

Synthesis of Eugenol Bio-based Reactive Epoxy Diluent and Study on the Curing Kinetics and Properties of the Epoxy Resin System

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Abstract In this study, monoglycidyl silyl etherated eugenol (GSE) was synthesized as reactive epoxy diluent, and the chemical structure of GSE, intermediates, and products were characterized by Fourier transform infrared spectroscopy (FTIR) and nuclear magnetic resonance (¹H-NMR). GSE existed as a potential bio-based reactive diluent for petroleum-based epoxy resin. The curing kinetics of EP/HHPA/GSE system was studied by non-isothermal DSC method. The kinetics parameters were calculated by using the Kissinger model, Crane model, Ozawa model, and β -*T* (temperature-heating rate) extrapolation, respectively. In addition, the effects of GSE on the thermo-mechanical properties and thermal stability of EP/HHPA/GSE systems were studied, indicating that GSE can effectively improve the toughness and thermal decomposition temperature of the epoxy system.

Keywords Bio-based epoxy; Reactive diluent; Eugenol; Curing kinetics

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INTRODUCTION

Bisphenol A (BPA) type epoxy based thermosetting resins are widely used for a variety of applications because of their good adhesion, relatively high moduli, mechanical strength, as well as their small curing shrinkage and low cost.^[1–6] Due to the high viscosity and poor process-ability of bisphenol A based resin, organic solvents are often used to reduce the viscosity of BPA-based epoxy curing system. However, most organic solvents are toxic, and they also cause serious environmental pollution and a substantial loss of oil resources. More and more environmental concerns and strict regulations give a push to the reduction of volatile organic compounds (VOC). An effective strategy for reducing VOC is the use of reactive diluent that can reduce the viscosity of epoxy resin and get involved in the curing reaction.^[7–12] Such diluents are usually glycidyl compound with low molecular weight, which include butyl glycidyl ether, benzyl glycidyl ether, allyl glycidyl ether, dodecyl and tetradecyl glycidyl ethers, 1,4-butanediol diglycidyl ether, etc.^[13–15]

The above-mentioned reactive diluents are based on non-renewable petroleum resources. It is an urgent task to develop sustainable and renewable polymeric materials. Recently, the use of natural resources to design reactive diluent has

been remaining the hot topic of research.^[16–22] For instance, Sahoo^[23] reported the synthesis of epoxidized linseed oil, which was proved an effective diluent for improving the processability of petro-based epoxy resin by reducing its viscosity and toughening the epoxy matrix. They also used the epoxidized soybean oil (ESO) based bioresin as suitable alternative to modify the virgin epoxy; the maximum 20 wt% of ESO could enhance the toughness of epoxy network and improve the impact strength by 60% as compared to that of virgin epoxy.^[24] Ding *et al.*^[25] reported the synthesis of furfuryl glycidyl ether (FGE) and examined the influences of FGE concentrations on the viscosity, thermal, and mechanical properties of BPA- type epoxy, and concluded that the optimum concentration of FGE was between 10 wt% and 15 wt%. Chen *et al.*^[9] synthesized polyepoxide cardanol glycidyl ether (PECGE) and studied the influence of PECGE addition on the viscosity of the diluent epoxy resin. It was found that the viscosity of the epoxy resin obtained was reduced without sacrificing its tensile strength, elongation at break, and heat-resistant property.

Eugenol, a monolignol commonly obtained from cloves, is widely used in perfumes, cosmetics, taste and food additives.^[26–31] It is also an potential building block to develop bio-based epoxy resin with advanced thermal and mechanical properties. For instance, Qin *et al.*^[27] synthesized the diglycidyl substituted eugenol by epoxidation of the double bond followed by glycidylation of the phenolic hydroxyl in the eugenol structure. Similar curing behavior, dynamic mechanical properties, and thermal stability were observed

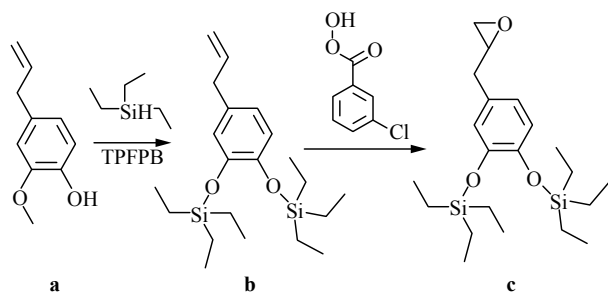
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when employing the anhydride curing agent. Caillo and co-workers^[28] reported the synthesis of tri(epoxized-eugenyl)-phosphate (TEEP) by treating phosphorus oxychloride with eugenol, followed by epoxidation with *m*-CPBA. The properties of the materials obtained were comparable to those of petro-based epoxy (DGEBA) when cured with the amine hardeners. Miao *et al.*^[32] reported the synthesis of bis(2-methoxy-4-(oxiran-2-ylmethyl)phenyl)furan-2,5-dicarboxylate (EUFU-EP) from 2,5-furandicarboxylic acid and eugenol and the biomass content of EUFU-EP was as large as 93.3%. It was found that the anhydride cured EUFU-EP resin showed better thermal properties, rigidity, flame retardancy, and high glass transition temperature (153.4 °C) when compared with those of BPA-based epoxy resin.

