

Modified Shape Memory Epoxy Resin Composites by Blending Activity Polyurethane

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ABSTRACT: A series of modified shape-memory epoxy resin composites were prepared by blending activity polyurethane (APU). Fourier transform infrared spectroscopy (FTIR), tensile tests, scanning electron microscope (SEM), dynamic mechanical analysis (DMA), and fold-deploy shape memory tests were used to characterize the structure, mechanical, morphology, thermodynamics, and shape memory performance of these materials. FTIR results suggest that APU has been introduced into the resin matrix resin. Tensile test results show that the addition of appropriate APU can increase the elongation at break significantly, compared with neat epoxy. SEM results indicate that the fracture mechanism has changed from brittle to ductile, suggesting that the brittleness of the material has been overcome. DMA results show that modified materials have lower glass transition temperature (T_g) and lower cross-linking density for shape memory function. Furthermore, the fold-deploy shape memory tests prove that the materials possess excellent shape memory properties. They can be deformed into different shapes and recover their original shapes fully within 2 min at T_g , while they are hardly affected by ninefold-deploy cycles. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

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INTRODUCTION

Shape-memory polymers (SMPs) are a class of novel smart materials, which have the capability to recover their primary shapes upon appropriate external stimulus,^{1,2} such as thermal treatment,³ light,⁴ electricity,⁵ and vapor.⁶ For materials to possess shape memory properties, they usually have two structures: permanent networks and reversible phases.^{7,8} Here, the function of permanent networks is to memorize the permanent shape, which can be achieved via chemical or physical cross-linking. On the other hand, the reversible phases are used to fix temporary shapes associated with either a glass transition or a melting transition.

Recently, shape-memory epoxy resins have attracted considerable attention for their lower cost, low density, easy control of the shape recovery temperature, high shape recoverability (up to 100%), and easy process ability compare with shape-memory alloys (SMAs).^{9–11} However, the disadvantage of materials limiting their application is brittleness.^{12–13} This is because the polymers contain many epoxy and benzene rigid groups. Therefore,

this study aims to search for a method to improve brittleness but not affect shape-memory properties.

Generally speaking, reducing the cross-link density and introducing flexible aliphatic chains are two effective methods to improve brittleness. In this article, we utilize various “theory curing degree” to change cross-link density and blend polymer with matrix to introduce flexible aliphatic chains. Here, “theory curing degree” is a theoretical numerical value based on calculation.¹⁴ We consider the value to be 100 when the molar ratio between epoxy group and curing agent is 1 : 1, and to be 90 when the proportion is 1 : 0.9, and so on. Polymer blending is an efficient method to obtain new materials with desirable performances.^{15–17} Normally, activity polyurethane (APU) has many unparalleled properties, for instance, practical and adjustable phase transition temperature ranges, low viscosity and good compatibility with epoxy resin, and, especially, high and reproducible shape recovery capabilities.^{18–22} Hence, a series of modified shape memory epoxy resin (SEP) composites by blending APU have been prepared for studying their performances.

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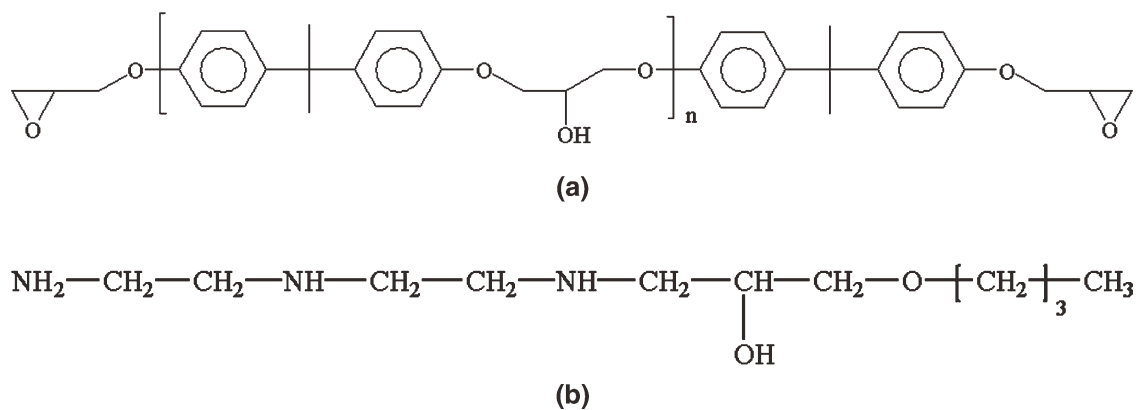


Figure 1. Chemical structures of epoxy resin and curing agent. (a) Epoxy resin E-51 (WSR 618). (b) Curing agent 593.

