

Toughening-Modified Epoxy-Amine System: Cure Kinetics, Mechanical Behavior, and Shape Memory Performances

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ABSTRACT: Shape memory epoxy resins are derived on reacting E51 with triethylenetetramine in presence of the toughening agent polypropylene glycol diglycidyl ether (PPGDGE). The curing behaviors are studied with differential scanning calorimetry. The toughening system shows a decrease in activation energy. Šesták–Berggren model is utilized to establish the kinetic equations. The fitting results prove that the equations can well describe the reactions. Tensile tests and dynamic mechanical analysis are used to analyze mechanical performances and thermodynamics. Shape memory properties are characterized by fold-deploy tests. The elongation at break increases as the concentration of PPGDGE increases. The toughening materials have lower glass transition temperature (T_g). The fixable ratios of all systems are greater than 99.5%. The shape recovery time decreases with increasing the PPGDGE concentration. The optimal system can fully recover its original shape in about 2 min at $T_g + 30^\circ\text{C}$, and exhibit the maximum fold-deploy cycles as 13 cycles. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40853.

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INTRODUCTION

In recent years, increased interests have focused on the shape memory materials, which can be used in electronics, aircraft, and aerospace fields, such as actuators and space deployable structure.^{1–4} For one polymer material to possess shape memory performance, it can be accomplished by changing the work temperature to below or above the temperature of the glass transition region (T_g).^{5,6} The shape memory polymer can be folded to various shapes by heating up it above T_g to make it soft. Cooling down the polymer below T_g leads to temporary fixation of the shape. The folded material can restore the original shape at a temperature above T_g .^{7–12} The above description indicates that shape memory polymer can achieve a repeatable process of folding and deployment. The driving factor of shape recovery performance is the elastic strain generated in deformation process.^{13,14}

So far, a great deal of polymers have been found with shape memory effects, such as transpolyisoprene, segmented polyurethane, polynorbornene, styrene-butadiene copolymers, and epoxy-based polymers.^{13,15–19} In these materials, shape-memory epoxy resins have attracted considerable attention recently for their excellent chemical resistance, easy processability, and high modulus.^{19–24} The remarkable properties result from the highly

cross-linked structure of epoxy resins. However, the highly cross-linked epoxy resins are usually relatively brittle^{25,26} and easy to emerge brittle failure during the process of folding and deployment. The unfavorable characteristics pose significant challenges on their shape memory property. Therefore, working on improving the toughness of the highly cross-linked epoxy resins is necessary. The improvement of toughness can not only lower the risk of damage caused by external force through increasing flexibility of materials, but also improve the maximum folding cycles of shape memory materials. Due to the toughened objects are shape memory materials, which require the toughening agent not to have an adverse effect on the shape memory properties, especially the ability of shape fixity. The low molecular weight aliphatic epoxy is a good and optional toughening agent, which has a good compatibility with the original epoxy, and can react with curing agent to form network structure as the original epoxy, without adversely affecting the shape memory properties of cured epoxy resins.

In this article, polypropylene glycol diglycidyl ether (PPGDGE) toughened shape memory epoxy resins were developed with different PPGDGE weight fractions to improve the toughness of epoxy resins. The cure kinetics and thermal performances of the epoxy systems were measured using the thermal analysis method of differential scanning calorimetry (DSC). The

mechanical properties were determined using an electron-mechanical universal material testing machine. The dynamic mechanical analysis (DMA) was also performed and the shape memory properties of shape fixation and shape recoverability characterization were examined. The results are discussed concerning the effects of the content of PPGDGE on the material's properties.

EXPERIMENTAL

Materials

The epoxy resin (Type E51 with an epoxy number of 0.51 mol/100 g) used in this study was purchased commercially, which was made by Bluestar New Chemical Materials Co., China. The triethylenetetramine (TETA) was used as cross-linking agent, which was obtained from Tianjin Tianda Chemical Reagent Co., China. The modifier used was PPGDGE with an epoxy number of 0.32 mol/100 g supplied by Xiya Reagent Co., China. The epoxy number was determined according to ASTM standard D 1652-11. All chemicals were used without any further purification.