In this work, we report the synthesis of monoglycidyl silyl etherated eugenol (GSE) as a reactive diluent for BPA-based epoxy resin. The addition of a small amount of GSE diluent to the BPA resin can significantly reduce the viscosity of the BPA resin due to the fact that silicone diluents (GSE) are more capable of lowering the surface tension of the resin system than conventional carbon chain-based diluents do. In addition, GSE is also a resin modifier that can participate in the curing reaction of BPA resin, and the bond energy of Si–O bond is much higher than that of C–C bond, which endows GSE-modified BPA resin with a potential increment of thermal stability. GSE was obtained *via* epoxidation of silyl etherate eugenol as shown in Scheme 1. The effect of GSE on the viscosity of BPA-based epoxy resin was evaluated. The curing kinetics, thermal, and mechanical properties of the cure epoxy/anhydride system with different BPA weight ratios were investigated.



Scheme 1 Synthesis of monoglycidyl silyl etherated eugenol

EXPERIMENTAL

Materials

Eugenol (99%), triethylsilane (98%), tris(pentafluorophenyl)borane (TPFPB; 97%), 3-chloroperoxybenzoic acid (*m*-CPBA; 85%), 2,4,6-tris(dimethylaminomethyl)phenol (DMP-30; 95%), *cis*-1,2-cyclohexanedicarboxylic anhydride (HHPA; 99%), and aluminum oxide were purchased from Shanghai Aladdin Industrial Co. Ltd. Epoxy resin (EP-44) was provided by Jiangsu Heli coating Co. Ltd.

Synthesis of Silyl Etherated Eugenol (b)

Scheme 1 shows the synthetic route to GSE. Eugenol (a, 8.2 g, 0.05 mol, 1.0 equiv.) and triethylsilane (11.6 g, 0.10 mol, 2.0

equiv.) were added to a 500 mL round bottom flask, and stirred for 10 min to get a uniform mixture. TPFPB (0.2 g, 0.4 mmol, 0.008 equiv.) was added to the reaction mixture as a catalyst, and the reaction evolved gas vigorously. The reaction mixture was passed through a neutral alumina column to remove TPFPB using dichloromethane as the solvent. The dichloromethane and unreacted triethylsilane were then removed by rotary evaporation under reduced pressure to give the triethylsilane-protected eugenol (19.33 g, 98%) as a yellowish liquid and the product was used without further purification. ¹H-NMR (400 MHz, CDCl₃, δ, ppm): 6.86 (d, 1H), 6.70 (s, 2H), 5.97 (td, 1H), 5.54 (s, 1H), 5.08 (m, 2H), 3.88 (s, 3H), 3.33 (d, 2H); (b) ¹H-NMR (400 MHz, CDCl₃, δ, ppm): 6.73 (d, 1H), 6.65 (s, 1H), 6.61 (d, 1H), 5.94 (dt, 1H), 5.04 (d, 2H), 3.26 (d, 2H), 0.99 (t, 18H), 0.74 (q, 12H).

Synthesis of GSE (c)

Silyl etherated eugenol (19.33 g) was dissolved in 300 mL of dichloromethane and reacted with *m*-CPBA at 0 °C for 2 h in an ice-water mixture and then transferred to room temperature for 48 h. Subsequently, the reactant was filtered and washed three times with 300 mL of saturated sodium bisulfite solution, then washed repeatedly with saturated sodium bicarbonate until the pH of the solution was neutral. The solution was dried with MgSO₄ for 24 h and the solvent was evaporated to obtain 17.02 g of GSE (c, yield 88%). ¹H-NMR (400 MHz, CDCl₃, δ, ppm): 6.74 (d, 1H), 6.71 (s, 1H), 6.65 (d, 1H), 3.09 (s, 1H), 2.81 (m, 1H), 2.77 (d, 1H), 2.66 (dd, 1H), 2.51 (s, 1H), 0.97 (t, 18H), 0.77 (q, 12H).

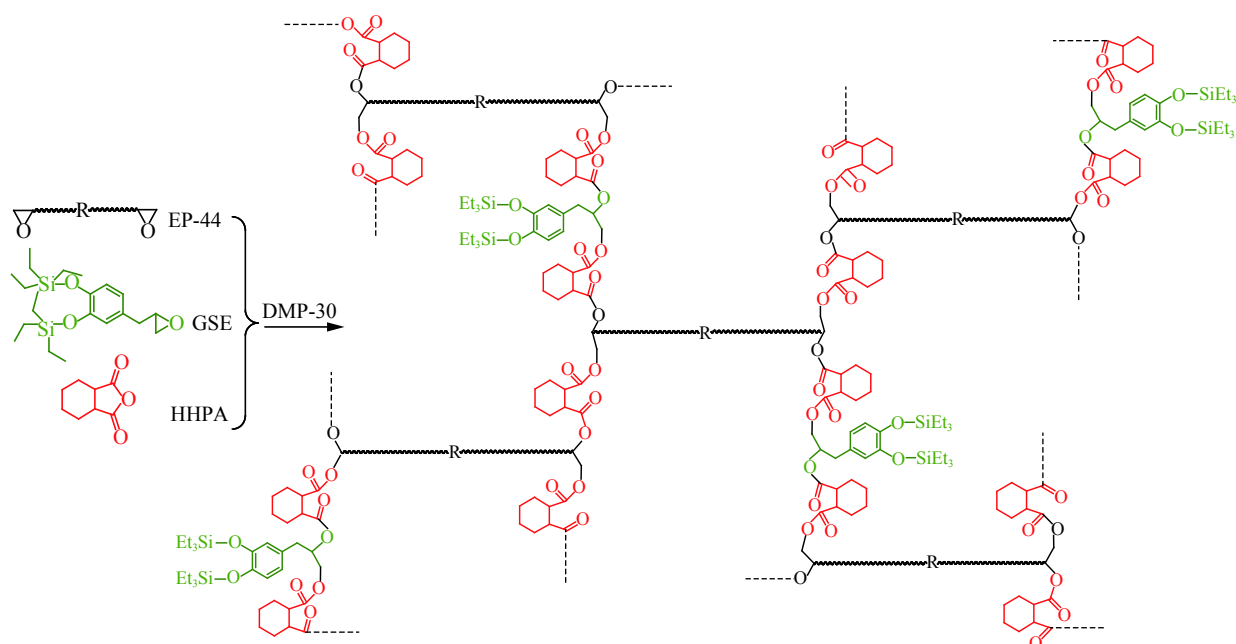
Preparation of Cured EP/HHPA/GSE Polymer

