An investigation on shape memory behaviors of epoxy resin system

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Shape-memory epoxy is receiving considerable attention because of its superior mechanical and thermal properties and excellent shape-memory performance. In this study, a novel series of shape-memory epoxy resins are prepared using hydro-epoxy, hexahydrophthalic anhydride, and diglycidyl 4,5-epoxy tetrahydro phthalate (TDE-85) to further improve the recovery force of shape-memory epoxy resins. The thermal, mechanical, and shape-memory properties of the shape-memory epoxy resin system are investigated by differential scanning calorimetry, dynamic mechanical analysis, bend test, and shape recovery test. Results indicate that the glass transition temperature (T_g), rubber modulus, and room-temperature bend strength increase as TDE-85 content increases. Investigation of the shape-memory behavior of the resin reveals that full recovery can be achieved after only several minutes when the temperature is equal to or above T_g. The shape recovery time decreases with the increase in TDE-85 content at T_g, T_g + 10 °C, and T_g + 20 °C. These results are attributed to the increase in TDE-85 content.

I. INTRODUCTION

Shape-memory polymers (SMPs) are a class of smart polymeric materials that can recover the original shape from a temporary shape by external stimuli on demand. Thermal-sensitive SMPs that use temperature change as their external stimulus are the most common SMPs.[1–9] Since the 1960s, covalently cross-linked polyethylene has found broad applications as heat-shrinking films or tubings. The importance of SMPs is gradually being taken seriously to date. In the past 50 years, SMPs have attracted considerable attention because of its unique properties.[10–12]

Common SMP chemical components include polynorbornene,[13] polycaprolactone,[14] polyurethane,[15–18] styrene copolymer,[19,20] and epoxy.[21,22] Among these SMPs, shape-memory epoxy resins have higher modulus and greater thermal and chemical stabilities than the others. They are commonly used as matrix materials in structural composites, which drastically improve the stiffness and shape recovery force of SMPs. Liu et al.[23] investigated the shape-memory properties of epoxy-based.

SMPs with different curing degrees. They found that epoxy-based SMPs with different curing degrees have excellent shape-memory performances and a wide range of well-separated transition temperatures. Xie and Rousseau[24] found that varying the cross-link density by substituting the diamine curing agent with a monoamine could tune the glass transition temperature (T_g) of epoxy-based SMPs. Liu et al.[25] filled shape-memory epoxy with 20 wt% SiC nanopowder, and found that the recovery force of the SMP nanocomposite was also higher than that of pure SMP.

Although shape-memory epoxies have several advantages than the other SMPs, the recovery force of shape-memory epoxy is relatively low, which limit their application.[26,27] To overcome these problems, a novel shape-memory epoxy resin system is prepared in this study using hydro-epoxy, hexahydrophthalic anhydride, and diglycidyl 4,5-epoxy tetrahydro phthalate. The thermal, mechanical, and shape-memory properties of the materials are systematically investigated by differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), bend test, and U-type shape-memory test. Fundamental trends are established between the chemical structure, cross-link density, T_g, rubbery modulus, bend strength, and shape-memory properties.

II. EXPERIMENTAL

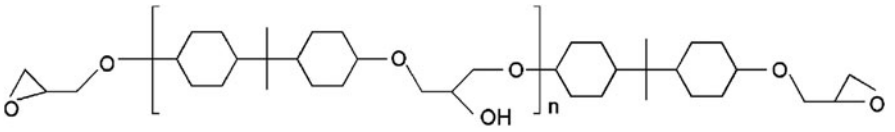
A. Materials

The chemical structures of the reactants are shown in Fig. 1. Hydro-epoxy resin (AL-3040) with an epoxy value of 0.43 eq/100 g was manufactured by Yantai Aolifu Chemical Industry Co., Ltd., People's Republic of China. The diglycidyl 4,5-epoxy tetrahydro phthalate (TDE-85,

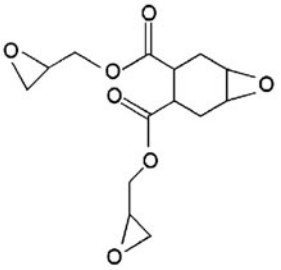
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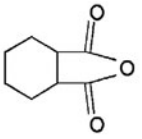
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Hydro-epoxy resin(AL-3040)



TDE-85



HHPA

FIG. 1. Chemical structures of the hydro-epoxy resin, TDE-85, and HHPA.

epoxy value 0.85 eq/100 g) was supplied by Tianjin Jindong Chemical Factory, People's Republic of China. The curing agent hexahydrophthalic anhydride (HHPA) was purchased from Zhejiang Alpharm Chemical Technology Co., Ltd., People's Republic of China. All chemicals were used as received. The detailed formulations of the shape-memory epoxy series are summarized in Table I. After mixing the three-part epoxy (AL-3040, HHPA, and TDE-85), degassing was carried out at 60 °C in a 25-inch Hg vacuum oven to obtain a bubble-free prepolymer. After degassing, the prepolymer solution was placed between two teflon-covered glass plates using a 4 mm thick rubber spacer. Thermal curing program was performed at 80 °C for 5 h, 120 °C for 4 h, and 150 °C for 2 h. Upon the completion of curing, the epoxy samples were demolded and cut into rectangular shapes for DMA, bend, and deformation-recovery tests.

TABLE I. Compositions of the shape-memory epoxy series.