EXPERIMENTAL

Materials

The epoxy resin matrix used in the current study was bisphenol A glycidyl ether epoxy resin (E-51), with an epoxy value of 0.51. The blending polymer was APU which was obtained from Hengchuang Insulated Material Co. Ltd.; the activity group was $-\text{COOH}$ and its content was 0.13 ± 0.02 mol/100 g. A modified amine 593 was used as curing agent; it was a transparent liquid with a long-chain structure; the amine value (mg KOH/g) was 500–600, and the viscosity was 80–100 mPa s (25°C). All materials were used without further processing. The chemical structures of reactants are shown in Figure 1.

The theoretical mass of curing agent for modified amine 593 was calculated from formula (1):

$$Y = \left(\frac{M}{n_H} \right) \times K \quad (1)$$

where Y is the mass of curing agent used in 100 g epoxy resin, M is the molecular weight of amine, n_H is the active hydrogen number in an amine molecule, and K is the epoxy value of E-51.

A series of modified systems were prepared according to eq. (1), the pure resin samples were named EP- b , and the modified systems were named aSEP- b , where SEP was the blending composite; a was the mass ratio of APU, and b was the theoretical curing degree.

Characterization Methods

FTIR (Nicolet750 FTIR Spectrometer) was used to detect the absorption peaks of curing pure epoxy resin and modified composites system. The specimens were prepared using the KBr pellet technique. The scanning scope was from 650 to 4000 cm^{-1} .

Tensile tests were carried out using a tensile tester (Instron 5500R) to evaluate the mechanical strength of materials. Samples were dumbbell, the width of the effective part was 4 mm, and the thickness was 2 mm. These specimens were elongated at the rate of 5 mm/min at room temperature.

The fracture surfaces of the notched impact samples were observed by scanning electron microscopy (SEM) using QUANTA 200F microscope (American). Surfaces of specimens were coated with gold, and the multiple of magnification was 500.

Thermodynamic properties including the glass transition temperature (T_g) and storage modulus (E_r) of the composites were researched by a dynamic mechanical thermal analyzer (American, TA Q800)DMA, performed in a nitrogen atmosphere from 25 to 150°C under the stretching mode. The heating rate was 3°C/min, and the resonance frequency was adjusted to 1 Hz. The sample size was 25 mm \times 5 mm \times (1 \pm 0.1) mm.

To investigate the shape memory performances of the composites, a fold-deploy shape memory test was performed as follows^{14,23}: first, a cured sample (size:150 mm \times (20 \pm 1.5) mm \times (2 \pm 0.2) mm) was heated to its T_g and then bent into a “U” shape encircling a central axis of diameter 12 mm; second, the U-shaped sample was cooled down at room temperature under a constant external force applied for several minutes, until the specimen became cool and rigid; finally, the system was reheated to recover its original shape at T_g , and the recovery time recorded when the recovery angle was 30, 60, 90, 120, 150, and 180°. The schematic diagram is shown in Figure 2.

RESULTS AND DISCUSSION

FTIR Analysis

The FTIR spectra of EP-100 and 30%SEP-100 were compared in Figure 3. However, the difference between the two curves was not very pronounced.

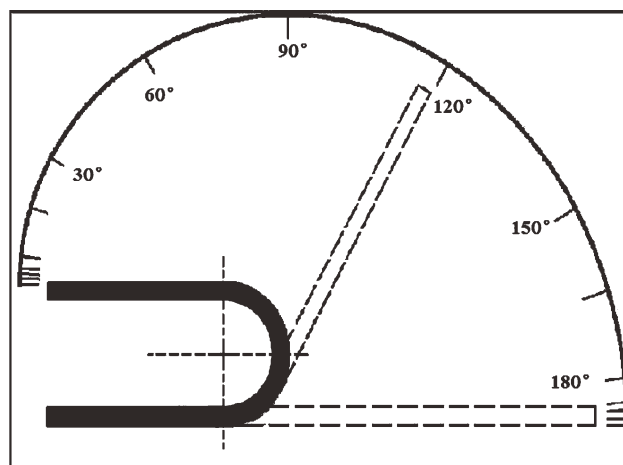


Figure 2. The schematic diagram of fold-deploy shape memory test.