Scheme 2 shows the curing mechanism of the EP/HHPA/GSE system. The reaction process of the anhydride-cured epoxy resin mainly consists of two parts. Firstly, DMP-30 attacks HHPA to form carboxylate anion, and then the carboxylate anion reacts with EP or GSE to form an oxyanion. The reaction is repeated until the epoxy resin is crosslinked and cured.

The acid anhydride curing agent HHPA (6.8 g) and DMP-30 curing accelerators (0.18 g) were dissolved in a certain amount of GSE, and the mixture was added to EP-44 (10 g) and heated to 60 °C for 10 min to be homogeneously mixed. The compound was degassed under vacuum and then poured into a Teflon mold and cured at the given temperature.

Characterizations

¹H-NMR spectra were recorded with a 400 MHz AVANCE III NMR spectrometer in CDCl₃ as reference. The FTIR spectrum was recorded with a NICOLET 6700 spectrometer instrument. DSC analysis was performed using a NETZSCH 214 instrument with nitrogen flow rate of 20 mL·min⁻¹. The samples were heated from 25 °C to 250 °C at heating rates of 5, 10, 15, 20, and 25 K·min⁻¹, respectively. The viscosity of the EP/GSE systems was measured by a Physica MCR-301 rotary rheometer, and the angular frequency was set from 0.1 rad·s to 100 rad·s. Thermal analysis of samples (EP/HHPA/GSE) was performed with a Diamond TG/DTA Instrument (PerkinElmer). The cured samples were measured from 25 °C to 800 °C at a heating rate of 10 °C·min⁻¹ under an air atmosphere. Dynamic mechanical analyses were



Scheme 2 The structure of cured EP/HHPA/GSE polymer network

performed with a TA Q800 analyzer Instruments (TA) at a frequency of 1 Hz. The cured samples were measured from room temperature to 200 °C at a heating rate of 3 °C·min⁻¹. The impact fracture surface of EP/HHPA/GSE systems was analyzed by a FEI Quanta FEG 250 (FESEM) Instrument. The fracture surfaces were sputter-coated with gold before taking the micrographs. Tensile test was performed according to ASTM 638 using Universal Testing Machine (INSTRON 5869) with the crosshead speed of 2 mm·min⁻¹. Five parallel samples were measured for each component and averaged.

RESULTS AND DISCUSSION

Synthesis and Characterization of GSE

Fig. 1 shows the ¹H-NMR spectra of GSE. After triethyl silylation, the signals at 5.54 ppm (5) and at 3.88 ppm (7) attributed to the phenolic hydroxyl group and the methyl group, respectively, completely disappeared (Fig. 1a), and the newly formed signals at 0.99 ppm (5) and 0.74 ppm (7) were attributed to the protons of triethylsilane (Fig. 1b). Furthermore, by comparing the signals of (5) and (7) (Fig. 1b), it could be found that the phenolic hydroxyl group and methyl group of all eugenol were replaced by triethylsilyl groups. The FTIR spectra shown in Fig. 2 also demonstrated the complete reaction of eugenol. After eugenol triethyl silylation, the band of C=C at 3500 cm⁻¹ (Fig. 2b) disappeared; instead, the band of Si—C bond appeared at 738 cm⁻¹ (Fig. 2c), indicating that the triethylsilane-protected eugenol was successfully synthesized.

Silylated eugenol was epoxidized by *m*-CPBA. The ¹H-NMR spectra show that the signals of double bonds at 5.94 and 5.04 ppm (1 and 3 in Fig. 1b) disappeared completely and new peaks belonging to oxiranes appeared at 3.09, 2.8, 2.77, 2.66, and 2.51 ppm (4, 6, and 8 in Fig. 1c). In Fig. 2(c),