Sample	AL-3040 (mol)	TDE-85 (mol)	HHPA (mol)	TDE-85 (mol%)
A	1	0	2	0
B	0.9	0.1	2.1	3.23
C	0.8	0.2	2.2	6.25
D	0.7	0.3	2.3	9.09
E	0.6	0.4	2.4	11.76

Note: TDG-85 (mol%) is the mole fraction of TDE-85, which is calculated by $n_{\text{TDE-85}}/(n_{\text{AL-3040}} + n_{\text{TDE-85}} + n_{\text{HHPA}}) \times 100\%$.

III. METHODS

A. Fourier transformed-infrared (FT-IR) spectra

Structural changes in the shape-memory epoxy resin were investigated using an FT-IR spectrometer (Nicolet iS10, Thermo-scientific, Waltham, MA) from 4000–500 cm^{-1}.

B. Differential scanning calorimetry

The thermal properties of the shape-memory epoxy resin were characterized using a differential scanning calorimeter (MDSC 2910, TA Instruments Corporation, New Castle, DE) carried out under nitrogen from 40 to 200 °C at a heating rate of 10 °C/min.

C. Dynamic mechanical analysis

The thermomechanical properties of the shape-memory epoxy resin were investigated using a dynamic mechanical analyzer (Q800, TA Instruments Corporation, New Castle, DE) in multifrequency-strain mode from 40 to 200 °C. The sample dimensions were 28 mm^3 × 13 mm^3 × 4 mm^3. The samples were heated at a rate of 3 °C/min, and an

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applied strain of 0.1% was oscillated at a constant frequency of 1 Hz.

D. Bend test

Three-point bending tests were carried out using a universal testing machine (Instron 4467, Instron Corporation, Canton, MA) with rectangular samples at room temperature (20 °C). The span was 64 mm, and the crosshead speed was 2 mm/min. The sample dimensions were 85 mm^3 × 15 mm^3 × 4 mm^3, and the bend strength under fixed deflection (1.5 mm × 4 mm) was measured.

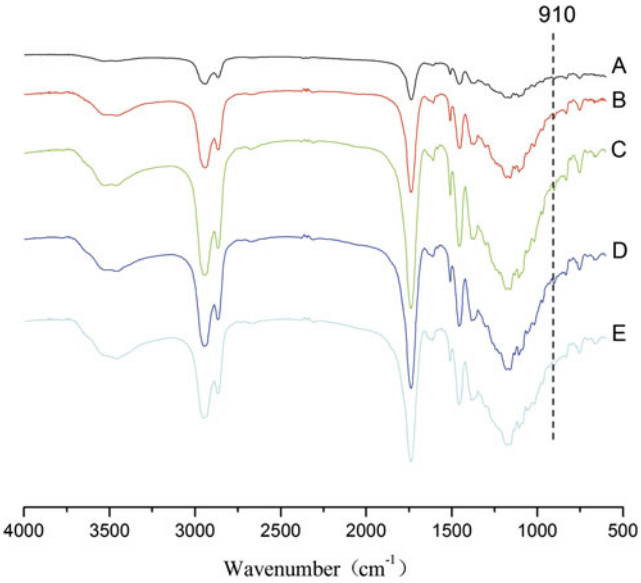


FIG. 2. FT-IR spectra of the shape-memory epoxy series.

E. U-type shape-memory test

Rectangular samples (85 mm^3 × 15 mm^3 × 4 mm^3) were used to evaluate the shape-memory properties of the epoxy resin. Five samples were measured under each condition. A shape-memory test was performed according to the following steps. (i) The samples were heated to T_g, T_g + 10 °C, and T_g + 20 °C in an oven and held for 10 min for full heating. The T_g values were obtained from DMA (tan δ). (ii) The samples were bent into U shapes, circling a center axis with a 10 mm diameter. The bending angle was recorded as θ_{first}. The U-shaped samples were then quickly removed from the oven and dipped into a cold water bath (20 °C) with a constant external force. Afterward, the U-shaped samples were left at room temperature for 2 h, and the bending angle was recorded as θ_{fixed}. (iii) To quantify shape-memory properties, the U-shaped samples were placed in an oven set to the temperature at which they were deformed, and the shape recovery process was observed. When the samples did not change, the recovery time was recorded. This recovery time was designated as the shape recovery time for the said temperature. The bending angle was then recorded as θ_{rec}. The shape fixity ratio (R_f) and shape recovery ratio (R_r) were calculated using Eqs. (1) and (2).

$$R_f = \theta_{fixed}/\theta_{first} \times 100\% \quad , \tag{1}$$

$$R_r = \theta_{fixed} - \theta_{rec}/\theta_{fixed} \times 100\% \quad . \tag{2}$$