Preparation of E51-TETA-PPGDGE Thermoset System

The storage modulus at rubbery state of fully cured pure E51 system was too high to accomplish large deformation as reported in our previous work,¹¹ so a theoretical curing degree (the rate of the number of reacted epoxy groups to the overall number of epoxy groups) of 80% was chosen for the research to assess the effect of toughening agent. The epoxy resin samples were marked as ETP-*x*, where *x* represented the mass ratio of PPGDGE to the total mass of TETA and PPGDGE. For instance, the neat resin was marked as ETP-0, and the toughening resin with 11 wt % of PPGDGE was marked as ETP-11%. In this study, four blends with different content of PPGDGE (*x* was 11, 15, 17, and 19%, respectively) were prepared. The E51-TETA-PPGDGE systems were made by the following procedure. The investigation samples were prepared by mixing the E51 and PPGDGE components in a required proportion and TETA was added. Then, the mixtures were degassed under vacuum to remove the entrapped air bubbles, poured into stainless steel molds, and cured for some time at certain temperature. The cure reactions of E51/PPGDGE with TETA are shown in Figure 1, which are proposed based on the reactions of epoxy-amino groups as described in other literatures.^{27,28} During the chemical reactions, the primary amino groups transform into secondary and tertiary amino groups by the epoxide ring-opening reactions. The cure temperature and cure time were determined from DSC studies, which will be discussed in detail later. After the samples were thoroughly cured, they were taken out to investigate the thermal performances, mechanical and shape memory properties.

Characterization Methods

The cure kinetics and curing process were examined by DSC. The nonisothermal DSC measurements were performed with Mettler DSC-1 analyzer for data acquisition, scanning over a temperature range from 20 to 200°C with different heating rates (5, 10, 15, and 20°C min⁻¹), conducted in a nitrogen atmosphere at a flow rate of 20 cm³ min⁻¹. The preparation of testing samples was in a dry atmosphere. Three to eight milligram

mixed E51-TETA-PPGDGE samples with different proportions were added to the aluminum pans and analyzed.

To study the effect of PPGDGE on the mechanical properties of final epoxy resin specimens, uniaxial tensile tests were conducted using an electromechanical universal material testing machine (Instron 5965). This machine was equipped with a measuring load cell at a crosshead velocity of 5 mm min⁻¹ and a gauge length of 10 mm at 20 ± 2°C. The dimensions of dumbbell-shaped samples were according to GB/T 1042.2/5A/2 standard in China. At least three specimens were tested, and the average was plotted.

The DMA was performed on a Mettler SDTA861e analyzer to obtain the storage modulus and loss tangent (tan δ) of the specimens. Shear mode was used with heating rate 3°C min⁻¹ from 20 to 150°C. The sample size was 10 × 10 × 2 mm³.

Shape memory performance analysis was performed as reported by our previous work.²⁹ The rectangular specimens [90 × (15 ± 0.2) × (2 ± 0.2) mm³] were used to quantify shape memory properties. The samples were heated at a bending temperature (*T_b*) above their *T_g* (e.g., *T_b* = *T_g* + 20°C) and held 10 min, then bended to U type at this temperature and cooled naturally to room temperature without removing the external force for 10 min. The maximum bending angle was 180°. After the external force was unloaded, a tiny recovery occurred and the bending angle became *θ_f*. The fixable ratio (defined as *θ_f*/180° × 100%) was measured. Subsequently, the samples were heated from room temperature to *T_b* and dynamic recovery occurred. The recovery time was recorded when the recovery angle was 180°.

RESULTS AND DISCUSSION

DSC Analysis

DSC investigations have been performed at variable heating rates in the temperature range of 20–200°C to determine the cure temperature according to the method described in another article.³⁰ To study the cure time at different cure temperatures, the cure kinetic equations were derived through the Šesták–Berggren (S–B) model.³¹ The S–B model is a two-parameter autocatalytic model, which gives a better description of the kinetic process compared with other nonisothermal autocatalytic models. The activation energy in the kinetic equation for the curing of epoxy resin was obtained by isoconversional method,³² which is much more accurate in detecting curing kinetics parameters than model-fitting method because of the model-free kinetics feature of isoconversional method.