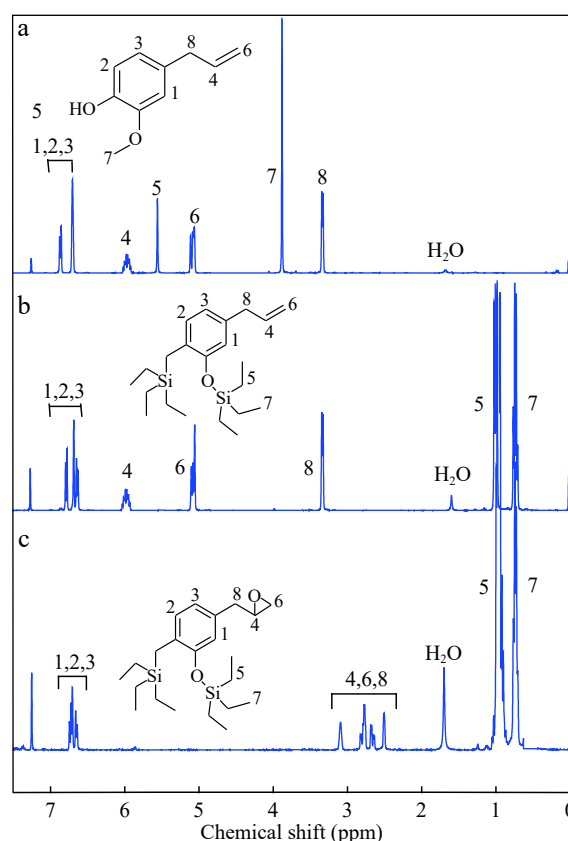


Fig. 1 ¹H-NMR spectra of (a) eugenol, (b) triethylsilane-protected eugenol, and (c) GSE

the band of C=C at 1639 cm⁻¹ disappeared completely. The new band at 829 cm⁻¹ was attributed to the epoxy group (Fig. 2d). The FTIR and ¹H-NMR results confirmed that the reactive diluent GSE was successfully synthesized.

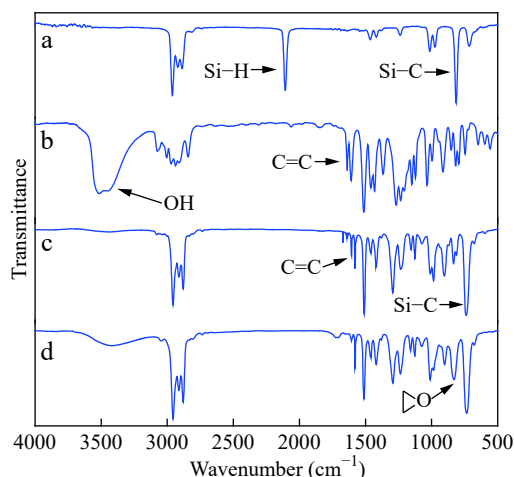


Fig. 2 FTIR spectra of (a) triethylsilane, (b) eugenol, (c) triethylsilane-protected eugenol, and (d) GSE

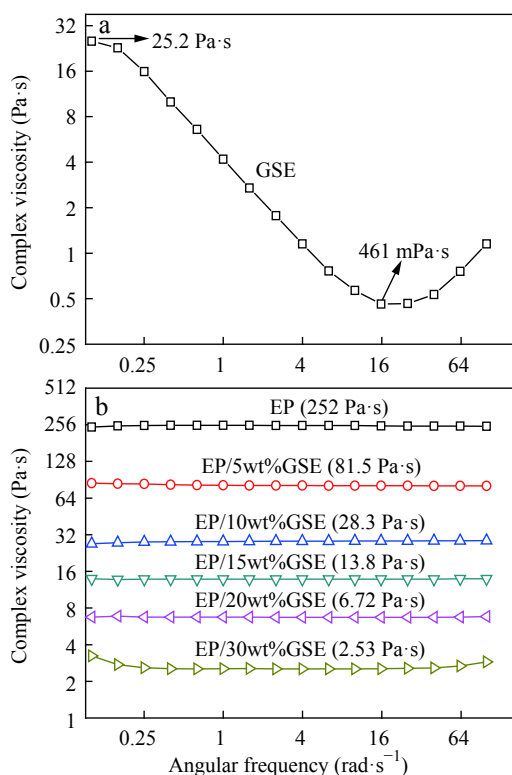


Fig. 3 The relation between viscosity and angular frequency of (a) GSE, and (b) EP/GSE system

Viscosity of the EP/ GSE System

The viscosity of EP/GSE system was investigated as shown in Fig. 3. Neat GSE was a non-Newtonian fluid with the minimum viscosity of 461 mPa·s (Fig. 3a) and the viscosity of neat EP was about 252 Pa·s (Fig. 3b). With the increasing content of diluent (GSE), the viscosity was 81.5 Pa·s (5 wt% GSE), 28.3 Pa·s (10 wt% GSE), 13.8 Pa·s (15 wt% GSE), 6.72 Pa·s (20 wt% GSE), and 2.53 Pa·s (30 wt% GSE) (Fig. 3b), respectively. Based on the above analysis, only a small amount of GSE added can reduce the viscosity of the epoxy resin significantly, which indicates that GSE is an effective reactive epoxy diluent.

Kinetic Parameters of EP/HHPA/GSE System

It is well known that most acid anhydride curing agents are in solid states at room temperature, and need to be dissolved to liquid state at a certain temperature before mixing with epoxy resin (EP-44). In this work, we used GSE as a diluent in the epoxy system. The liquid HHPA, GSE, DMP-30, and EP-44 were mixed to form a homogenous solution for the next DSC test.

Fig. 4 shows the DSC thermograms of EP/HHPA/GSE system at a heating rate of 15 K·min⁻¹. Compared with the epoxy resin system without adding GSE, the temperature value corresponding to the exothermic peak of the resin system shifts toward the high temperature direction as the GSE content increases. Besides, the addition of GSE would also lead to changes in the total heat release of the EP/HHPA/GSE system; the specific values are summarized in Table 1. The reaction enthalpy value of the GSE-added resin system was reduced as compared with that of neat epoxy resin. This might be attributed to the steric hindrance effect of the benzene ring structure on the epoxy group in GSE molecule, which resulted in the decrease of heat released in the resin system.