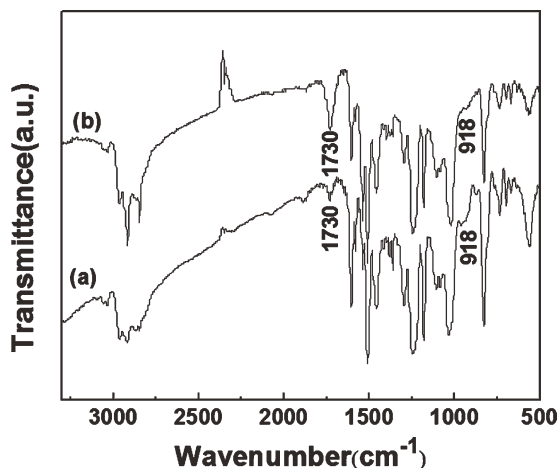


Figure 3. FTIR spectra of EP-100 (a) and 30%SEP-100 (b).

Same points: The absorption bands at 2970 and 2868 cm^{-1} were attributed to saturated C-H stretching vibration. The distortion vibration absorbance peak of C-H appeared at 1453 and 1374 cm^{-1} , respectively. In addition, the stretching vibration of ethers and carbonyls was superimposed, with a peak showing from 1225 to 1344 cm^{-1} . The peaks at 1593 and 1535 cm^{-1} corresponded to the distortion vibration of N-H, and the band at 1104 cm^{-1} was the characteristic absorbance peak of ether C—O—C; these indicated that the curing agent had reacted with matrix resin. The characteristic epoxy peak was observed at 918 cm^{-1} ; however, the peak was inconspicuous, indicating that a majority of epoxy groups had opened their rings and reacted with the curing agent.

Different points: The stronger absorption peak at 1730 cm^{-1} observed in Figure 3(b) represented the —COOH characteristic absorbance peak of APU, suggesting that APU had been introduced by blending APU with E-51.

Tensile and Strength Analysis

The Effect of Different Curing Degrees. Mechanical properties of different curing degrees in 30%SEP systems are listed in Table I. Tensile strength increased with curing degree whereas elongation at break declined. The elongation at break indicated toughness of the polymer. The results also suggested that reducing the degree of cure could improve brittleness; however, the effect was minor because when the degree of cure was less than 80%, the increase of elongation at break was not obvious. On the other hand, the tensile strength of 30%SEP-60 showed a reduction of 23.78% compared with that of 30%SEP-100. A possible reason for this is that fewer effective cross-link networks are formed with the decrease of curing degree, resulting in unreactive resin remaining in the polymers, which produced a plasticization effect but with a reduction in tensile strength. When the curing degree was reduced to a certain extent (under 70%), the cross-link networks were too few to provide adequate strength for resisting macro-deformation, thus the tensile strength and elongation at break changed slightly with the decrease of curing degree. From the above analysis, we concluded that 80% was the optimum curing degree.

The Effect of Different Toughened Degrees. The impact of different toughened degrees on the tensile strength and elongation at break are shown in Table II. The elongation at break of pure epoxy resin system and the 30%SEP-80 system was 1.90% and 3.57%, respectively, showing an enhancement of 87.90%. The elongation at break of 30%SEP-80 blends increased suddenly, which could be explained as follows: The APU as toughening agent dispersed in the curing cross-link nets. When the content of APU was under 25%, the cross-link nets restricted the movement of APU chains, and the distribution of APU chains in the matrix resins was discontinuous. However, when APU content exceeded 30%, the curing cross-link nets could not restrict the movement of chains effectively; the chains would “overflow” beyond the nets, and the APU chains in the resin formed a continuous distribution. APU contained many pliable chains which played a role in improving brittleness; thus, the elongation at break increased suddenly in APU 30 wt %. However, when the APU content was 35 and 40%, the elongation at break was less marked due to the limiting effect of APU chains providing the plasticization. The results suggested that the 30% content was the “inflexion”. On the other hand, with the increase of toughness, tensile strength evidently reduced. In epoxies, low cross-link network density was found to result in lower yield strength and higher fracture toughness than the denser cross-linked epoxy system,^{24,25} hence, a longer-chain structure offered by APU might reduce the cross-linking density, and, therefore, influence tensile strength.