Cure Temperatures. The nonisothermal DSC was carried out for the three epoxy resin systems (ETP-0, ETP-11%, and ETP-15%) with different contents of PPGDGE, at variable heating rates (5, 10, 15, and 20°C min⁻¹). The initial cured temperature (*T_i*), peak temperature (*T_p*), and final temperature (*T_f*) for all the three samples at different heating rates (*β*) are shown in Figure 2. To eliminate the influence of heating rate, the data were linear fitted, then *T_i*, *T_p*, and *T_f* of the resin systems can be determined by extrapolating to *β* = 0.³⁰ The results obtained from the linear fitting for the three samples are listed in Table I.

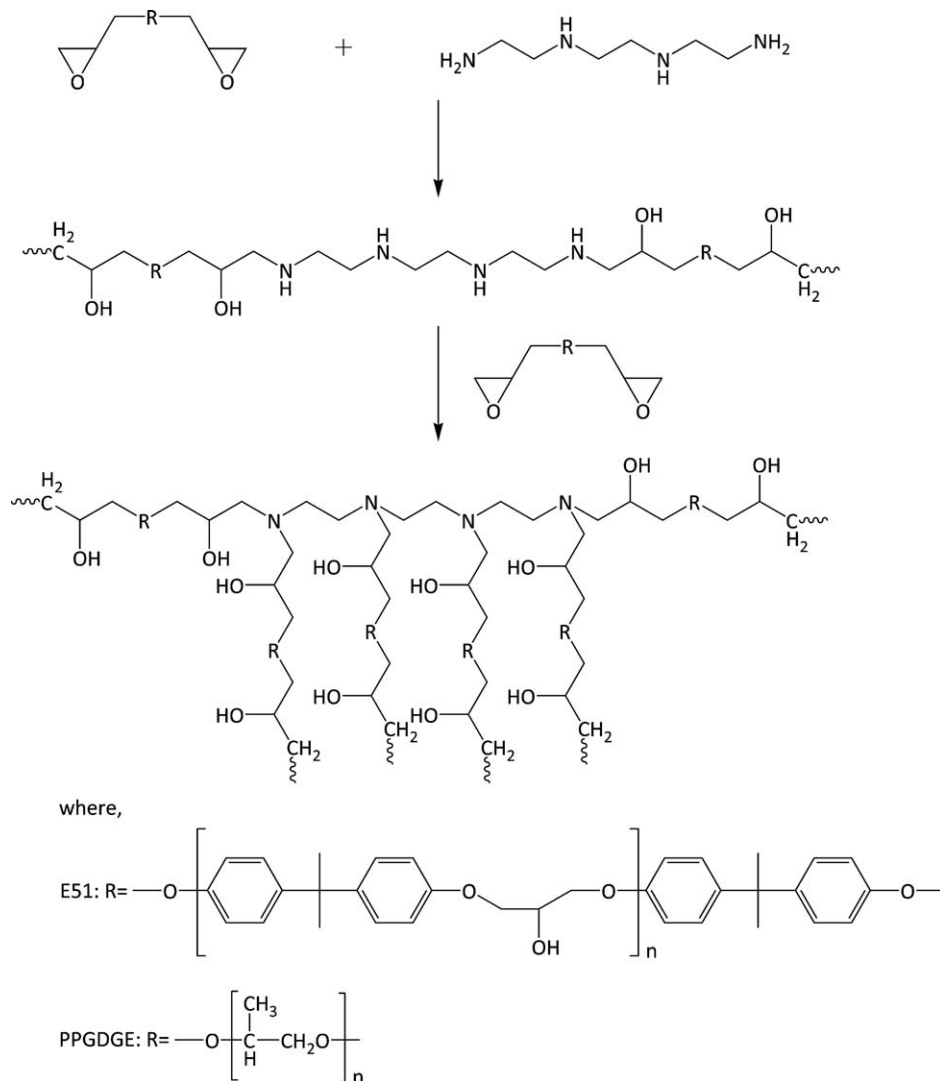


Figure 1. Cure reactions of E51/PPGDGE with TETA.