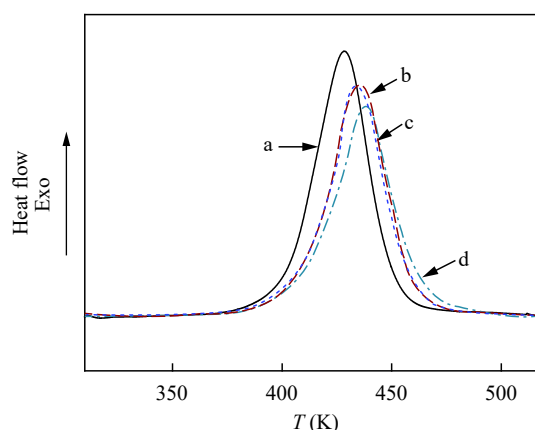


Fig. 4 DSC thermograms of EP/HHPA/GSE system at heating rate of 15 K·min⁻¹: (a) EP/HHPA, (b) EP/HHPA/5wt%GSE, (c) EP/HHPA/10wt%GSE, and (d) EP/HHPA/15wt%GSE

Table 1 DSC parameters of EP/HHPA/GSE system

Samples	Enthalpy of reaction (J·g ⁻¹)	Peak temperature T_p (K)
EP/HHPA	282.5	434.60
EP/HHPA/5wt%GSE	271.9	440.45
EP/HHPA/10wt%GSE	273.8	441.85
EP/HHPA/15wt%GSE	247.4	443.95

In the complex system of EP/HHPA/GSE, when 10 wt% GSE was added, the system possessed the maximum reaction enthalpy (273.8 J·g⁻¹). This composition was used for further kinetic analysis.^[24]

Fig. 5 shows the non-isothermally cured DSC curves of the EP/HHPA/10wt% GSE system at different heating rates. The corresponding thermodynamic parameters are listed in Table 2. As can be seen, the reaction initiation temperature (T_i) and termination temperature (T_p) rose with the increase

of rate β , and the peak temperature (T_p) also moved toward the high temperature direction. ΔH is the total amount of heat released per unit mass of sample at different heating rates. According to the analysis results, during the curing process of EP/HHPA/GSE system, ΔH decreased with the increasing heating rate, which indicated that the higher the heating rate, the lower the solidification degree of the system.

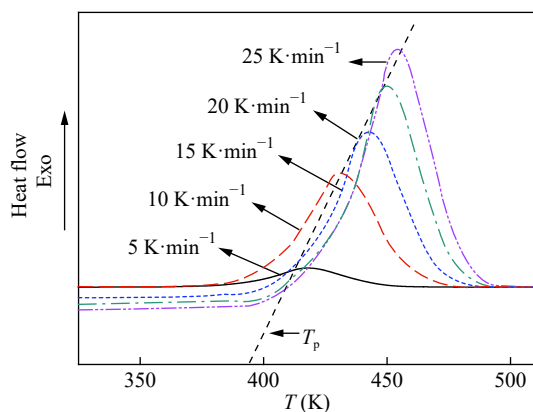


Fig. 5 DSC curves of EP/HHPA/GSE system

Table 2 Characteristic temperatures from DSC curves

β (K·min ⁻¹)	T_i (K)	T_p (K)	T_f (K)
5	380.65	418.05	448.45
10	391.15	431.05	460.55
15	404.55	442.35	470.25
20	422.15	449.95	477.25
25	430.75	454.15	481.25

Determination of Kinetic Parameters of EP/HHPA/GSE System

The study of curing kinetic parameters has important theoretical significance for its application. The purpose of analyzing the curing reaction kinetics of EP/HHPA/GSE system is to establish the relationship between curing rate and curing degree with time and temperature, to study the system properties and the effect of curing conditions on the curing behavior, and then to optimize the curing process.

Curing kinetic parameters, such as apparent activation energy (E_a) and reaction order n , are important for understanding the curing reaction. The value of E_a reflects the ease of the system curing, and the curing reaction occurs only when the energy of the system is greater than E_a . In addition, the complexity of system curing is usually evaluated by the number of reaction order (n). The linear relationships between $\ln(\beta/T_p^2)$ and $\ln\beta$ to $(1/T_p)$ were obtained by processing the DSC data obtained at different heating rates us-

ing Kissinger, Ozawa, and Crane equations. Then, the n -order dynamic model equation of the system solidification could be determined by the parameters obtained from the linear fitting method (4).

The kinetic equations for epoxy systems all follow Eq. (1), and Eq. (2) can be obtained by differential processing and simplification of Eq. (1).

$$\frac{d\alpha}{dt} = K(T)(1-\alpha)^n \quad (1)$$

$$\ln\left(\frac{\beta}{T_p^2}\right) = \ln\left(\frac{AR}{E_a}\right) - \left(\frac{E_a}{RT_p}\right) \quad (2)$$

$$A = [\beta E_a \exp(E_a/RT_p)]/RT_p^2 \quad (3)$$

The data were fitted by Eq. (3) to obtain the relationship between $\ln(\beta/T_p^2)$ and $(1/T_p)$ (Fig. 6a). After calculation, E_a equaled 60.66 kJ·mol⁻¹. Eq. (4) was derived from Eq. (3). Based on the calculated value of E_a , the value of A could be obtained, and are listed in Table 3.

