

Morphologies and Mechanical and Thermal Properties of Highly Epoxidized Polysiloxane Toughened Epoxy Resin Composites

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Abstract: A novel highly epoxidized polysiloxane was synthesized to modify the diglycidyl ether of bisphenol-A (DGEBA). The mechanical and thermal properties as well as the morphology of the cured epoxy resins were examined by tensile testing, impact testing, fracture testing, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and environmental scanning electron microscopy (ESEM). The chemical structure of the highly epoxidized polysiloxane (HEPSO) was confirmed by Fourier transform infrared spectroscopy (FTIR), ^{29}Si nuclear magnetic resonance spectroscopy (^{29}Si NMR), and gel permeation chromatography (GPC). The T_g increased by approximately 8 °C after introducing HEPSO. TGA in air showed that the initial degradation temperature for 5% weight loss (T_d 5%), the temperature for 50% weight loss (T_d 50%) and the residual weight percent at 800 °C (R_{800}) were increased after introducing HEPSO. The addition of 4 phr HEPSO2 resulted in the highest increase in tensile strength, impact strength and fracture toughness (K_{IC}). The morphology of the fracture surfaces show that the miscibility of polysiloxane with epoxy resin increased with increasing epoxide group in HEPSO. The high epoxide groups in HEPSO can react during the curing process, and participate chemically in the crosslinking network. HEPSO is expected to improve significantly the toughness and thermal stability of epoxy resin.

Keywords: epoxy, polysiloxane, hydrolysis and condensation, toughness, morphology, thermal properties.

Introduction

Epoxy resins have been widely used as adhesive for the copper clad laminate, because of their low cost, superior mechanical properties, excellent thermal resistance, and good processability. However, lead-free soldering puts forward higher requirements for the thermal stability of the epoxy resin. And the brittleness of the epoxy resins becomes more serious with the improvement of thermal stability. Thus, improving the toughness of the epoxy resin becomes the urgent affairs of the copper clad laminate.

Polysiloxane is considered to be one of the most suitable toughening agents for epoxy resins, owing to its high flexible backbone of Si-O-Si, low glass transition temperature, excellent thermal and oxidative stability as well as low surface tension and good weather ability.^{1,2} However, pure poly (dimethylsiloxane) (PDMS) had very little use as a toughen-

ing agent because of the poor compatibility between soft segments of PDMS and polar hard segments in epoxy which largely resulted from the lack of hydrogen bonding.^{3,4} To improve the compatibility of polysiloxane with epoxy matrix, a large number of researches have been conducted, including using silane coupling agents,^{5,6} introducing polar functionality to polysiloxanes (such as capped with hydroxide,⁷ amino,⁸⁻¹⁰ epoxide,¹¹⁻¹³ carboxyl¹⁴ and isocyanate group¹⁵), adding block or graft silicone to make polysiloxane homogeneously dispersed in the matrix,¹⁶⁻²⁰ and chemical incorporation of PDMS into the main chain of epoxy.²¹⁻²³ Unfortunately, there still existed some drawbacks in these systems, such as the swift decline of glass transition temperature with an increase of the PDMS soft segment.

It was interesting to found in our primary studies that introducing high epoxide groups into polysiloxane by hydrolysis and condensation reaction, can improve the compatibility of polysiloxane with epoxy resin, and the highly epoxidized polysiloxanes can increase the toughness and

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thermal properties simultaneously. However, there are few reports on producing highly epoxidized polysiloxane by hydrolysis and condensation reaction to make polysiloxane homogeneously dispersed in the epoxy matrix.²⁴

In this paper, novel highly epoxidized polysiloxanes with different content of epoxide groups were synthesized to improve the toughness of an epoxy resin by a hydrolysis and condensation reaction between 3-glycidoxypropyl trimethoxysilane (GPTMS) and APTES bearing 3-glycidoxypropyl poly(methylsilane) (AGPMS) which is prepared by ring-opening reaction of 3-glycidoxypropyl poly(methylsilane) (GPPMS) with γ -aminopropyl triethoxysilane (APTES). The effects of GPTMS content relative to AGPMS and addition content on the morphologies and the mechanical properties were investigated by environmental scanning electron microscopy (ESEM), tensile testing, impact testing and fracture testing. The thermal stability of the cured epoxy resins was examined by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) as well.

Experimental

Materials. Diglycidyl ether of bisphenol A (DGEBA) with epoxide equivalent weight of 185 g eq.⁻¹ was purchased from Shell Chemical Co., Netherlands. The curing agent was 4,4-diaminodiphenylmethane (DDM), supplied by Shanghai SSS Reagent Co., Ltd., China. 3-Glycidoxypropyl poly(methylsilane) (GPPMS) was supplied by Shanghai Sili Industry & Trade Co., Ltd., China. γ -Aminopropyl triethoxysilane (APTES) and 3-glycidoxypropyl trimethoxysilane (GPTMS) were from Silicone Co., Ltd., China. Dibutyltin dilaurate was purchased from Shanghai Lingfeng Chemical Reagent Co., Ltd., China.