From the above analysis, we concluded that 30%SEP-80 blend has the optimum mechanical properties.

SEM Analysis

SEM micrographs for varies toughened degrees composites are shown in Figure 4. The fracture surface of the neat matrix was smooth and clean with a bearded edge, suggesting it was brittle rupture; a few holes that were observed could be the result of retained bubbles during mixing and drying of the samples [Figure 4(a)]. As APU increased, the fracture surfaces appeared more rugged with a feather-like appearance, which indicated that toughness had increased; however, it still remained brittle [Figure 4(b)]. Figure 4(c–d), on the other hand, showed very coarse fracture surfaces with the appearance of many rugged filaments called “dimples”, a characteristic of ductile rupture. The above analysis revealed that the nature of fracture mechanism had changed from brittle to ductile when the degree of toughness exceeded 20%. From the above results, the addition of APU overcame brittleness effectively.

Table I. Mechanical Properties of Different Curing Degrees in 30%SEP Systems

Mechanical properties	30% SEP-60	30% SEP-70	30% SEP-80	30% SEP-90	30% SEP-100
Tensile strength (MPa)	33.9	35.3	37.7	38.6	44.45
Elongation at break (%)	3.63	3.57	3.57	2.94	2.84

Table II. Mechanical Properties of Different Toughened Degrees in SEP-80 Systems

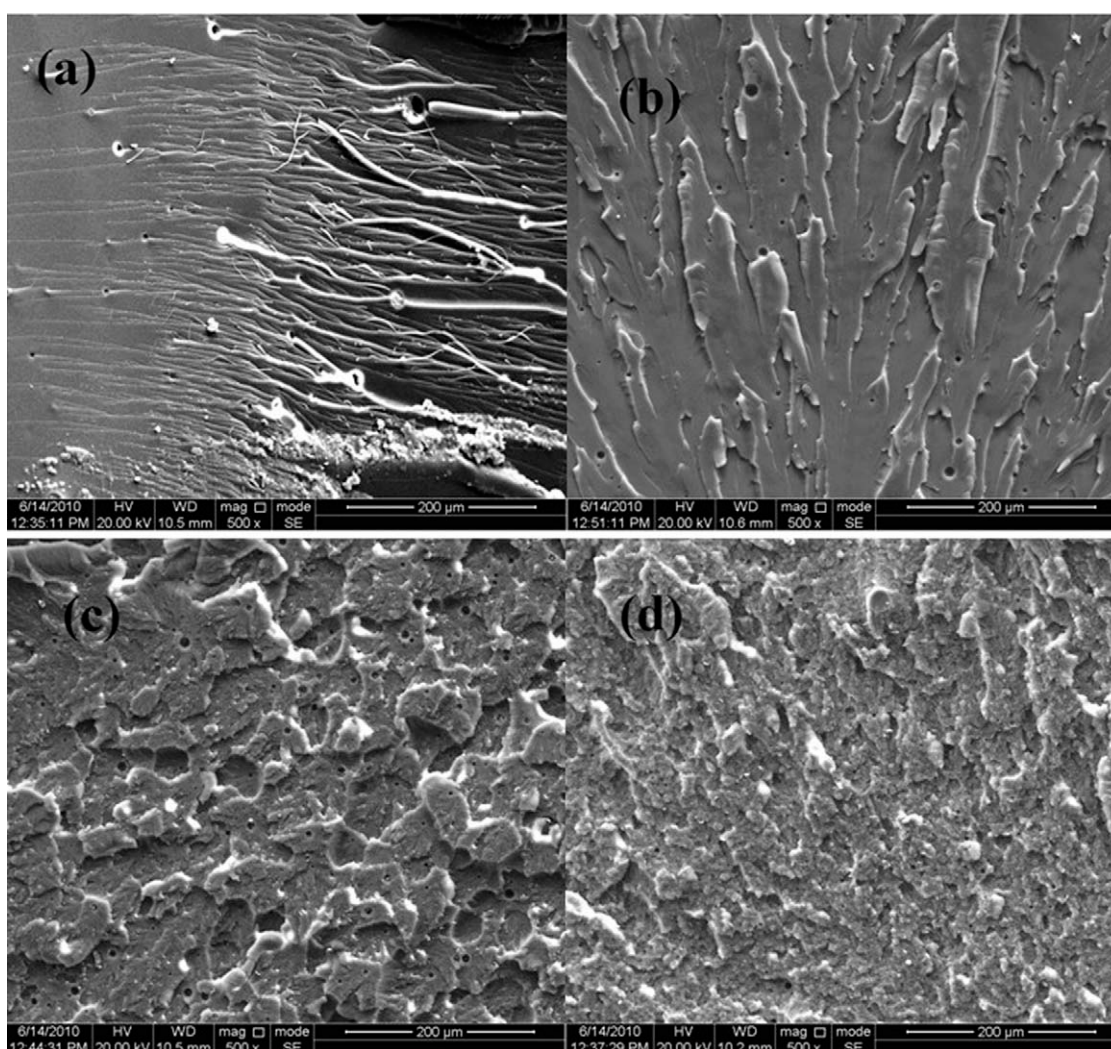
Mechanical properties	SEP-80	10% SEP-80	20% SEP-80	25% SEP-80	30% SEP-80	35% SEP-80	40% SEP-80
Tensile strength (MPa)	64.6	52.8	45.9	44.9	37.7	30.9	24.2
Elongation at break (%)	1.90	2.22	2.26	2.27	3.57	3.68	3.79