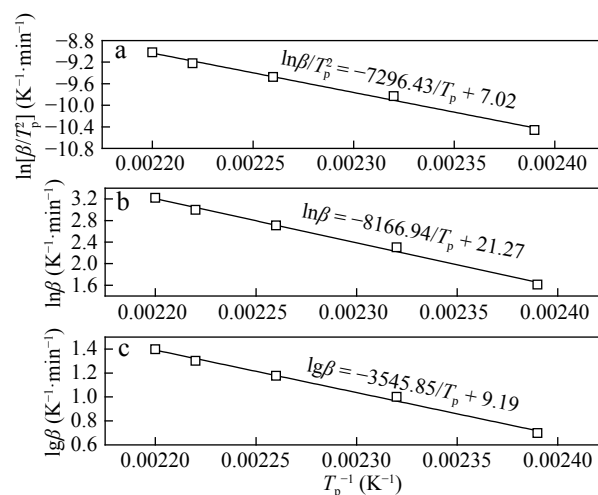


Fig. 6 The relation between (a) $\ln(\beta/T_p^2)$ and $1/T_p$, (b) $\ln\beta$ and $(1/T_p)$, and (c) $\lg\beta$ and $(1/T_p)$

According to related research, n of the curing system can be obtained by Crane Eq. (4). When the value of (E_a/nR) in the equation is much larger than the value of $2T_p$, Eq. (4) can be simplified to the form of Eq. (5). The linear relationship between $\ln\beta$ and $(1/T_p)$ was calculated by Eq. (5) (Fig. 6b), and the slope and the number of reaction stages n were -8166.94 and 0.893, respectively.

$$\frac{d\ln\beta}{d(1/T_p)} = -(E_a/nR + 2T_p) \quad (4)$$

Table 3 The kinetics parameters of curing reaction

β (K·min ⁻¹)	$\ln(\beta/T_p^2)$ (K ⁻¹ ·min ⁻¹)	$\ln\beta$ (K·min ⁻¹)	$\lg\beta$ (K·min ⁻¹)	T_p^{-1} (K ⁻¹)	A (min ⁻¹)
5	-10.462	1.609	0.699	0.00239	7.935×10^6
10	-9.830	2.303	1	0.00232	8.818×10^6
15	-9.476	2.708	1.176	0.00226	8.150×10^6
20	-9.223	2.996	1.301	0.00222	7.950×10^6
25	-9.018	3.219	1.398	0.00220	8.396×10^6
Average					8.358×10^6

$$\frac{d \ln \beta}{d(1/T_p)} = -\frac{E_a}{nR} \quad (5)$$

The Ozawa equation is another curing kinetic model. Compared with the Kissinger equation, it has the advantage of avoiding the experimental error caused by the assumption of reaction mechanism function. Therefore, the Ozawa Eq. (6) can be used to test the activation energy value obtained by Kissinger equation.

$$\lg \beta = \lg \left[\frac{AE_a}{Rf(\alpha)} \right] - 2.315 - 0.4567 \frac{E_a}{RT_p} \quad (6)$$

At different heating rates, α values at the exothermic peak temperature, T_p , are approximately identical. According to the theory, the linear fitting straight line equation of $\lg \beta - T_p^{-1}$ is shown in Fig. 6(c). After calculation, E_a of 64.55 kJ·mol⁻¹ was obtained. By comparison, it could be seen that the calculation results obtained by these two methods are similar, which shows that the assumption of the n -order reaction model in the EP/HHPA/GSE curing process was proved. The average value of E_a was 62.61 kJ·mol⁻¹.

Determination of the Dynamic Equation of EP/HHPA/GSE System

The curing kinetic Eq. (8) was obtained by combining Eqs. (1) and (7), and Eq. (9) was obtained by integrating Eq. (8). The above E_a , A , and n values were introduced into Eq. (9) and the final solidification kinetic Eq. (10) of the EP/HHPA/GSE polymer system was determined. The relationship between α and t was reflected by Eq. (10) as shown in Fig. 7. It can be concluded that the higher the reaction temperature of the EP/HHPA/GSE system, the longer the reaction time (t) and the higher the conversion rate (α).

$$K = A \exp(-E_a/RT_p) \quad (7)$$

$$\frac{d\alpha}{dt} = A \exp(-E_a/RT)(1-\alpha)^n \quad (8)$$

$$\alpha(t) = 1 - [1 + (n-1)A \exp(-E_a/RT)t]^{\frac{1}{1-n}} \quad (9)$$

$$\alpha(t) = 1 - [1 - 8.94 \times 10^5 \exp(-7.53 \times 10^3/T)t]^{\frac{1}{9.35}} \quad (10)$$

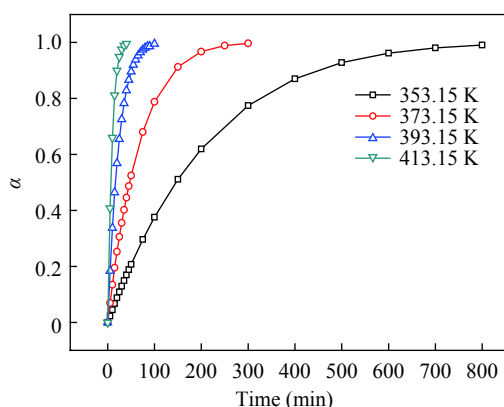


Fig. 7 The relationship between α and t of EP/HHPA/GSE system

Determination of Curing Temperature of EP/HHPA/GSE System

Table 2 indicates that as the heating rate increased, the

initial temperature of the curing reaction in EP/HHPA/GSE polymer system and the peak temperature of the maximum exothermic peak moved toward the high temperature. This suggested that the curing reaction was not only a thermodynamic process, but also a dynamic process. We employed the curing temperature at heating rate of 0 K·min⁻¹ by T - β extrapolation as the reliable curing temperature of the system.