Preparation of APTES Bearing 3-Glycidoxypropyl Poly(methylsilane)(AGPMS). APTES bearing 3-glycidoxypropyl poly(methylsilane) (AGPMS) was prepared by the ring-opening reaction of GPPMS with APTES. 100 g GPPMS, 11.1 g APTES and 111 g toluene were placed in a three-necked

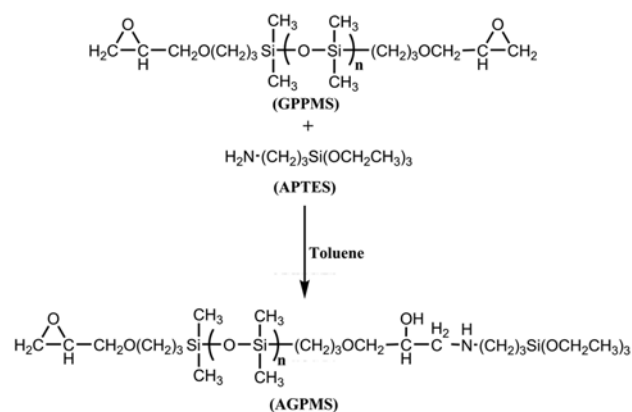


Figure 1. Preparation of APTES bearing 3-glycidoxypropyl poly(methylsilane) (AGPMS).

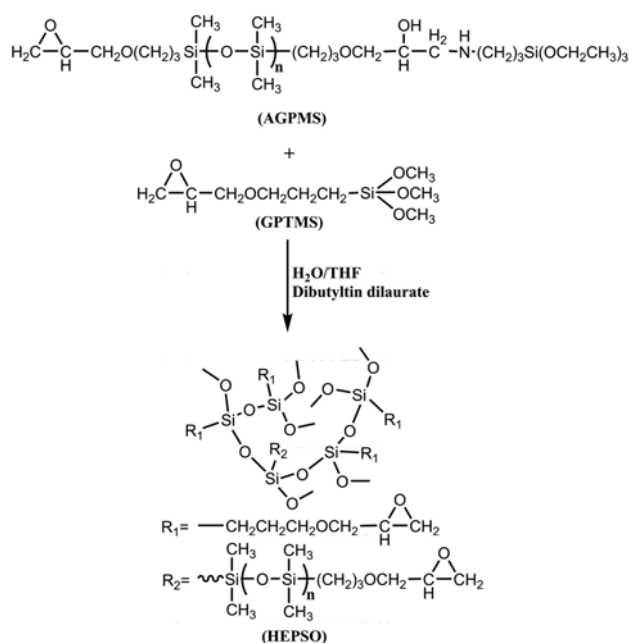


Figure 2. Preparation of highly epoxidized polysiloxane (HEPSO).

round-bottomed flask with magnetic stirring, thermometer, and reflux condenser. After purging with nitrogen at room temperature for 1 h, the mixtures were heated to 110 °C and reacted for 6 h under the protection of nitrogen. The solvent was removed on a rotary evaporator. The obtained product (AGPMS) was a light yellow transparent oil liquid. The synthetic scheme is shown in Figure 1.

Preparation of Highly Epoxidized Polysiloxane (HEPSO). Highly epoxidized polysiloxanes (HEPSOs) were prepared by the hydrolysis and condensation reaction of AGPMS with GPTMS using dibutyltin dilaurate as catalyst. Calculated amount of AGPMS, GPTMS, distilled water, dibutyltin dilaurate, and tetrahydrofuran were placed in a three-necked round-bottomed flask with magnetic stirring, thermometer and reflux condenser. After mixing the reactants and solvent by vigorous stirring for 10 min, the mixtures were heated to 65 °C and reacted for 5 h. The solvent and water were removed quickly on a rotary evaporator. The obtained product (HEPSO) was a colorless transparent viscous liquid. The synthetic scheme is shown in Figure 2, and the compositions used in this preparation were shown in Table I.

Preparation of Epoxy Thermosets Containing HEPSO. All the samples were cured under the same conditions using DDM as curing agent. The HEPSOs were added to DGEBA in an oil bath at 90 °C with continuous stirring until homogeneous mixtures were obtained. After that, a stoichiometric amount of DDM relative to DGEBA was added to the systems with vigorous stirring until homogeneous blends were obtained. Then the whole mixtures were degassed with a vacuum oven. The above mixing process for all samples

Table I. The Preparation and the GPC Measurements of the HEPSOs

Sample	AGPMS (g)	GPTMS (g)	H ₂ O (g)	Dibutyltin Dilaurate (g)	THF (g)	M_n^a	PDI ^b
HEPSO1	20.0	10.0	3.46	0.30	75.0	6,025	2.86
HEPSO2	20.0	20.0	4.60	0.40	100	3,922	2.88
HEPSO3	20.0	40.0	6.90	0.60	150	2,574	2.49

^aNumber-average molecular weight. ^bPolydispersity Index.

Table II. Preparation of HEPSO Modified Epoxy Resins

Sample	Polysiloxanes	DGEBA/Polysiloxanes/DDM Weight Ratio
Neat epoxy	-	100/0/26.7
HEPSO1-4	HEPSO1	100/4/27.0
HEPSO2-2	HEPSO2	100/2/26.9
HEPSO2-4	HEPSO2	100/4/27.2
HEPSO2-8	HEPSO2	100/8/27.6
HEPSO2-12	HEPSO2	100/12/28.1
HEPSO3-4	HEPSO3	100/4/27.3

took us about 20 min. Finally, the ternary mixtures were poured into preheated stainless steel moulds and cured at 90 °C for 3 h, plus 150 °C for 2 h and 180 °C for 2 h, in vacuum, to access a complete curing reaction. The thermosetting blends containing HEPSO up to 12 wt% were prepared. The compositions used in this study were shown in Table II.

Measurement.