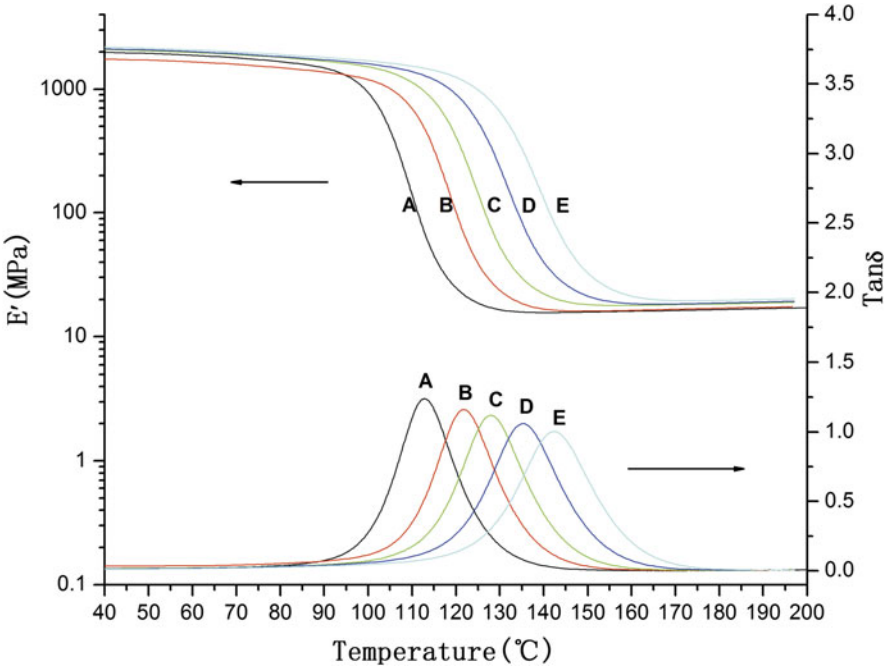


FIG. 3. DMA curves of the shape-memory epoxy series.

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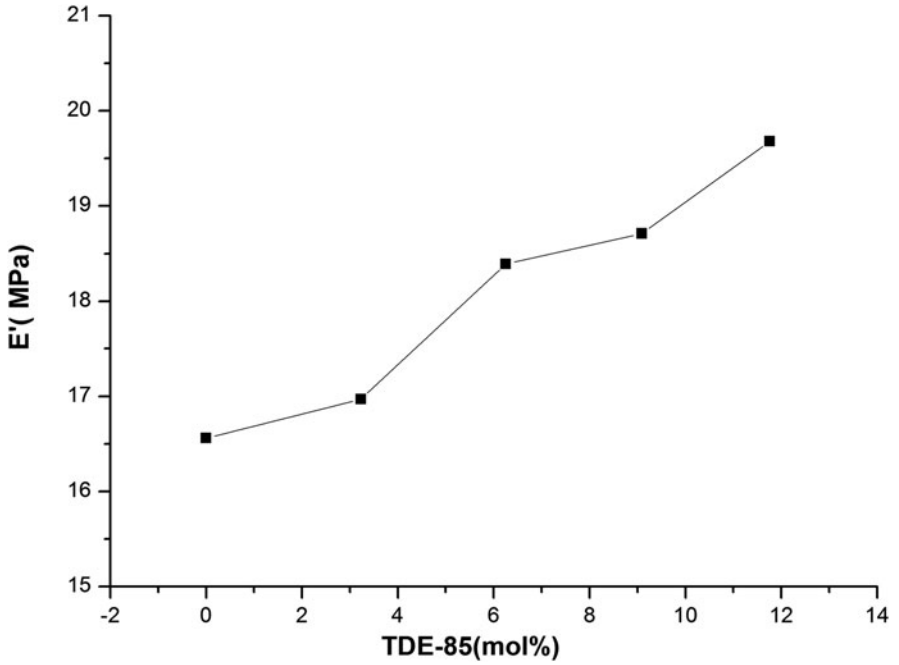


FIG. 4. Relationship between storage modulus and TDE-85 content at 180 °C.

IV. RESULTS AND DISCUSSION

A. FT-IR

Figure 2 shows the FT-IR spectra of the shape-memory epoxy resins from 4000–500 cm^{-1}. No absorption was observed for each polymer at 910 cm^{-1}, which is the characteristic absorption of the epoxy group. The shape-memory epoxy network is based on the reaction of HHPA with a stoichiometric amount of a blend of hydro-epoxy resin and TDE-85; hence, this finding indicates that the epoxy has completely reacted with the curing agent. HHPA contains a carbonyl group (C=O) in its molecular structure; hence, all polymers show strong absorptions at 1740 cm^{-1} because of the stretching vibration of the C=O bond. According to Fig. 2, the absorption of carbon-oxygen double bonds becomes stronger as the TDE-85 content increases in the polymer network. The molar ratio of the carbonyl group in the polymer network improves as the TDE-85 content increases because of the carbonyl groups in TDE-85.

B. Thermal and dynamic mechanical analyses

In this study, the peak of the tan δ versus temperature curve is defined as DMA T_g. A good SMP usually exhibits a change on storage modulus (E') for more than 2–3 orders below and above DMA T_g. Figure 3 shows that the E' below DMA T_g is approximately two orders of magnitude larger than that above DMA T_g, indicating that the shape-memory epoxy resin meets the requirements. For instance, the E' of sample C at 25 °C is 2120 MPa,

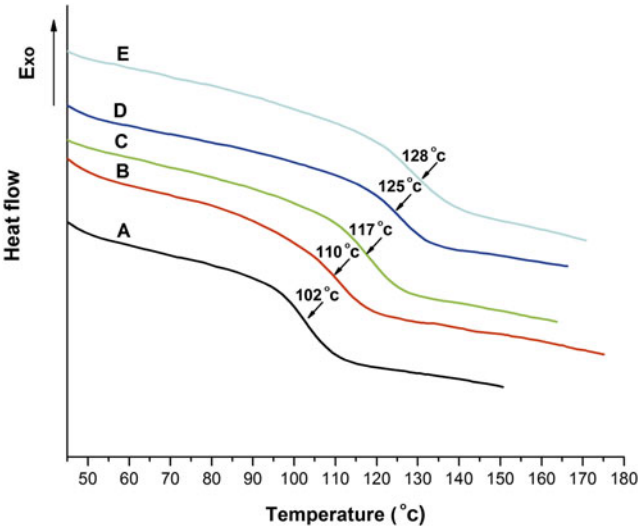


FIG. 5. DSC curves of the shape-memory epoxy series.