The observed data indicate that T_p , T_p and T_f of the three samples remain nearly unchanged. T_i is near room temperature, which proves that TETA is a kind of room-temperature cross-linking agent. The curing reaction can be carried out at low temperature over long periods of time, or performed at high temperature within a short period of time. Both of the two ways have their own weak points. The former can cause incomplete reaction and a low glass transition temperature of cured epoxy resin. The latter will bring large numbers of flaw on cured epoxy resin due to the fast and drastic reaction. To compensate for the deficiencies of isothermal curing process, the temperature programmed mode was used. Based on the theoretical analysis as well as the practical curing process, three cure temperatures (35, 100, and 140°C) were adopted in the temperature programmed process. The specific cure time at different temperatures will be determined later according to the cure kinetic equations.

Isoconversional Method. The activation energy E_a was estimated by the Flynn–Wall–Ozawa (FWO) isoconversional method³³ that obtains the variational activation energy with the

extent of conversion (α). The FWO equation is expressed as follows:

$$\lg \beta = \lg \left(\frac{AE_a}{G(\alpha)R} \right) - 2.315 - 0.4567 \frac{E_a}{RT} \quad (1)$$

where, β is the heating rate (5, 10, 15, and 20°C min⁻¹ in this article), A is the pre-exponential factor, $G(\alpha)$ is the integral mechanism function, R is gas constant, and T represents the absolute temperature corresponding to a given conversion α at different heating rates. To calculate E_a of the cure reaction, the slope of $\lg \beta$ versus $1/T$ was yielded, which equals $-0.4567E_a/R$.

The dependencies of the activation energy E_a obtained from the slope on conversion α for ETP-0 and ETP-11% are shown in Figure 3. As shown in Figure 3, the activation energy E_a varies with the extent of conversion α . E_a depends not only on temperature but also on the reaction mechanism and the diffusion rate of reactive groups. An increase in the activation energy is observed at the initiation of curing reaction, because the initial viscosity of the mixture is very low. Low viscosity leads to better mixing and hence better reaction, so the initial activation