FTIR and ²⁹Si NMR: The infrared spectrum (FTIR) was recorded with a WQF-410 FTIR (BRAIC, China). ²⁹Si NMR was performed on a 400 MHz Brüker NMR spectrometer (Brüker, Germany) with CDCl₃ as solvent.

GPC: The molecular weight and polydispersity index of the HEPSOs were determined on a Waters 515-410 gel permeation chromatography (GPC, Waters, USA) with calibration by polystyrene standards, and the measurements were carried out at 25 °C with tetrahydrofuran as the eluent at the rate of 1.0 mL min⁻¹.

DSC: The differential scanning calorimetry (DSC) measurements were performed on a Pyris-1 thermal analysis apparatus (Diamond DSC, Perkin-Elmer, USA) in a dry nitrogen atmosphere. The instrument was calibrated with standard indium. All samples (about 13 mg), cut into small pieces, were first heated to 200 °C and held at this temperature for 3 min to remove the thermal history, followed by quenching to 50 °C, then heated from 50 to 200 °C. A heating rate of 20 °C min⁻¹ was used in all cases. Glass transition temperature (T_g) was taken as the midpoint of the heat capacity change.

TGA: A Pyris-1 series thermal analyzer (Pyris-1 TGA, Perkin-Elmer, USA) was used to investigate the thermal stability of the silicon-modified epoxy resins. For the analysis, cured epoxies were cut into small pieces and about 15 mg of

sample was taken and heated in air from 50 to 800 °C at the heating rate of 10 °C min⁻¹ in all cases.

Tensile Testing: The tensile strength of the cured specimens was measured with a RGM-3030 Electric Universal Testing Machine (REGER, China) at a cross-head speed of 10 mm min⁻¹ according to ASTM D638-08. The gage length of the specimens was 7.62 mm. The values were taken from an average of at least five specimens.

Impact Testing: The impact strength of the cured specimens was tested with a Charpy impact tester (WPM Leipzig, Germany) at 25 °C. The specimens were unnotched, and the average dimensions of the samples were 60 mm (length) × 6.0 mm (width) × 4.5 mm (thickness). (errors < ±0.1 for width and thickness and < ±0.2 for length). The direction of the impact was from the direction of thickness. The reported results of impact testing were an average of at least five samples.

Fracture Testing: Fracture tests were carried out using single edge notched specimens machined from the cast sheets. The specimens had a nominal length, L , of 60 mm, width, W , of 12.0 mm and a thickness, B , of 6.0 mm. A 5.5 mm deep notch was cut using a steel saw, and then a fresh razor blade was sawing across the notch root to initiate a natural pre-crack. All the specimens considered valid for fracture tests had a nominal crack length to specimen width ratio, a/w , of 0.45-0.55 according to ASTM D 5045-99. The pre-cracked, single edge notched, fracture specimens were examined under three-point bending until failure. Tests were performed with a RGM-3030 Electric Universal Testing Machine (REGER, China) at a cross-head speed of 2 mm min⁻¹. The mode I stress intensity factor, K_{IC} , at the point of fracture initiation, was determined using the following equation:

$$K_{IC} = \left(\frac{P}{B\sqrt{W}} \right) f(x)$$

where P is the maximum applied force, B is the thickness of specimen, W is width of the specimen, x is the value of a/w and f is a geometry factor given by the following equation:

$$f(x) = 6\sqrt{x} \frac{[1.99 - x(1-x)(2.15 - 3.93x + 2.7x^2)]}{(1+2x)(1-x)^{3/2}}$$

ESEM: The fracture surfaces of the specimens from impact tests were observed with environmental scanning electron microscopy (ESEM; QUANTA400, FEI, USA) with

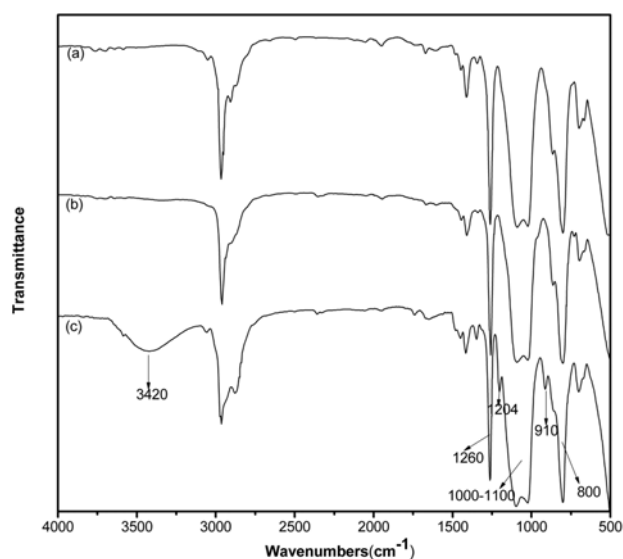


Figure 3. FTIR spectra of (a) GPPMS, (b) AGPMS, and (c) HEP SO.

an accelerating voltage of 20 kV.

Results and Discussion

Synthesis and Characterization. The chemical structure of HEP SO was confirmed by FTIR, ^{29}Si NMR and GPC spectroscopic analyses.