DMA Analysis

The thermodynamics properties of the blending polymers are shown in Figure 5, while the main data are listed in Table III.

The shape of $\tan\delta$ -temperature curves for various modified blends are similar, with the curves showing a consistent shift to a lower T_g with increasing toughened degree; the module-temperature curves also shifted to a lower T_g [Figure 5(a)]. Compared with neat resin samples, T_g of the modified system declined to about 15°C, suggesting that the heat resistance only

declined a little by adding APU. On the other hand, T_g of modified blends decreased as the toughened degree increased, due to APU including many flexible chains and active $-\text{COOH}$ groups. The reaction activity of $-\text{COOH}$ provided by APU was less than the epoxy group; it rarely reacted with curing agent and formed fewer effective networks compared with neat resin; thus, with the increase of APU, cross-linking density decreased. Generally speaking, crosslink-density, one of the most important factors influencing T_g , led to a lower T_g because of lower

**Figure 4.** SEM micrographs of APU/epoxy samples (a) EP-80, (b) 10%SEP-80, (c) 20%SEP-80, and (d) 30%SEP-80.

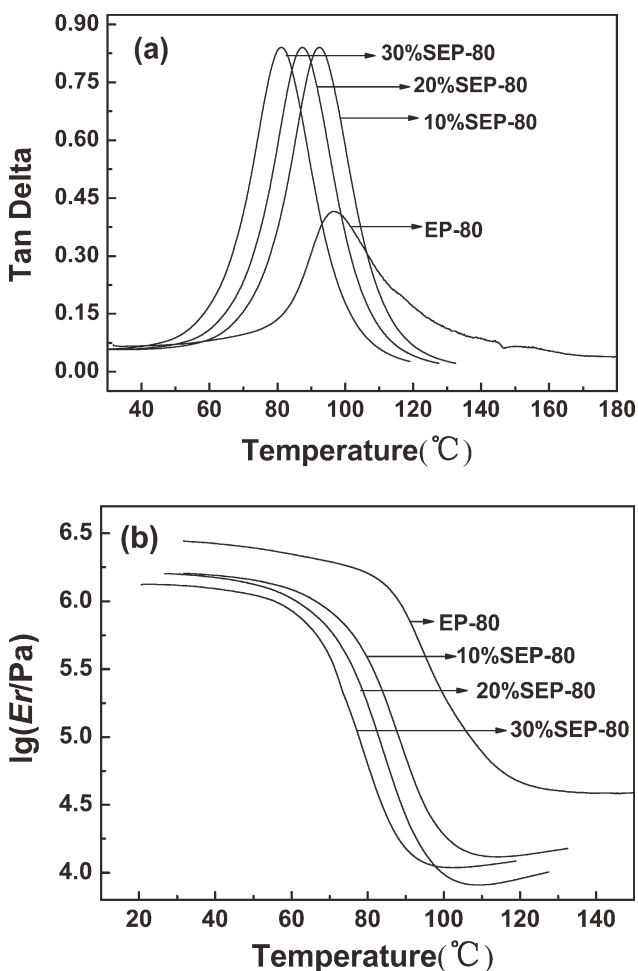


Figure 5. DMA curves of APU/epoxy samples [(a) $\tan \delta$; (b) $\lg(E_r/Pa)$].