In this work, the value of heating rate was taken as the horizontal coordinate, and the values of T_i , T_p , and T_f were taken as the vertical coordinates to obtain the linear relationship, as shown in Fig. 8.

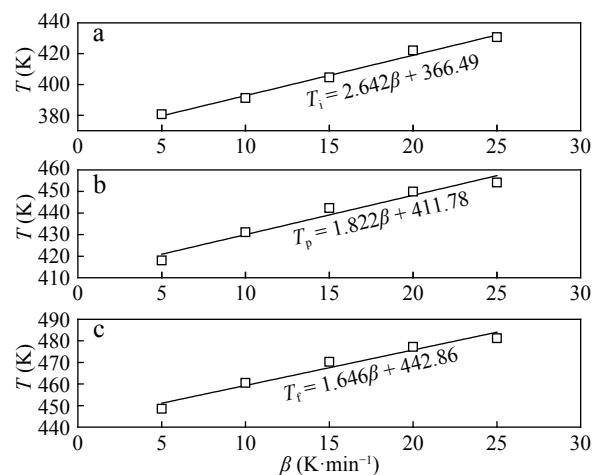


Fig. 8 The extrapolation plots of β - T : (a) T_i , (b) T_p , and (c) T_f

According to the results, the peak starting temperature was 366.49 K (gel temperature 93.34 °C), the peak temperature was 411.78 K (curing temperature 138.63 °C), and the peak end temperature was 442.86 K (post-cure temperature 169.71 °C). Based on the above results, the complete process of EP/HHPA/GSE system was cured at 95 °C for 1 h, at 140 °C for 2 h, and at 170 °C for 3 h, successively.

Thermal Stability

TGA tests of the EP/HHPA/GSE systems were carried out under the air atmosphere as shown in Fig. 9. Thermal decomposition of the resin mainly comprises two parts: firstly, as the temperature increases, the side chain of the resin begins to oxidize and is accompanied by carbonization of the main chain; secondly, the carbonized backbone begins to decompose until it disappears completely. With the increase of GSE content, there was no significant difference between oxidation of the resin side chain and carbonization of the main chain, while a significant retardation effect was observed in the decomposition process of the resin backbone. The initial decomposition temperature of the EP/HHPA resin backbone was 487 °C, and the resin decomposed completely at 595 °C. The initial and complete decomposition temperatures of the resin were increased to 495 and 627 °C, respectively, with only 5 wt% GSE added. When 15 wt% GSE was added, the initial and complete decomposition temperatures were 502 and 643 °C, respectively. As a result, the addition of the diluent GSE could increase the thermal decomposition temperature of the EP/HHPA/GSE system.

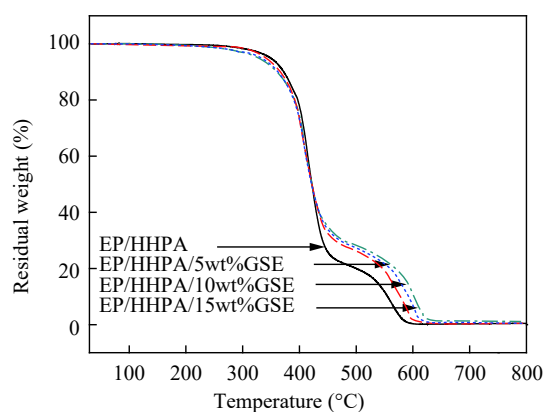


Fig. 9 TGA curves of EP/HHPA/GSE resin systems

Dynamic Mechanical Properties

Fig. 10 shows the plots of loss tangent $\tan\delta$ versus temperature for EP/HHPA/GSE resin systems. As can be seen, glass transition temperature (T_g) of epoxy/HHPA cured resin was 134.33 °C, and T_g s of EP/HHPA/GSE were 120.04 °C for 5 wt% GSE, 111.97 °C for 10 wt% GSE, and 102.73 °C for 15% GSE, respectively. The T_g s of the system decreased with the increase of diluent GSE. Because the crosslinking density of the epoxy resin was significantly reduced and the molecular chain mobility was enhanced as the content of diluent increased, T_g of the EP/HHPA/GSE system was reduced.

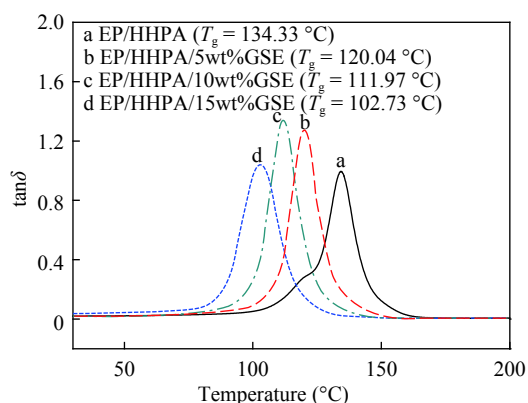


Fig. 10 Plots of $\tan\delta$ versus temperature for EP/HHPA/GSE resin systems

Mechanical Properties

Fig. 11 shows the stress-strain curves of the EP/HHPA/GSE systems, and the tensile properties are summarized in Table 4.

