stress-strain behaviors of B₂₁ depend on the temperature as illustrated in Figures 5(b), 5(d), and 5(f). Comparing with the stress-strain behaviors of B₂₁ at 15°C and 72°C, B₂₁ at 42°C exhibits an interesting phenomenon of the stress maintaining almost constant when the strain increased from 31% to 34%. This is mainly because the sample B₂₁ is consisted of two layers, including A₁₀ layer in the rubbery state and A₀₂ layer in the glassy state at 42°C, respectively. Additionally, A₁₀ layer of B₂₁ does not break at the strain of approximately 25%, whereas the sample A₁₀ breaks. This result might be due to the powerful interfacial adhesion of the two layers. For comparison, stress-strain behavior for pure EP at different

FIGURE 5: Stress-strain behavior of the samples at 15°C (a, b), 42°C (c, d), and 72°C (e, f).

temperatures is displayed in Figure 6. A notable difference between EP composites and pure EP is that the failure strain of EP composites is greatly improved due to the addition of PEG in EP matrix.

3.4. Shape Memory Behavior

3.4.1. DSME. The four cycles of thermomechanical behavior of the composites are shown in Figure 7, and the detailed

FIGURE 6: Stress-strain behavior of the pure EP at 15°C, 42°C, and 72°C.

FIGURE 7: Thermomechanical cyclic behavior of (a) A_{10} , (b) A_{00} , (c) A_{01} , and (d) A_{02} .

TABLE 3: Shape fixity and shape recovery of A_{02} , A_{01} , A_{00} , and A_{10} (N = number of thermomechanical cycles).

$N^{(a)}$	Fixity ratio (%)				Shape recovery ratio (%)			
	A_{10}	A_{00}	A_{01}	A_{02}	A_{10}	A_{00}	A_{01}	A_{02}
1	75	82	90	93	98	99	99	99
2	74	80	89	90	98	99	99	99
3	73	79	88	89	98	98	98	99
4	70	78	87	88	96	97	97	97

^(a)Thermomechanical cycle number.

FIGURE 8: Triple-shape memory cycles of the sample for B_{21} .

data are summarized in Table 3. On the basis of DMA curves (Figure 6(a)), the rubbery state and glassy state of the samples A_{02} and A_{01} can be achieved at 72°C and 42°C, and those of the samples A_{00} and A_{10} can be achieved at 42°C and 20°C, respectively. The composites deformed in their rubbery state and generated a decrease in conformational entropy of the constituent polymer network chains. Then, the cooling down of the deformed material triggered vitrification, which kinetically traps the SMP in its low entropy state as a result of a significant reduction in chain mobility. Shape recovery is later initiated by reheating the material under stress-free conditions and allowing for the relaxation of polymer chain segments (with regained mobility) to their original entropically favored conformational state [11]. Additionally, it should be noted that the shape fixities of A_{00} and A_{10} are relatively low while the samples A_{01} and A_{02} display better shape fixities at 87–93% for the four cycles, which may be contributed from the addition of nanosilica particles. Furthermore, The shape recovery effect of all the samples was 96%–99%, especially the sample A_{02} that is better than the others. This finding is coincident with previous analysis.

3.4.2. TSME. The triple-shape memory capability for B_{21} is shown in Figure 8. The sample was first strained to 2.5% at 72°C, which was followed by cooling down to 42°C. After the stress was released, the strain instantaneously shrunk to 1.96%. At this step, the shape fixity was decided by the

FIGURE 9: Illustration of triple-shape memory effect of B_{21} : shape (C) original shape, shape (B) first temporary shape, and shape (A) second temporary shape.

molecular frozen of A_{02} because rubbery state of A_{10} tended to recoil the sample. At last, the shape fixity ratio R_{fB} of 78% was achieved. Then, the sample was stretched to 5% at 42°C, followed by cooling down to 15°C and the subsequent releasing of the stress, and the strain shrunk from 5% to 4.5%. At 15°C, although both A_{02} and A_{10} were in glassy state, A_{02} had a tendency to keep shape B, resulting in R_{fA} of 84%. Finally, the sample was reheated to 42°C and 72°C; the strain was 2% and 0.04% at 42°C and at 72°C, respectively. $R_{rB} = 97\%$ and $R_{rC} = 100\%$ were calculated based on (4).

The TSME is further demonstrated visually in Figure 9. B_{21} was cut into a rectangular film of dimensions 50 mm × 5 mm × 2 mm (shape C). Shape C was first heated in an oven at 72°C and then quickly deformed to a “U” shape and quenched in a water bath at 42°C; some minor recovery occurred due to the not so perfect shape fixing ratio, but most of the deformation was kept and fixed at a temporary shape B (progress 1). After this, shape B was transformed into shape A and immersed in a water bath of 15°C; shape A was fixed at the same time (progress 2). Reheating to 42°C and 72°C, shape B and shape C recovered in turn (progress 3 and 4). Shape B and shape C behaved just the corresponding shape at the right temperature due to their excellent shape recovery ratio.

4. Conclusions

A novel bilayer epoxy system shape memory composites with TSME have been successfully synthesized and designed. The triple-shape memory nanocomposites were prepared by casting together two different shape memory composites exhibiting outstanding shape recovery effect. By varying the amount of PEG and nanosilica particles, we prepared a series of nanocomposites layers with different T_g . The dispersibility of the nanosilica particles and the failure strains of the nanocomposites were significantly improved by the addition

of PEG. The mechanical and shape memory fixity properties of the composites were significantly improved by the addition of nanosilica particles.

Conflict of Interests

The authors declare that they do not have any commercial or associative interest that represents a conflict of interests in connection with the work submitted.

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