but only 17.97 MPa at 165 °C. Figure 3 also reveals that E' increases as the TDE-85 content increases. For a clearer illustration, Fig. 4 reveals the relationship between E' and TDE-85 content at 180 °C. In the shape-memory epoxy resin network, the average molecular weight between cross-link points decreases with increasing tri-functional epoxy resin (TDE-85) content, thereby increasing the cross-link density of the polymer network. Thus, E' increases with increasing TDE-85 content. Figure 4 also reveals that these shape-memory epoxy resins have higher E' than the other shape-memory

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epoxies.[23,28] Thus, these shape-memory epoxy resins have higher recovery force.

A closer examination of Fig. 3 reveals that the DMA T_g of the polymer increases with increasing TDE-85 content. For instance, the DMA T_g of sample A is only 113 °C, whereas the DMA T_g of sample E is 142 °C. T_g is the essential transition temperature from the freezing to free-motion states of segments in a polymer network. In the shape-memory epoxy resin network, the cross-link density increases with increasing TDE-85 content.

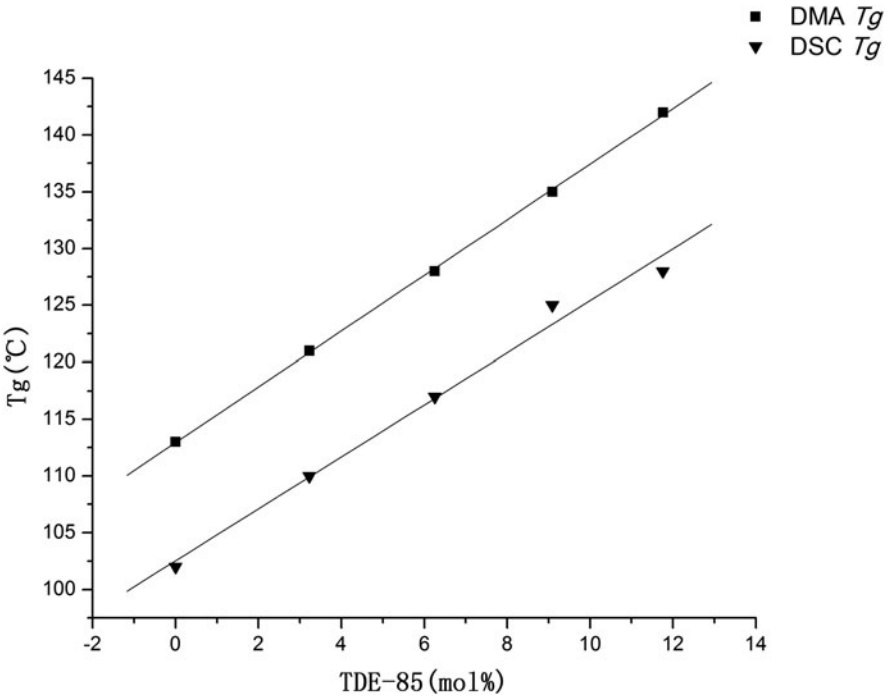


FIG. 6. T_g values of the shape-memory epoxy series.

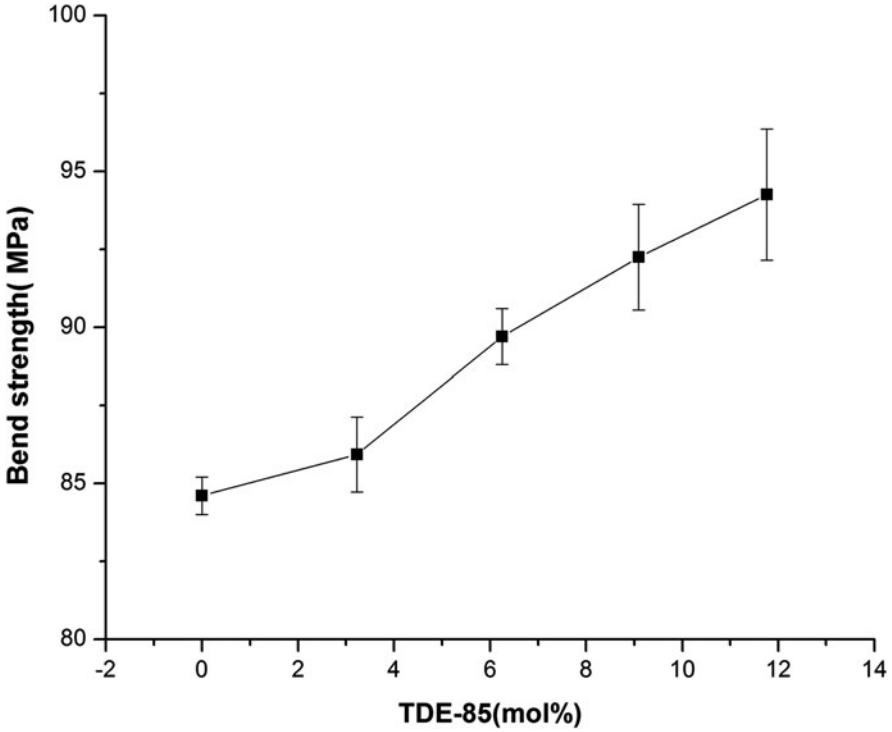


FIG. 7. Relationship between bend strength and TDE-85 content at room temperature.