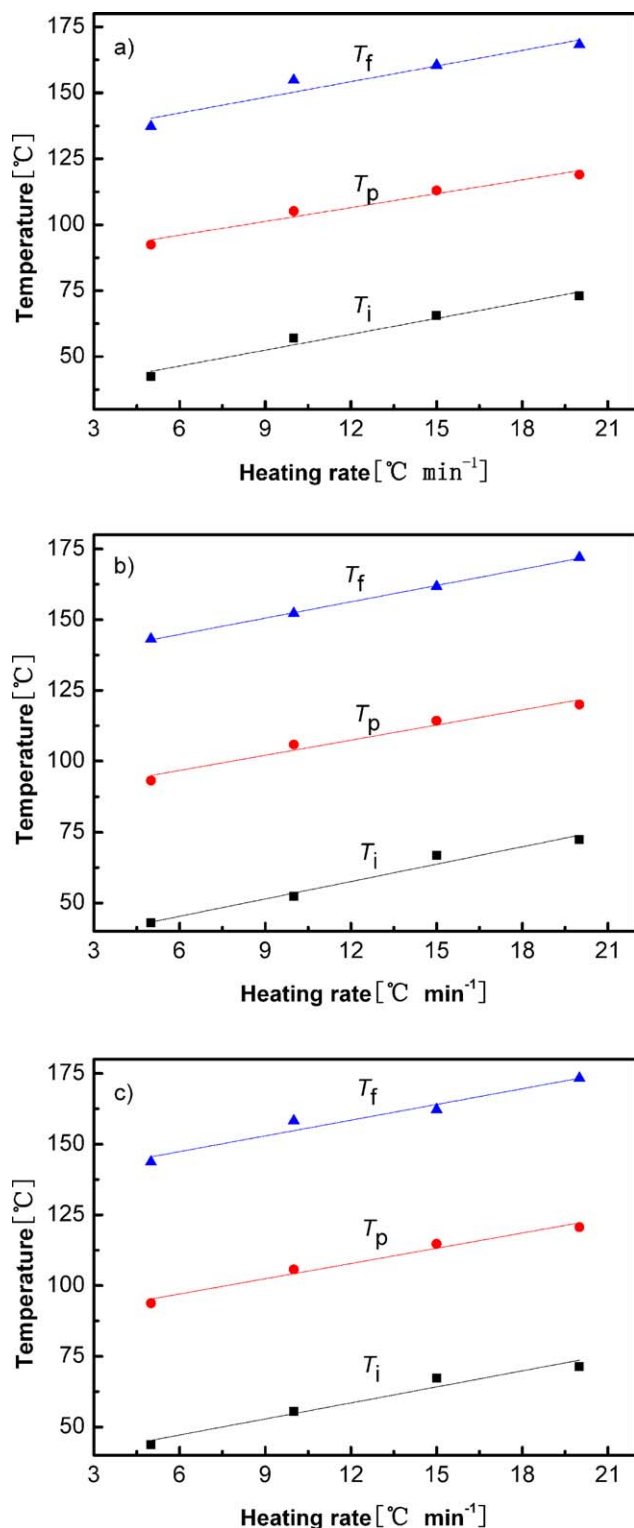


Figure 2. Plots of characteristic cure temperatures for epoxy resins with different contents of PPGDGE: (a) ETP-0, (b) ETP-11%, and (c) ETP-15%. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

energy E_a is low. Then, the activation energy starts to decrease with increasing in conversion α , as the autocatalytic effect grows in importance as curing reaction continues. The OH groups

Table I. Results of Linear Fitting for Three Epoxy Resin Systems

Sample designation	T_i ($^{\circ}\text{C}$)	T_p ($^{\circ}\text{C}$)	T_f ($^{\circ}\text{C}$)
ETP-0	34.42	85.51	130.50
ETP-11%	32.25	86.00	130.92
ETP-15%	35.84	86.25	136.25

generated by the epoxy-amine reaction lead to the autocatalysis. A number of examples of analyzing epoxy-amine autocatalytic reaction can be found elsewhere.^{34–36} As the molecular weights increase continually, the activation energy gradually increases due to the high diffusion resistance.

The average values of E_a for ETP-0 and ETP-11% are calculated to be 67.44 and 62.59 kJ mol^{-1} , respectively. The calculational results will be used for the establishment of cure kinetic equations. The activation energy of resin system decreases when the toughening agent PPGDGE is added. This is attributed to the fact that the viscosity of the reactants decreases obviously by adding PPGDGE, which enhances the mobility of reactive groups.

Prediction of Cure Time. For the determination of cure kinetic equations of the ETP-0 and ETP-11% epoxy systems, the two-parameter S–B autocatalytic model^{31,37} was adopted. The S–B model is expressed as follows:

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E_a}{RT}\right) \alpha^m (1-\alpha)^n \quad (2)$$

where t is the reactive time, m and n are the kinetic exponents. The kinetic parameters A , m , and n for the two epoxy systems were calculated by fitting the obtained experimental data to S–B model for each T and α at $5^{\circ}\text{C min}^{-1}$ by the multiple regression analysis. Table II lists the obtained values of A , m , and n for the ETP-0 and ETP-11%. The cure kinetic equations for the two epoxy systems can be established by substituting their values into the S–B model. The equations of ETP-0 and ETP-11% are given in eqs. (3) and (4), respectively.