Figure 3 shows the FTIR spectra of GPPMS, AGPMS, and HEP SO. The FTIR spectrum of AGPMS (Figure 3(b)) is very similar to the FTIR spectrum of GPPMS (Figure 3(a)), which can be explained that the N-H and O-H ratio in the whole AGPMS molecule is so small that the absorption peaks for them can not be presented. Compared with the FTIR spectrum of AGPMS, the peaks at 3420 cm^{-1} (O-H of Si-OH), 1204 cm^{-1} (Si-OH), and 910 cm^{-1} (oxirane group) appear at FTIR spectrum of HEP SO shown in Figure 3(c), which indicates the occurrence of the hydrolysis and condensation reaction between AGPMS and GPTMS. And the strong peak at 3420 cm^{-1} (O-H of Si-OH) indicates the condensation reaction was not completely finished, which can also explain the liquid state of HEP SO. Other characteristic absorptions of HEP SO structure are at 1260 cm^{-1} (Si-C), $1100\text{--}1000\text{ cm}^{-1}$ (Si-O-C, Si-O-Si), and 800 cm^{-1} (C-H of Si-CH₂ and Si-CH₃).

Figure 4 shows the ^{29}Si NMR spectra of AGPMS and HEP SO. The ^{29}Si NMR spectrum shown in Figure 4(a) also establishes the structure of AGPMS. The peak at 7.4 ppm attributes to O-Si(CH₃)₃, the peaks at $-18.9\text{--}-23.9\text{ ppm}$ represent the absorptions of O-Si(CH₃)₂-O, and the peak at -45.2 ppm attributes to -CH₂-Si(OCH₂CH₃)₃. And the molar ratio of GPPMS and APTES was 1/1, plus the weak reactivity of the epoxide groups of the GPPMS and the big steric hindrance of the -NH-, indicate that most AGPMS has the

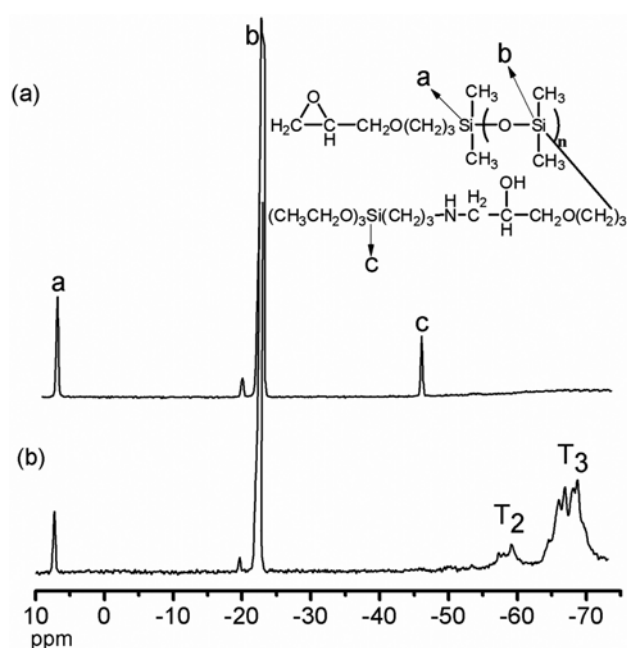


Figure 4. ^{29}Si NMR spectra of (a) AGPMS and (b) HEP SO.

structure shown in Figure 1. Compared with the ^{29}Si NMR spectrum of AGPMS, the peak at -45.2 ppm attributing to -CH₂-Si(OCH₂CH₃)₃ disappears, and the peaks at $-57.0\text{--}-60.3\text{ ppm}$ belonging to (SiO)₂-Si-OH and (SiO)₂-Si-OCH₃ (T₂) and the peaks at $-65.2\text{--}-68.9\text{ ppm}$ representing the absorption of Si-(OSi)₃ (T₃) appear at the ^{29}Si NMR spectrum of HEP SO (Figure 4(b)), which further indicates the occurrence of the hydrolysis and condensation reaction between AGPMS and GPTMS.

As shown in Table I, the average molecular weights of the HEP SO1, HEP SO2, and HEP SO3 measured by GPC were 6,025, 3,922, and 2,574, respectively. These results show that the GPTMS was successfully linked into the AGPMS during the hydrolysis and condensation reaction, and the average molecular weight of the product from the hydrolysis and condensation reaction decreases with the increase of the GPTMS content relative to AGPMS.

Miscibility of HEP SO/DGEBA Blends and Morphology of the Cured Sample. Although the GPPMS has epoxide groups at the end of the polysiloxane, when DGEBA was directly blended with GPPMS, macroscopic phase separation was serious, part of GPPMS went to the surface of the epoxy resin during the curing process. Figures 5 and 6 show the morphologies of the cured blends obtained from SEM examination. As observed from the Figures 5(a-d), the HEP SO dispersed well in the epoxy matrix, which indicates that the miscibility of GPPMS with epoxy resin was improved by incorporating APTES and GPTMS. However, there were also particles in the epoxy matrix, and the number of the particles increased with increasing HEP SO2 content. While the size of the HEP SO2 particles did not increase with the