It can be easily seen that as the GSE content increased, the tensile strength and tensile modulus gradually decreased. The reason might be that since the bio-based diluent acts as a small molecule plasticizer,^[24] higher diluent content would reduce the cross-linking density of the system, which was manifested by an increase in elongation at break. It could also be confirmed by the reduced T_g described in the previous section.

SEM Micrographs

Fig. 12 shows the SEM micrographs of impact fracture

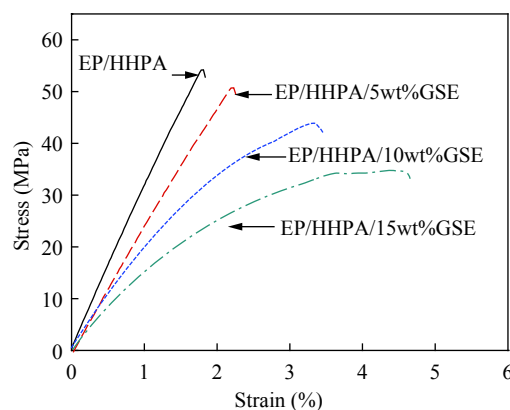


Fig. 11 Stress-strain curves of EP/HHPA/GSE system

Table 4 Tensile properties of EP/HHPA/GSE system

Sample	Tensile strength (MPa)	Strain at break (%)	Tensile modulus (MPa)
EP/HHPA	53.4 ± 2.8	1.8 ± 0.2	2191.3 ± 64.5
EP/HHPA/5wt%GSE	50.1 ± 3.1	2.4 ± 0.1	1934.2 ± 58.2
EP/HHPA/10wt%GSE	44.5 ± 2.6	3.3 ± 0.1	1710.7 ± 43.3
EP/HHPA/15wt%GSE	32.8 ± 1.8	4.6 ± 0.3	1076.1 ± 40.7

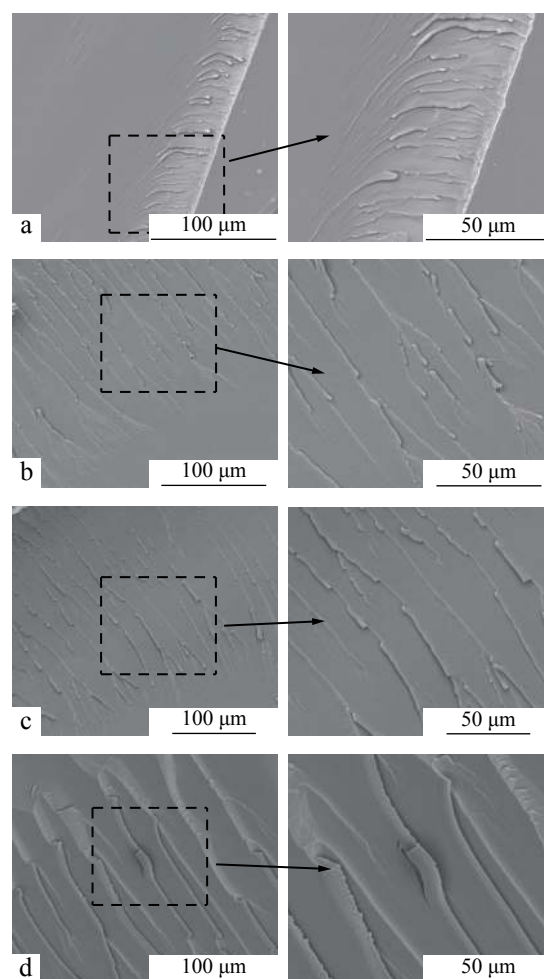


Fig. 12 SEM micrographs of the impact fractured surface of EP/HHPA/GSE systems: (a) EP/HHPA, (b) EP/HHPA/5wt%GSE, (c) EP/HHPA/10wt%GSE, and (d) EP/HHPA/15wt%GSE

surface of the EP/HHPA/GSE systems. Fracture surface of the neat epoxy resin was mostly smooth and tidy, and only a small portion had a long strip texture. As the content of GSE increased, the area of long strip-like texture in the field of view gradually enlarged and the surface became rougher. This was attributed to the fact that the addition of GSE reduced the crosslink density in material system and eliminated the internal stress partially.

CONCLUSIONS

Monoglycidyl silyl etherated eugenol (GSE) was successfully synthesized and used as reactive diluent for epoxy/anhydride curing system. Based on EP/HHPA/GSE curing kinetic studies, the value of pre-exponential factor A was calculated to be $8.358 \times 10^6 \text{ min}^{-1}$, the apparent activation energy E_a was $62.61 \text{ kJ} \cdot \text{mol}^{-1}$, and the reaction stages n was 0.893. According to the extrapolation results of T - β plot, the gel temperature was 366.49 K (93.34 °C), the curing temperature was 411.78 K (138.63 °C), and the post-cure temperature was 442.86 K (169.71 °C). The effects of GSE on the thermo-mechanical properties and thermal stability of EP/HHPA/GSE systems were studied, which indicated that GSE can effectively improve the toughness and thermal decomposition temperature of the epoxy system.

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