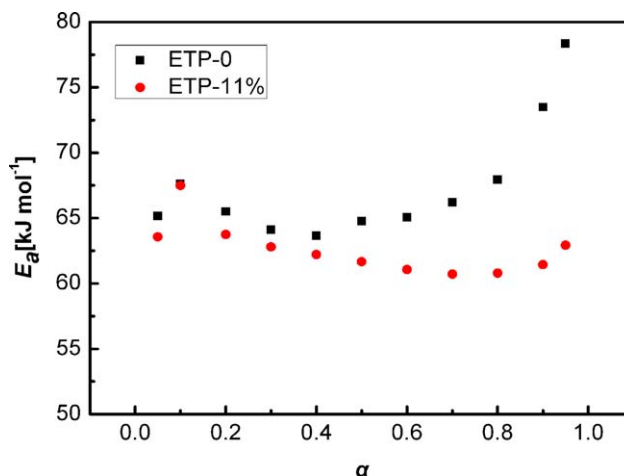


Figure 3. Dependencies of the activation energy E_a on conversion α for ETP-0 and ETP-11%. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table II. Kinetic Parameters Estimated by Šesták–Berggren Model for ETP-0 and ETP-11%

Sample designation	A	m	n	Adj. R-square
ETP-0	1.8198×10^9	0.3289	2.0138	0.9959
ETP-11%	3.3129×10^8	0.3150	1.6418	0.9967

$$\frac{d\alpha}{dt} = 1.8198 \times 10^9 \exp\left(-\frac{67440}{RT}\right) \alpha^{0.3289} (1-\alpha)^{2.0138} \alpha \in (0, 1) \quad (3)$$

$$\frac{d\alpha}{dt} = 3.3129 \times 10^8 \exp\left(-\frac{62590}{RT}\right) \alpha^{0.3150} (1-\alpha)^{1.6418} \alpha \in (0, 1) \quad (4)$$

The accuracy of the obtained kinetic equations can be estimated by comparing the experimental curves with the calculated curves by plotting $d\alpha/dt$ versus α .³⁸ The plots are shown in Figure 4 for the ETP-0 and ETP-11% resin systems. It is observed that the calculated curves are in good agreement with the experimental data, implying that the reactions well conform to the autocatalytic kinetic equations.

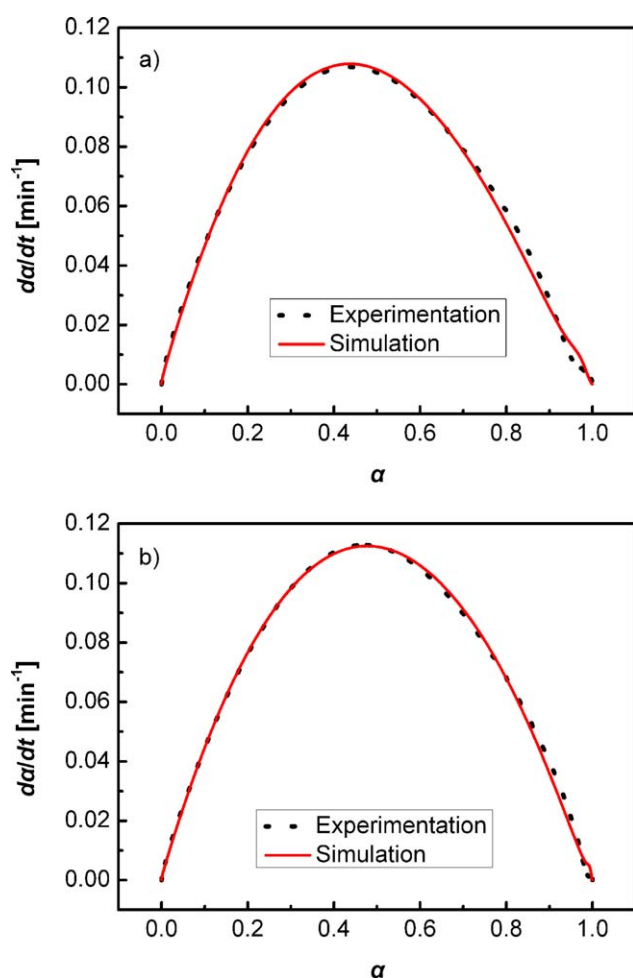


Figure 4. Comparison of experimental and calculated DSC curves for (a) ETP-0 and (b) ETP-11%. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table III. Mechanical Properties of Different Toughened Degrees in Epoxy Resin Systems