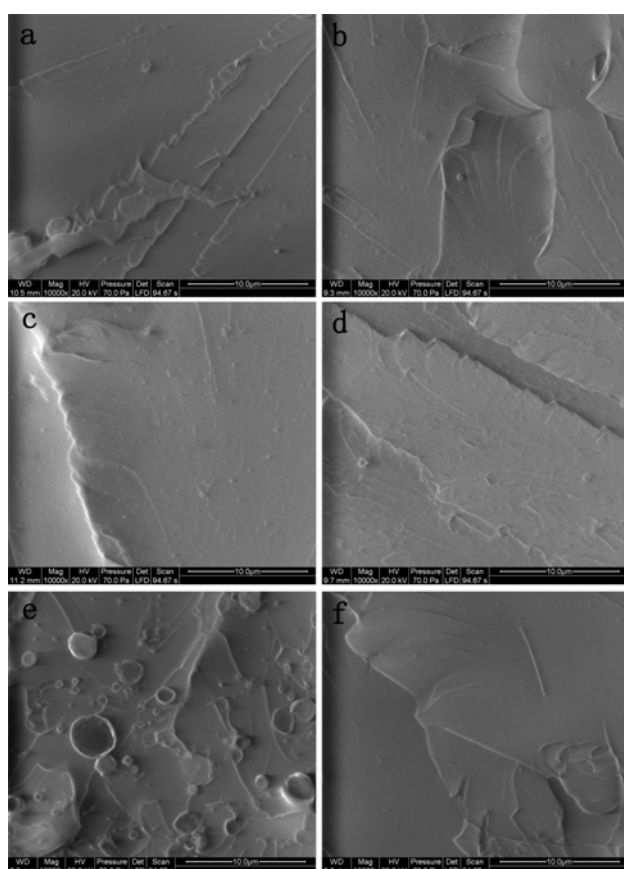


Figure 5. SEM images of fracture surfaces of cured epoxy resins, (a) HEPSO2-2, (b) HEPSO2-4, (c) HEPSO2-8, (d) HEPSO2-12, (e) HEPSO1-4, and (f) HEPSO3-4.

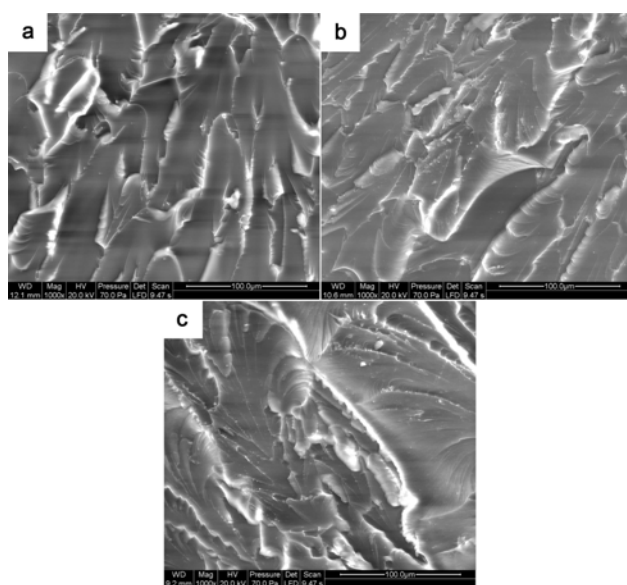


Figure 6. SEM images of fracture surfaces of cured epoxy resins at high magnification, (a) neat epoxy resin, (b) HEPSO2-2, and (c) HEPSO2-4.

increase of HEPSO2 content, which is different from the common rubber modified epoxy resins^{25,26} and further indicates the improvement of the miscibility of GPPMS with epoxy resin. And for the HEPSO1 modified epoxy resin (Figure 5(e)), the phase separation was very serious, and for the HEPSO3 modified epoxy resin (Figure 5(f)), there was almost no visible particle in the epoxy matrix, which further indicates that miscibility of polysiloxane with epoxy resin was improved by introducing the GPTMS, and the miscibility increased with the increase of the GPTMS in the HEPSO.

And from Figure 6(a), the fracture surface was relatively smooth and glassy, which is typical of a brittle thermosetting polymer,^{27,28} and these observations agree well with the low measured toughness of the material, where impact strength and K_{IC} were 19.33 kJ m^{-2} and $2.35 \text{ MPa m}^{1/2}$, respectively. The fracture surfaces of the HEPSO2-2 and HEPSO2-4 showed rougher features and more micro cracks than that of the unmodified epoxy, as shown in Figure 6(b) and (c), which was consistent with the good toughness of the HEPSO2-2 and HEPSO2-4.

Mechanical Properties. The mechanical properties of HEPSO-modified epoxy resins were determined in terms of tensile strength, impact strength, and stress intensity factor (K_{IC}).

Tensile Properties: The tensile strength of the cured epoxy resins are shown in Figures 7 and 8. Clearly, the tensile strength can be enhanced by the addition of HEPSO with appropriate contents. In general, the addition of soft phase like rubber and polyurethane, etc., to epoxy resins results in reduction of the tensile strength.^{29,30} This is also observed for the high HEPSO2 content cases as shown in Figure 7. Nonetheless, Figure 7 shows that the tensile strength of the blend containing 2 and 4 phr HEPSO2 is slightly enhanced by the addition of HEPSO. The addition of a low content HEPSO produced the second phase particles uniformly distributed in the modified epoxy system (as shown in Figure

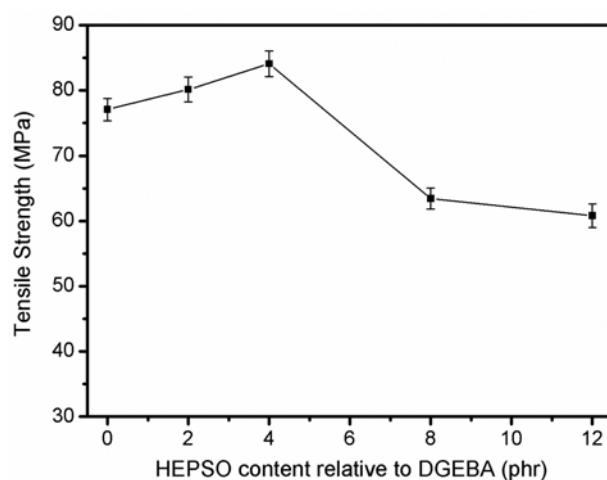


Figure 7. Tensile strength of the modified epoxy resins as a function of the HEPSO contents.