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Consequently, the segment movement is hindered, leading to increase in DMA T_g. Similar results have been reported for other shape-memory epoxies.[29]

Figure 3 also reveals the decrease in relaxation peak height of the polymer with increasing TDE-85 content. Relaxation peak height is associated with molecular mobility, revealing that molecular mobility decreases with increasing TDE-85 content.

These polymers are further characterized using DSC, and the curves are shown in Fig. 5. The T_g values obtained from the DSC analysis are also marked in Fig. 5. In the discussion below, DSC T_g is used to represent the T_g value measured by DSC. As shown in Fig. 5, all polymers exhibit distinct DSC T_g values ranging from 102 to 128 °C, which gradually increase with increasing TDE-85 content. For a clearer illustration, T_g values obtained from DSC and DMA are summarized in Fig. 6. The T_g values obtained from DSC are approximately 12 °C lower than those obtained from DMA. This difference may be attributed to the frequency effect in the DMA test, consistent with previous studies.[30,31]

C. Mechanical property analysis

The relationship between bend strength and TDE-85 content at room temperature is shown in Fig. 7. The bend strength gradually increases with increasing TDE-85 content at room temperature. For instance, the bend strength of sample A at 25 °C is only 84.61 MPa, whereas that of sample E is 94.25 MPa. Notably, the bend strength of the material is increased by 11.39% with the addition of 11.76 mol% TDE-85. In the epoxy network, the cross-link points are completely responsible for carrying the load; thus, increase in bend strength is expected with increasing cross-link density.

D. Shape-memory property analysis

To investigate the shape-memory properties of the epoxy series, the samples were tested at T_g, T_g + 10 °C, and T_g + 20 °C using the U-type shape-memory test. The T_g values were obtained by DMA (tan δ). According to the results, the shape fixity ratio of the shape-memory epoxy series (sample A through E) can reach 100% regardless of the deformation temperature used. The results also

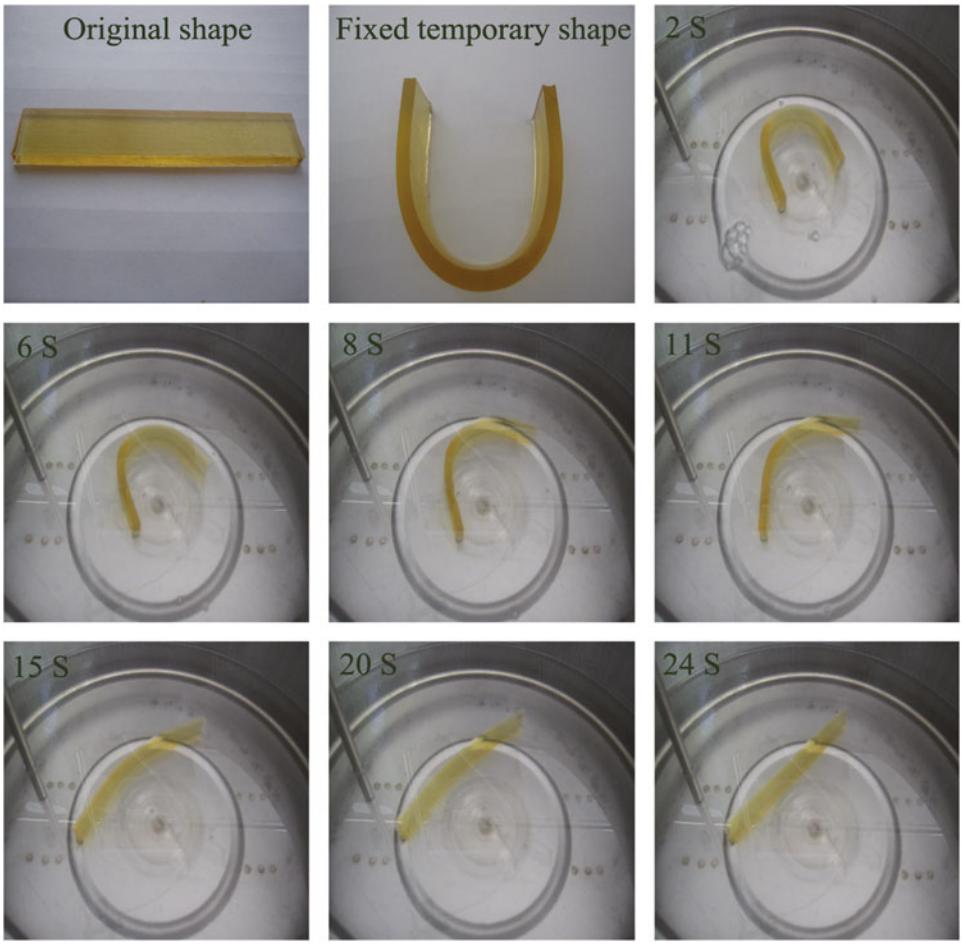


FIG. 8. The shape recovery process of sample C in a 130 °C paraffin oil bath.