Sample designation	Tensile strength (MPa)	Elongation at break (%)
ETP-0	84.4	5.2
ETP-11%	72.3	6.4
ETP-15%	60.8	7.5
ETP-17%	53.9	7.8
ETP-19%	52.8	7.9

The kinetic equations were useful for roughly predicting the cure time at a given temperature for a given resin system. We have determined three cure temperatures (35, 100, and 140°C) in the temperature programmed process. Here, the final cure temperature (140°C) of ETP-11% resin system is taken as an example to illustrate the predicting method of the cure time. By substituting the final cure temperature in eq. (4), the expression for curing rate could be arrived at as in eq. (5):

$$\frac{d\alpha}{dt} = 4.0426 \alpha^{0.3150} (1-\alpha)^{1.6418} \alpha \in (0, 1) \quad (5)$$

The cure time could be calculated using eq. (6):

$$t = \frac{\alpha}{d\alpha/dt} = 0.2474 \frac{\alpha^{0.6850}}{(1-\alpha)^{1.6418}} \alpha \in (0, 1) \quad (6)$$

Under nonideal conditions, the extent of conversion α cannot arrive at 100%. The values of cure time t for ETP-11% at the final cure temperature is calculated to be 150 min when α is 98%. To ensure the more complete conversion and the higher T_g , the final temperature should be properly increased,³⁰ so the reactants were maintained at this temperature for 3 h. Following the above studies, all the resin systems were cured under the same cure schedule of 35°C-3 d, 100°C-3 h, and 140°C-3 h.

Mechanical Properties Analysis

The change in mechanical property with the enhancement in toughening agent-content is used as the main index to determine whether the material is toughened. Accordingly, tensile tests of the resin systems were conducted to identify the tensile strength and the elongation. Each tensile value of the resin system represents the average of three experiments. The tensile strength and elongation at break values for the resin systems with different toughened degrees are shown in Table III. For the ETP series, with the increase in concentration of PPGDGE, the tensile strength decreases, and the elongation increases. These changes in mechanical properties are possibly due to the differences in structures and molecular weights of the two epoxy resins. The inhomogeneity of the cross-linking network of obtained products can cause the decrease of tensile strength. Conversely, PPGDGE is a kind of aliphatic compounds with long-chain structures, the segments of which confer more flexibility to the resin system, and help improve the elongation. The elongation at break indicates the toughness of the resin system. Better toughness is achieved at the cost of tensile strength. ETP-17% will be used for the following DMA analysis because of the more appropriate strength and elongation.

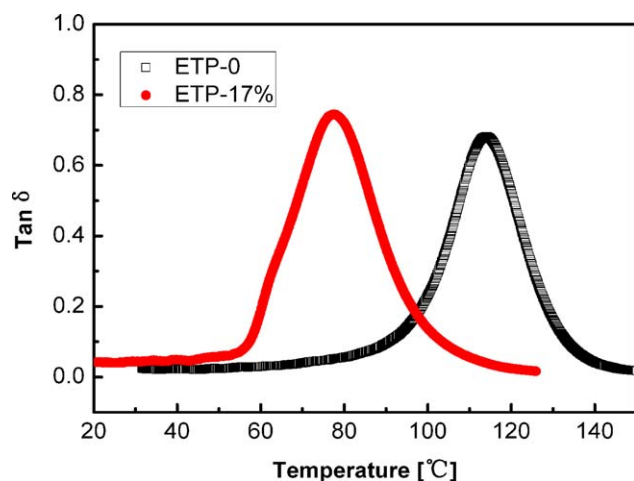


Figure 5. Loss tangent as a function of temperature for ETP-0 and ETP-17%. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Dynamic Mechanical Analysis