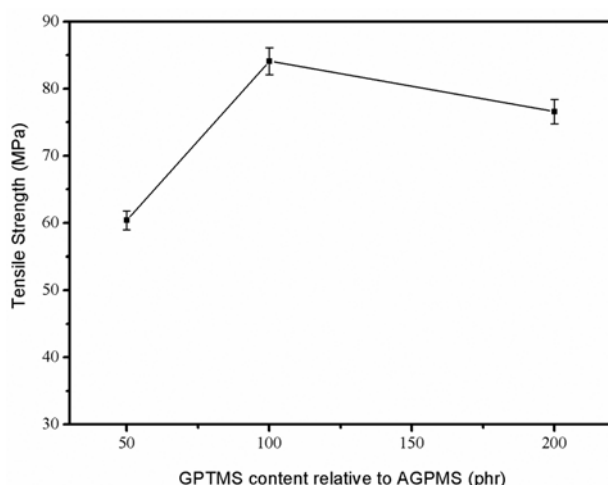


Figure 8. Tensile strength of the cured epoxy resins modified with HEPsOs (4 phr) as a function of the GPTMS contents relative to AGPMS.

6(b) and 6(c)). In rubber-toughened epoxy resins, the dispersed soft silicone rubber particles are assumed to effectively reduce the internal stress in epoxy resins caused during curing, which is attributed to the complete separation of rubber phase from epoxy matrix and acts as a stress relieving agent.³¹ Experimentally, it is clear that soft second phases with fine sizes are beneficial to enhancement of the tensile strength of epoxy resins.^{32,33} Similarly, the uniformly distributed soft second HEPsO phase with a small droplet size can release internal stress caused during curing to enhance the tensile strength. The dependence of the tensile strength of modified epoxy resins on the HEPsO content as shown in Figure 7 is determined by the two competing effects of reduced internal stress and lowered strength by introduction of soft HEPsO phase. In other words, on the one hand the addition of soft second HEPsO phase would reduce internal residual stress, leading to the increased tensile strength; on the other hand, the interaction strength between epoxy matrix and the HEPsO phase is relatively low, when the blend containing more than 8 phr HEPsO, the space between the HEPsO phases is so small that the crosslinking structure of the matrix is damaged, resulting in the lower tensile strength. This can also be confirmed by the Figure 8. As can be seen, when the GPTMS content relative to AGPMS was 50 phr, the tensile strength of modified epoxy resin was 60.37 MPa, which was lower than the neat epoxy resin (77.09 MPa), and when the GPTMS contents were 100 and 200 phr, the tensile strength were 84.09 and 76.57 MPa, respectively. This can be explained that when the GPTMS content was 50 phr, the size of the HEPsO phase was so large that the crosslinking structure of the matrix was damaged and the interaction strength between HEPsO phase and epoxy matrix was not strong, as a result the tensile strength decreased; and when the GPTMS con-

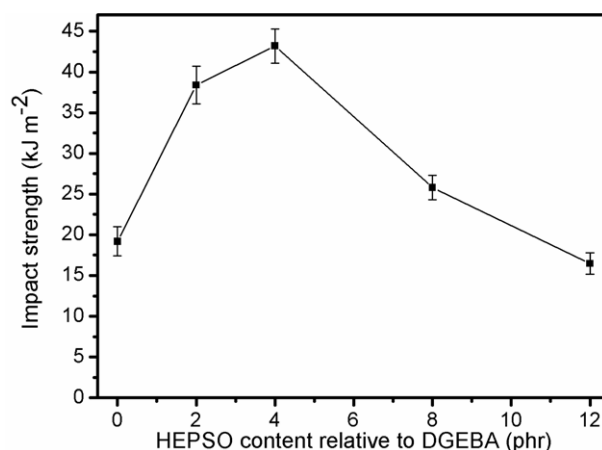


Figure 9. Impact strength of the modified epoxy resins as a function of the HEPsO contents.

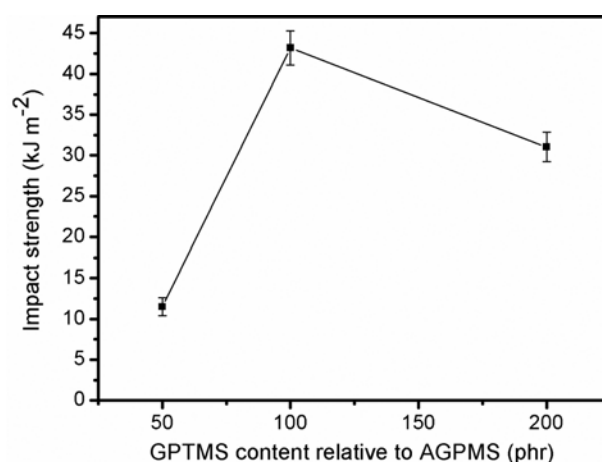


Figure 10. Impact strength of the cured epoxy resins modified with HEPsOs (4 phr) as a function of the GPTMS contents relative to AGPMS.

tent was 200 phr, the compatibility of HEPsO with epoxy matrix was so well that few particles which reduced internal residual stress existed, resulting in a lower tensile strength relative to the HEPsO2 modified epoxy resin. Consequently, at relatively low addition levels, the tensile strength of the epoxy resin can be increased by introducing the HEPsO which has proper compatibility with epoxy matrix.