cross-link density. Furthermore, the height of internal friction peak $\tan \delta$ clearly increased. This could be explained by the production of carbamate ($-COO-$) due to the chemical reaction of $-COOH$ and $-OH$. The carbamate has a stronger polarity and, therefore, the friction, brought about by the movement of molecular chains, increased. The above results indicated that adding modifier reduced the materials' heat resistance, but not detrimentally.

It was generally recognized that the prominent shape memory materials must have a stable high-elastic state, and the mechanical modulus usually changed about two orders of magnitude when the ambient temperature varied. Figure 5(b) shows that

Table III. DMA Data for APU/Epoxy Shape Memory Composites

Samples	EP-80	10% SEP-80	20% SEP-80	30% SEP-80
$T_{gl}/^{\circ}C$	96.95	92.62	87.47	81.12
$\Delta \lg E_r$	1.862	2.098	2.193	2.099

$\Delta \lg E_r = \lg E_r(\text{maximum}) - \lg E_r(\text{minimum})$.

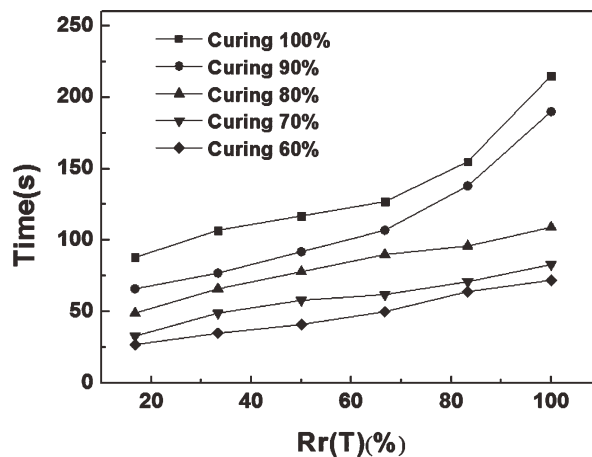


Figure 6. The effect of curing degree on the shape recovery ratio of 30%SEP systems.

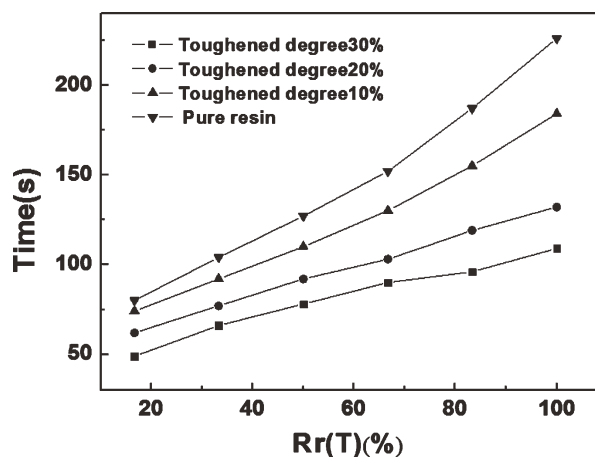


Figure 7. The effect of toughened degree on the shape recovery ratio of SEP-80 systems.

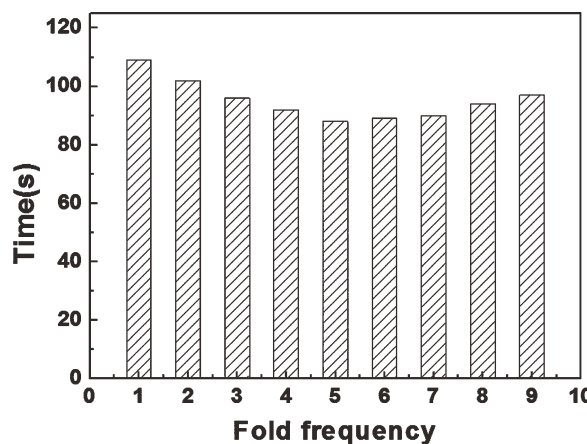


Figure 8. The effect of fold frequency on the shape recovery ratio of 30%SEP-80 system.