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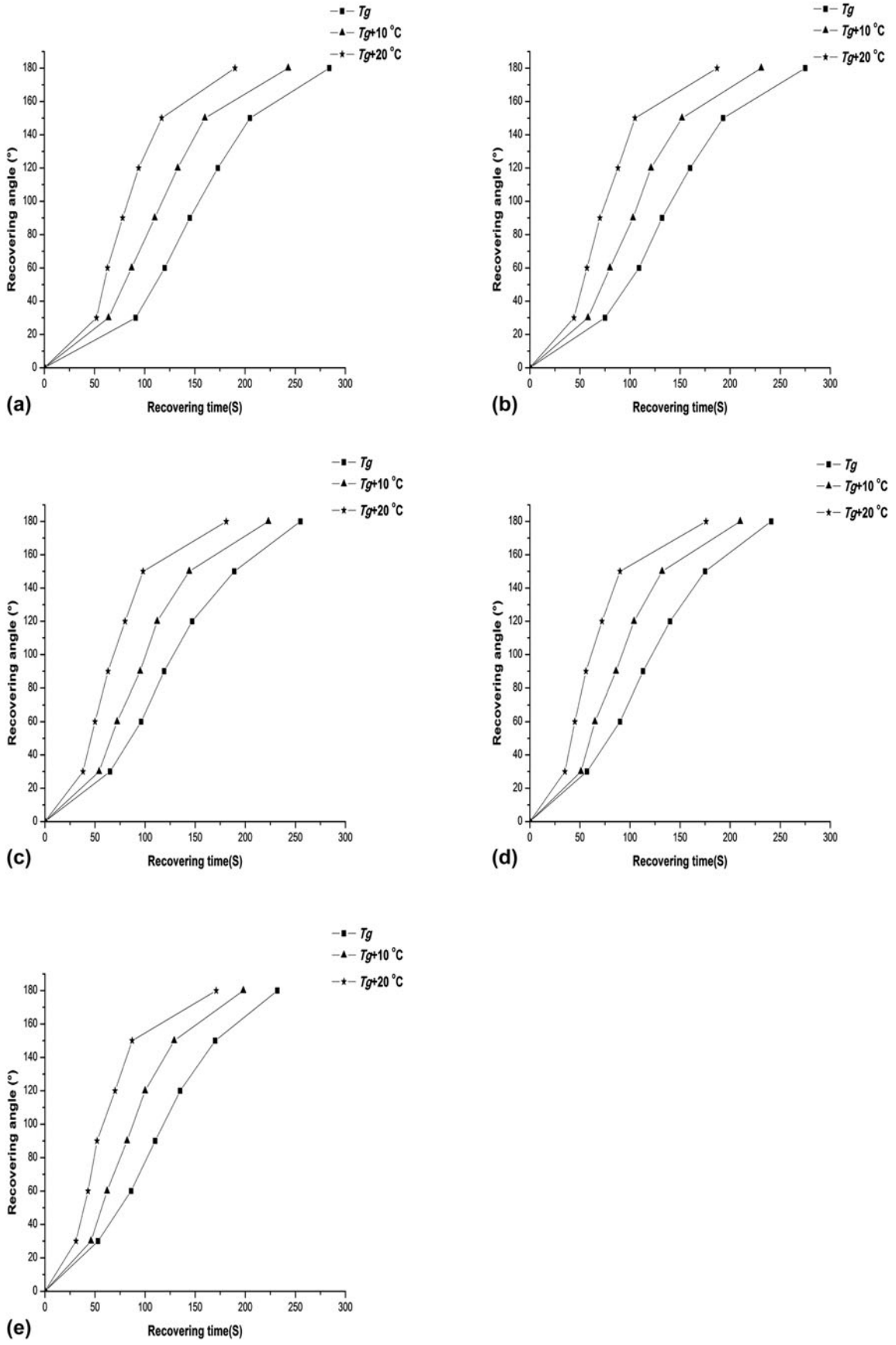


FIG. 9. Relationship between recovering angle and recovering time of the shape-memory epoxy series at different temperatures.

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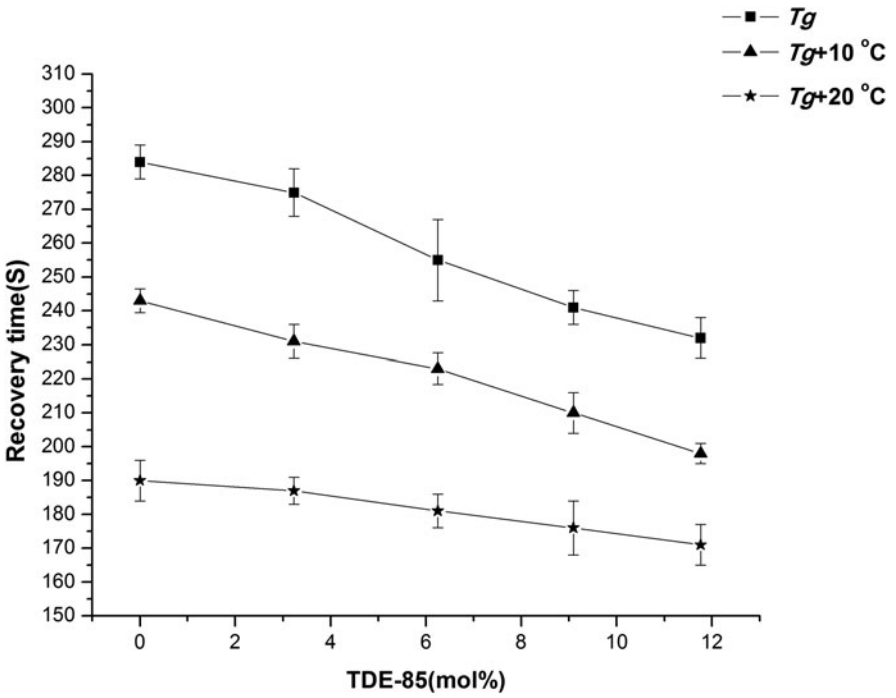