Impact Properties and Fracture Toughness: The impact strength and stress intensity factor (K_{IC}) were measured to investigate the toughness of the HEPsO-modified epoxy resins.

As shown in Figure 9, impact strength of cured resins toughened with HEPsO2 reaches a maximum value by using 4 phr HEPsO2. Further addition of HEPsO2 decreased the impact strength of toughened resins but the value was still higher than the neat epoxy by addition of 8 phr HEPsO2. Figure 10 exhibits the dependence of the impact strength of epoxy resins with HEPsOs (4 phr) on the GPTMS content

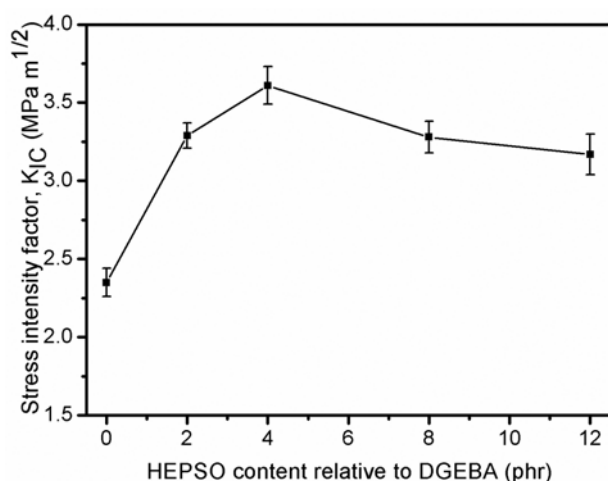


Figure 11. The stress intensity factor (K_{IC}) of modified epoxy resins as a function of the HEPISO contents.

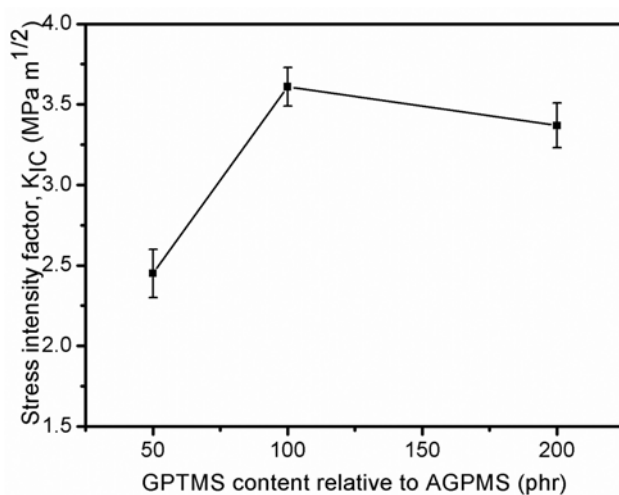


Figure 12. The stress intensity factor (K_{IC}) of the cured epoxy resins modified with HEPISOs (4 phr) as a function of the GPTMS contents relative to AGPMS.

relative to AGPMS. Obviously, when the GPTMS content was 50 phr, the impact strength value was 11.9 kJ m^{-2} , which was greatly lower than the neat epoxy resin (19.33 kJ m^{-2}), and when the GPTMS contents were 100 and 200 phr, the impact strength values were 43.2 and 31.03 kJ m^{-2} , respectively.

The stress intensity factor (K_{IC}) exhibits the similar trend as the impact strength. Figure 11 shows the stress intensity factor (K_{IC}) of cured resins as a function of the amount of silane. The K_{IC} value of cured resin toughened with HEPISO2 increased by the addition of 4 phr HEPISO2, but there was no additional increase between 4–12 phr. And the K_{IC} value of the HEPISO modified epoxy resin reached a maximum when the GPTMS content was 100 phr, as shown in Figure 12.

Impact strength and K_{IC} values of modified epoxies first increased with the increase in HEPISO2 content before 4 phr, which may be due to high-energy absorption, and resil-

ient behavior of the flexible siloxane molecule,³⁴ as well as the defects and the lower crosslinking density of the network caused by the incorporating polysiloxanes. When the modifier content increased to 8 wt% and 12 wt%, the dispersed polysiloxane particles were so many that the particles seem to be contacted each other, as shown in Figure 5(c) and 5(d) (above), which might affect the crosslinking structure of the epoxy networks, and consequently the lower impact strength and K_{IC} values. And the impact strength and K_{IC} of modified epoxies both reach the maximum values, when the GPTMS content was 100 phr relative to AGPMS. This phenomenon can be explained that when the GPTMS content was 50 phr, the HEPISO could not well disperse in the epoxy matrix, phase separation was very serious, and large agglomerates existed in the epoxy matrix, which acted as defects and then initiated failure to reduce impact strength and the toughness of the epoxy resin (K_{IC}), and when the GPTMS content was 200 phr, the compatibility of HEPISO with epoxy matrix was so well that fewer particles which played an important role in toughening epoxy resins, existed, resulting in a lower impact strength and K_{IC} values relative to the HEPISO2 modified epoxy resin.

Glass Transition Temperature from DSC Measurements.