Figure 9. Visual demonstration of shape memory properties for 30%SEP-80 (a: original/permanent shapes, b: fixed temporary shapes, c: recovered shapes). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the storage modulus of modified system had changed by more than two orders of magnitude when the temperature changed from 20 to 120°C. This augured well for the property of shape memory materials, which are further examined by the following tests:

Shape Memory Performance

The Effect of Curing Degree on the Shape Recovery Ratio. Figure 6 shows the recovery time of 30%SEP systems with various curing degrees under T_g , according to Table III. All samples recovered their original shape within 4 min, proving that the materials had an excellent shape memory property. It could be seen that the recovery time increased with curing degree. However, the recovery speed of 30%SEP-100 and 30%SEP-90 was significantly slower when the recovery rate exceeded 60%. We reasoned that the cross-linking density here played an important role in limiting recovery. In the 30%SEP-100 and 30%SEP-90 systems, the cross-linking density was higher than others as well as permanent networks, so the binding between the molecular chains would be stronger and movement of segments would be more difficult; therefore, it would take a longer time for complete recovery. However, the difference was not very obvious between 30%SEP-60, 30%SEP-70, and 30%SEP-80 blends, which indicated that the materials possessed excellent shape recovery performance when curing degree was less than 80%.

The Effect of Toughened Degree on the Shape Recovery Ratio. Figure 7 illustrated the recovery time of SEP-80 systems in various toughened degrees under T_g , according to Table III. All specimens recovered rapidly to their original shape, an expected result. With adding of various proportions of modifier, the recovery time declined proportionately. APU contained many pliant chains dispersed evenly in epoxy resin and, therefore, offered more reversible phases. When the blending samples were in a rubbery state under T_g , the pliant chains as reversible phases would have more strength to recover; hence, the high toughened degree system would return to their primitive shapes quickly.

The Effect of Fold Frequency on the Shape Recovery Ratio. Repeatability of shape memory recovery was an important performance parameter for SMPs, characterizing the fatigue resistance of materials. Figure 8 shows the relation between fold frequency and recovery time of 30%SEP-80 at T_g (80°C). The results suggested that the recovery rate of all materials could reach 100%, and no noticeable changes (deformation strain,

shape fixity, and shape recovery) occurred, even with a specimen of a ninefold frequency. The parabolic-like trend of the bar diagram, showed that the recovery time of a fivefold specimen was shortest, about 88 s. This phenomenon was due to the aliphatic chains as reversible phases moving a small amount to overcome friction with frequent bending; thereafter, the molecule became more submissive. Thus, the resistance occurring in multiple cycles improved, and recovery time was reduced. However, material fatigue would occur in high temperature cyclic deformation for many times, demonstrating that the polymer had lost some of its shape memory property. Hence, the shape recovery time increased.

Visual Demonstration of Shape Memory Properties for 30%SEP-80. The shape memory properties of a representative specimen, 30%SEP-80, were visualized in Figure 9. Starting from the original (permanent) rectangular shapes [Figure 9(a)], 30%SEP-80 could be deformed into different shapes through bending and twisting. Upon cooling under load, these deformed temporary shapes [Figure 9(b)] were fixed. Subsequent heating at 80°C allowed complete recovery of the original rectangular shapes [Figure 9(c)] within about 109 s. The recovered shapes were indistinguishable from the original shapes, confirming excellent shape fixity and recovery.

CONCLUSION

A series of modified shape memory epoxy resin (SEP) composites by blending activity polyurethane (APU) were prepared for studying their pervasive performances. The results showed that the appropriate proportion was 30% mass ratio of APU and 80% theory curing degree. Tensile strength of 30%SEP-80 blending was 37.7 MP, elongation at break increased 87.90% compared with the neat epoxy. The fracture mechanism changed from a brittle to ductile, which proved that brittleness had been improved greatly, and T_g was 81.12°C, which was suitable for shape memory materials. 30%SEP-80 system possessed excellent shape memory properties, as shown by recovering its original shape fully within 2 min at glass transition temperature following deformation into different shapes; in addition, there was little effect from a nine-fold deploy cycle.

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