FIG. 10. Relationship of shape recovery time and TDE-85 content at different temperatures.

show that full recovery can be observed after only several minutes at T_g, T_g + 10 °C, and T_g + 20 °C; hence, the shape recovery ratio of the series can reach 100%. Figure 8 shows a series of photographs on the shape recovery process of sample C in a 130 °C paraffin oil bath. The U-shaped specimen is obtained by vacuum casting. The U-shaped specimen is heated to 130 °C in an oven and held for 10 min for full heating. The specimen is then deformed into a straight shape through bending. Upon cooling under load, the deformed temporary shape is fixed. Full recovery is observed after only 16 s when the specimen is placed in a 130 °C paraffin oil bath.

Figure 9 shows the relationship between recovery angle and recovery time of the shape-memory epoxy series at T_g, T_g + 10 °C, and T_g + 20 °C. Figure 9 reveals that the slope of the curve is generally higher from 30° to 150°, indicating a relative low recovery rate at the start and terminal stage. This phenomenon can be explained by the possibility that the release of internal stress is followed by a relatively strong friction between the segments at the start stage, thereby decreasing the recovery rate. At the final stage, the stored strain energy is released in large quantities at the incipient stage, thereby slowing the recovery rate. The same trend of shape recovery rate has been reported in the literature.[32]

The relationship between shape recovery time and TDE-85 content at T_g, T_g + 10 °C, and T_g + 20 °C is shown in Fig. 10. The shape recovery time gradually decreases with increasing TDE-85 content. In the U-type shape-memory test, the strain energy is stored in the form of internal stress in a temporary shape. Figure 3 shows that E' increases with increasing TDE-85 content, indicating that more strain energy is stored as AG-80 content increases, during which the sample is deformed. Thus, the shape recovery time decreases with increasing TDE-85 content.

V. CONCLUSION

A shape-memory epoxy resin system is prepared using hydro-epoxy, HHPA, and diglycidyl 4,5-epoxy tetrahydro phthalate. The effect of TDE-85 content on the thermal, mechanical, and shape-memory properties of shape-memory epoxy resin is studied in detail. DSC and DMA measurements on the shape-memory epoxy resins show that the T_g and rubber modulus gradually increase as TDE-85 content increases. The room-temperature bend strength of the material increases with increasing TDE-85 content. The U-type shape-memory test on these shape-memory epoxy resins shows that they have excellent shape-memory performances. The shape recovery time of shape-memory epoxy resin systems decreases with increasing TDE-85 content. These results are attributed to the increase in TDE-85 content.