The glass transition temperature (T_g) is an excellent indicator for the thermal stability of epoxy formulated samples.³⁵ The DSC curves of the HEPISO modified epoxy resins are shown in Figure 13. Obviously, the T_g s of the epoxy resins were slightly increased by introducing silicone compounds. This result can be explained as follows: when HEPISOs were incorporated into epoxy resin, they could react with DDM and DGEBA by their epoxide groups and Si-OH, and enter into the crosslink network. They could function as crosslink sites to some extent and lead to higher crosslink density and consequently higher T_g .³⁶ But the T_g s were not greatly influenced by the content of HEPISO2. On the one hand, with the increase of the HEPISO2 content in epoxy resin, more epoxide groups and Si-OH react during the curing process,

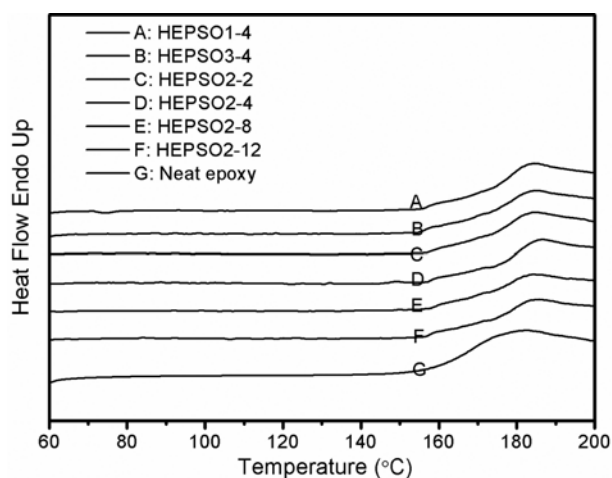


Figure 13. DSC curves of the cured epoxy resins.

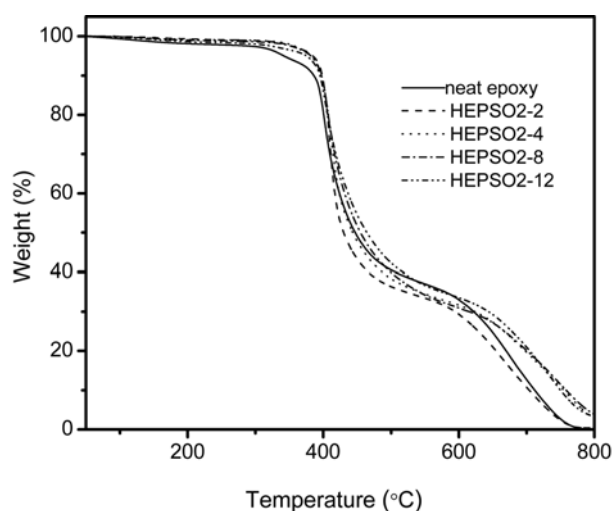


Figure 14. TGA curves of HEP SO-modified epoxy resins in air.

which increases the crosslink density and the T_g s; on the other hand the polysiloxane has good flexibility, plus the number of the HEP SO2 particles increases with the increase of the HEP SO2, as a result, the crosslinking structure of the epoxy resin is destroyed and consequently the T_g decreases. These two competing effects finally lead to the similar T_g s. At the same addition (4 phr), with the increase of the GPTMS segments in the HEP SO, more and more epoxide groups react during the curing process, which increases the crosslink density and the T_g s. While the HEP SO1, HEP SO2, and HEP SO3 modified epoxy resins exhibit similar T_g s. This can be explained that more and more polysiloxane segments introduced into the crosslinking network, which plastified the epoxy resin and consequently decreased the T_g s, plus the addition was small, the difference of the T_g s was so small that it can not be examined by DSC measurement.

Thermal Degradation of the Cured Epoxy Resins by TGA Analysis. TGA is usually utilized to study the thermal stability of polymeric materials. The results of TGA analysis of the cured samples under air atmosphere are shown in Figure 14. The initial degradation temperature for 5% weight loss (T_d 5%), the temperature for 50% weight loss (T_d 50%) and the residual weight percent at 800 °C (R_{800}) could be higher than the neat epoxy resin. These results indicate that the thermal stability improved as siloxane components were incorporated into the cured networks.³⁷ This increasing thermal stability may be due to the high thermal stability of the silicone compound and the protecting effect of the silica layer formed during the decomposition process, where silica greatly restrains the oxidation weight loss of the polymeric materials, and results in high the residual weight for the polymers at 800 °C.³⁸ While T_d 50% of HEP SO2-2 is lower than that of the neat epoxy resin. This can be explained that the HEP SO2 decomposed and transferred to the surface of the epoxy resin at the high temperature, in HEP SO2-2 the

HEP SO2 content was so small that it could not form protect layer in the surface of the epoxy resin; and the HEP SO2 affected the network of the epoxy resin, which made the decomposition more easily.

Conclusions

For the first time, a serial novel highly epoxidized polysiloxanes were synthesized to modify the epoxy resin. This kind of polysiloxanes can effectively toughen the epoxy resin. The traditional rubber toughener can significantly enhance the toughness of the resin system but decreases the glass transition temperature. HEP SO was found to have the best balance of properties, an addition of 4 phr HEP SO2 resulted in the highest increase in the tensile strength, impact strength, and K_{IC} , the glass transition temperature and thermal stability were also improved at relatively low addition levels. This can be attributed to the high epoxidized groups in polysiloxane, which reacted during the curing process, and chemically participated in the crosslinking network. The morphologies of the fracture surfaces of the cured epoxy resins show that the miscibility of polysiloxane with epoxy resin increased with the increase of the epoxide group in HEP SO, and the fracture surfaces of HEP SO2-2 and HEP SO2-4 show rougher features and more micro cracks than that of the unmodified epoxy, which further indicates the good toughness of the HEP SO2-2 and HEP SO2-4.

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