To further explore the effect of toughening agent on the toughness of resin system, DMA was performed. Figure 5 shows the loss tangent ($\tan \delta$) for ETP-0 and ETP-17% as a function of temperature. The temperature corresponding to $\tan \delta$ peak was considered as T_g . The obtained T_g values for different compositions were used for determination of the temperature conditions for evaluating the shape memory performances. The T_g value of ETP-17% is about 40°C lower than that of ETP-0. This phenomenon is possibly attributed to the much lower density of PPGDGE. The density of PPGDGE is more than 10 times that of E51. A lower density will lead to the decrease of cross-link points per unit volume and lower cross-link density. As a result, the segmental mobility is proportionally increased, leading to a lower T_g .³⁹ The $\tan \delta$ represents the internal friction,⁴⁰ which is caused by the movement of molecular chains, as reflected in the $\tan \delta$ peak height.¹¹ The higher peak height of ETP-17% declares that the segmental mobility and the internal friction are increased. The broadening of the $\tan \delta$ curve is also important as it implies the better fracture toughness, which can be quantified by calculating the relative change in the full width half maximum (FWHM).⁴¹ As shown in Figure 5, the FWHM of ETP-17% is broader than that of ETP-0, implying that PPGDGE helps improve the fracture toughness.

Evaluation of Shape Memory Properties

The shape memory properties of ETP-0, ETP-17%, and ETP-19% were studied at a bending temperature corresponding to $T_g + 30^\circ\text{C}$. The shape memory characteristics of the three resin systems are shown in Table IV. The fixable ratio was measured and calculated to be greater than 99.5%. The difference between the maximum bending angle and θ_f is always less than 1° in the process for fold-deploy test. The repeatability of the shape memory fold-deploy cycles is also an important performance parameter to characterize the fatigue resistance of resin systems.¹⁹ As shown in Table IV, for the ETP-0 resin system, the maximum fold-deploy cycles are nine cycles. The fracture damage occurred after nine cycles because of the material fatigue by repeated fold-

Table IV. Shape Memory Characteristics of Different Toughened Degrees in Epoxy Resin Systems

Sample designation	Fixable ratio (%)	Maximum fold-deploy cycles	Recovery time (s)
ETP-0	>99.5	9	154
ETP-17%	>99.5	13	141
ETP-19%	>99.5	13	122

deploy cycles. For the ETP-17% and ETP-19% resin systems, the maximum fold-deploy cycles can arrive at 13 cycles, because the PPGDGE molecular chain benefits the segmental mobility, and the resins become more toughened. Table IV also includes the shape recovery time for the ETP series, recovery time decreases with an increase in PPGDGE content. The reason can be explained that the lower density of PPGDGE molecules causes a lower cross-link density and a looser network of cured resin, which is advantageous for the segmental mobility as reflected in the decreased shape recovery time. The resin systems can recover their original shape within several minutes, proving that the shape memory properties of the cured materials are excellent.

CONCLUSIONS

A series of shape memory epoxy resins were synthesized by curing epoxy and curing agent TETA with varying content of toughening agent PPGDGE. DSC analysis was used to generate the cure kinetic equations capable of predicting the cure schedule at a given temperature for a given resin system. Based on the theoretical analysis as well as the practical curing process, the temperature programmed process was adopted as: 35°C -3 d, 100°C -3 h, and 140°C -3 h. The use of the isoconversional method revealed the decrease of the activation energy for the toughening resin system. The model-fitting reaction kinetic analysis with the S-B method proved that the curing reactions well conformed to the autocatalytic kinetic equations. The increase in the PPGDGE content of the mixture led to an improvement in elongation and fracture toughness. Nevertheless, better toughness was achieved at the cost of tensile strength. The T_g of the blend decreased when the toughening agent PPGDGE was added. The fold-deploy shape memory test showed that the shape memory properties of the cured materials are excellent. The shape fixable ratios of all systems were greater than 99.5%. The maximum fold-deploy cycles were increased to 13 cycles for ETP-17% and ETP-19% resin systems. Increasing the PPGDGE concentration improved the shape recovery as reflected in the decrease of recovery time without affecting the shape fixable ratio.

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