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REFERENCES

1. K. Hearon, C.J. Besset, A.T. Lonnecker, T. Ware, W.E. Voit, T.S. Wilson, K.L. Wooley, and D.J. Maitland: A structural approach to establishing a platform chemistry for the tunable, bulk electron beam cross-linking of shape memory polymer systems. *Macromolecules* **46**, 8905 (2013).
2. Y.K. Bai, C. Jiang, Q.H. Wang, and T.M. Wang: Multi-shape-memory property study of novel poly(ε-caprolactone)/ethyl cellulose polymer networks. *Macromol. Chem. Phys.* **214**, 2465 (2013).
3. T. Xie, X.C. Xiao, and Y.T. Cheng: Revealing triple-shape memory effect by polymer bilayers. *Macromol. Rapid Commun.* **30**, 1823 (2009).
4. L. Domeier, A. Nissen, S. Goods, L.R. Whinnery, and J. McElhanon: Thermomechanical characterization of thermoset urethane shape-memory polymer foams. *J. Appl. Polym. Sci.* **115**, 3217 (2010).
5. N. Lakhera, C.M. Laursen, D.L. Safranski, and C.P. Frick: Biodegradable thermoset shape-memory polymer developed from poly(β-amino ester) networks. *J. Polym. Sci., Part B: Polym. Phys.* **50**, 777 (2012).
6. J.T. Fulcher, H.E. Karaca, G.P. Tandon, and Y.C. Lu: Thermomechanical and shape memory properties of thermo-setting shape memory polymer under compressive loadings. *J. Appl. Polym. Sci.* **129**, 1096 (2013).
7. L. Sun, W.M. Huang, Z. Ding, Y. Zhao, C.C. Wang, H. Purnawali, and C. Tang: Stimulus-responsive shape memory materials: A review. *Mater. Des.* **33**, 577 (2012).
8. W.M. Huang, Y. Zhao, C.C. Wang, Z. Ding, H. Purnawali, C. Tang, and J.L. Zhang: Thermo/chemo-responsive shape memory effect in polymers: A sketch of working mechanisms, fundamentals and optimization. *J. Polym. Res.* **19**, 9952 (2012).
9. X.L. Wu, W.M. Huang, and H.X. Tan: Characterization of shape recovery via creeping and shape memory effect in ether-vinyl acetate copolymer (EVA). *J. Polym. Res.* **20**, 150 (2013).
10. L. Santo: Shape memory epoxy foams: New materials for aerospace applications. *Mater. Sci. Forum* **706**, 165 (2012).
11. L. De Nardo, S. Bertoldi, M.C. Tanzi, H.J. Haugen, and S. Farè: Shape memory polymer cellular solid design for medical applications. *Smart Mater. Struct.* **20**, 035004 (2011).
12. Y.Y.F. Chan Vili: Investigating smart textiles based on shape memory materials. *Text. Res. J.* **77**, 290 (2007).
13. D. Yang, W. Huang, J.H. Yu, J.S. Jiang, L.Y. Zhang, and M.R. Xie: A novel shape memory polynorbornene functionalized with poly(ε-caprolactone) side chain and cyano group through ring-opening metathesis polymerization. *Polymer* **51**, 5100 (2010).
14. D.M. Le, K. Kulangara, A.F. Adler, K.W. Leong, and V.S. Ashby: Dynamic topographical control of mesenchymal stem cells by culture on responsive poly(Iμ-caprolactone) surfaces. *Adv. Mater.* **23**, 3278 (2011).
15. N.G. Sahoo, Y.C. Jung, H.J. Yoo, and J.W. Cho: Influence of carbon nanotubes and polypyrrole on the thermal, mechanical and electroactive shape-memory properties of polyurethane nanocomposites. *Compos. Sci. Technol.* **67**, 1920 (2007).
16. M. Milad, R.N. Mohammad, and B. Mehdi: Effect of block ratio and strain amplitude on thermal, structural, and shape memory properties of segmented polycaprolactone-based polyurethanes. *J. Mater. Sci.* **49**, 7575 (2014).
17. J.J. Han, G.X. Fei, G. Li, and H.S. Xia: High intensity focused ultrasound triggered shape memory and drug release from biodegradable polyurethane. *Macromol. Chem. Phys.* **214**, 1195 (2013).
18. B. Xu, Y.Q. Fu, W.M. Huang, Y.T. Pei, Z.G. Chen, J.T.M. De Hosson, A. Kraft, and R.L. Reuben: Thermal-mechanical properties of polyurethane-clay shape memory polymer nanocomposites. *Polymer* **2**, 31 (2010).
19. B. Richard, G. Korey, and M.W. Lisa: Mechanical and curing properties of a styrene-based shape memory polymer. *J. Intell. Mater. Syst. Struct.* **21**, 677 (2010).
20. P.Z. Fei and K.A. Cavicchi: Synthesis and characterization of a poly(styrene-block-methylacrylate-random-octadecylacrylate-block-styrene) shape memory ABA triblock copolymer. *ACS Appl. Mater. Interfaces* **2**, 2797 (2010).
21. D.M. Feldkamp and I.A. Rousseau: Effect of the deformation temperature on the shape-memory behavior of epoxy networks. *Macromol. Mater. Eng.* **295**, 726 (2010).
22. N. Zheng, G.Q. Fang, Z.L. Cao, Q. Zhao, and T. Xie: High strain epoxy shape memory polymer. *Polym. Chem.* **6**, 3046 (2015).
23. Y.Y. Liu, C.M. Han, H.F. Tan, and X.W. Du: Thermal, mechanical and shapememory properties of shape memory epoxy resin. *Mater. Sci. Eng., A* **527**, 2510 (2010).
24. T. Xie and I.A. Rousseau: Facile tailoring of thermal transition temperatures of epoxy shape memory polymers. *Polymer* **50**, 1852 (2009).
25. Y.P. Liu, K. Gall, M.L. Dunn, and P. McCluskey: Thermomechanics of shape memory polymer nanocomposites. *Mech. Mater.* **36**, 929 (2004).
26. Q.H. Meng and J.L. Hu: A review of shape memory polymer composites and blends. *Composites, Part A* **40**, 1661 (2009).
27. I.S. Gunes and S.C. Jana: Shape memory polymers and their nanocomposites: A review of science and technology of new multifunctional materials. *J. Nanosci. Nanotechnol.* **8**, 1616 (2008).
28. J.S. Leng, X.L. Wu, and Y.J. Liu: Effect of a linear monomer on the thermomechanical properties of epoxy shape-memory polymer. *Smart Mater. Struct.* **18**, 095031 (2009).
29. K. Wei, G.M. Zhu, Y.S. Tang, T.T. Liu, and J.Q. Xie: The effects of crosslink density on thermo-mechanical properties of shape-memory hydro-epoxy resin. *J. Mater. Res.* **28**, 2903 (2013).
30. S.J. Sheng, X. Hu, F. Wang, Q.Y. Ma, and M.F. Gu: Mechanical and thermal property characterization of poly-L-lactide (PLLA) scaffold developed using pressure-controllable green foaming technology. *Mater. Sci. Eng., C* **49**, 612 (2015).
31. R.C. Zhang, R. Li, A. Lu, Z.J. Jin, B.Q. Liu, and Z.B. Xu: The glass transition temperature of poly(phenylene sulfide) with various crystallinities. *Polym. Int.* **62**, 449 (2013).
32. K. Wei, G.M. Zhu, Y.S. Tang, G.M. Tian, and J.Q. Xie: Thermomechanical properties of shape-memory hydro-epoxy resin. *Smart Mater. Struct.* **21**, 055022 (2012).

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