

Rigid Biphenyl-contained Epoxy Resins with Improved Thermal Resistant Properties*

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Abstract Biphenyl-contained monomer of 1,4-bis[2-(3,4-epoxy cyclohexyl ethyl) dimethylsilyl] biphenyl (BP-SiH-EP) was prepared *via* hydrosilylation reaction of 1,4-bis(dimethylsilyl) biphenyl (BP-SiH) and 1,2-epoxy-4-vinylcyclohexane in the presence of Karstedt's catalyst. ¹H-NMR, ¹³C-NMR and FTIR were used to characterize the structure of the obtained monomer. BP-SiH-EP was then cured by methyl hexahydrophthalic anhydride (MeHHPA) with 1-cyanoethyl-2-ethyl-4-methylimidazole as an accelerator. The polymerization behavior was studied by DSC. The results of DMA measurement demonstrate that the cured BP-SiH-EP/MeHHPA can maintain high storage modulus (>1 GPa) in a wide range of temperature up to 176 °C. According to the damping factor curve of DMA, cured BP-SiH-EP/MeHHPA exhibits a high glass transition temperature (T_g) of 192 °C, which is 20 °C higher than that of cured 1,4-bis[2-(3,4-epoxy cyclohexyl ethyl) dimethylsilyl] benzene (DEDSB)/MeHHPA. TGA results show that cured BP-SiH-EP/MeHHPA has good thermal stability ($T_{5\%} = 339$ °C) due to the high heat-resistance of rigid biphenyl group. Moreover, the crosslinking density of cured BP-SiH-EP/MeHHPA should be lower than that of cured DEDSB/MeHHPA estimated from their chemical structures, which conflicts with the calculated results based on the rubber elasticity equation. The inconsistency indicates that the calculated crosslinking densities are not comparable, possibly owing to their differences in the rigidity of polymer chains and intermolecular interaction.

Keywords Epoxy resin; Hydrosilylation; Biphenyl group; Thermal property; Crosslinking density

INTRODUCTION

Epoxy resins are widely used in many fields such as aerospace, electronics, automobiles and architectures^[1, 2] due to their extraordinary properties including excellent adhesion properties, strength, high chemical resistance and durability^[3–5]. However, such materials have some disadvantages, *e.g.* the traditional epoxy resins prepared from epichlorohydrin and bisphenol A show poor thermal resistant properties, harmful residue of chloride ions to the electrical insulation, and usual degradation under UV radiations^[6, 7]. To improve the thermal resistant properties, the corresponding functional groups such as rigid big aromatic group, have been introduced to the structure of epoxy resins^[8, 9], but the rigid aromatic groups commonly endow the resins with high melting point or high viscosity. Moreover, the olefin oxidation by peroxide, *e.g.* 3-chloroperoxybenzoic acid^[10] is also used to improve the resins' thermal properties despite its high cost and danger of explosive.

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Another method for preparation of epoxy is hydrosilylation, which is described as the catalytic addition of Si—H bonds with double bond of olefinic epoxy^[11, 12]. There are mainly two kinds of olefinic epoxy precursors: linear aliphatic epoxy (*e.g.* allyl glycidyl ether) and cycloaliphatic epoxy (*e.g.* 1,2-epoxy-4-vinylcyclohexane). The glass transition temperature (T_g) of cured cycloaliphatic epoxy resins is usually higher than that of linear aliphatic epoxy resins^[13, 14]. Rigid groups, such as silphenylene group and biphenyl group, can be introduced to modify epoxy resins, which may increase the stiffness and T_g of cured epoxy resins, and decrease the water absorption^[15, 16].

Herein, we report the introduction of biphenyl group into the structure of monomer by hydrosilylation reaction for the preparation of 1,4-bis[2-(3,4-epoxycyclohexylethyl)dimethylsilyl]biphenyl (BP-SiH-EP), by which the chlorine residual in the resins can be avoided. The epoxy monomer was cured with methylhexahydrophthalic anhydride (MeHHPA) as the hardener. The curing behavior, dynamic mechanical property, crosslinking density and thermal stability of the cured resin were investigated and compared with those of cured 1,4-bis[2-(3,4-epoxycyclohexylethyl)dimethylsilyl]benzene (DEDSB)/MeHHPA^[15].

EXPERIMENTAL

Materials

Tetrahydrofuran (THF, pre-dried over Na) was purchased from ACROS. 4,4'-Dibromobiphenyl (PPDBr, 98%) was purchased from TCI. *p*-Dibromobenzene (PDBB, 99%) and Karstedt's catalyst solution (Pt, ~ 2% in xylene) were purchased from Aladdin. Chlorodimethylsilane (ClMe₂SiH, 95%), 1,2-epoxy-4-vinylcyclohexane, 1-cyanoethyl-2-ethyl-4-methylimidazole (2E4MZ-CN) and MeHHPA were supplied by Energy-Chemical Co. Ltd. DEDSB was prepared according to the method described in the reference^[15].

Characterization

¹H-NMR and ¹³C-NMR spectra were recorded with a Bruker DMX-500 Spectrometer using CDCl₃ as solvent. Fourier transform infrared (FTIR) spectroscopy was performed on a Nicolet Magna-IR 550 II FTIR spectrophotometer operating at a resolution of 4 cm⁻¹ and using KBr pellets. Thermal gravimetric analysis (TGA) was performed on a Shimadzu DTG-60H simultaneous DTA-TG apparatus with a heating rate of 10 K/min under nitrogen purge rate of 35 mL/min. Differential scanning calorimetry (DSC) was measured on a TA Q200 calorimeter. Dynamic mechanical analysis (DMA) was carried out on TA Q800 instrument by the 3-point bending method at a heating rate of 3 K/min with the test frequency at 1 Hz.

Synthesis

Preparation of BP-SiH 1

Magnesium powder (4.08 g, 3.5 mmol), THF (40 mL) and ClMe₂SiH (3.5 g, 37 mmol) were added in a 100 mL three-necked round-bottom flask equipped with a reflux condenser under nitrogen protection. After the mixture was heated to 40 °C, PPDBr (5 g, 16 mmol) was added slowly and then stirred for 3 h. After the reaction was completed, the mixture was condensed on a rotary evaporator, and then poured into deionized water (30 mL). The mixture was extracted with ethyl acetate (15 mL × 3). The combined organic phase was washed with deionized water (100 mL), dried over sodium sulfate for 12 h, and then filtered, concentrated. 4.0 g of the colorless liquid product BP-SiH 1 was obtained in 93.0% yield. ¹H-NMR (500 MHz, CDCl₃, δ): 7.49–7.71 (m, 8H), 4.58 (s, 2H), 0.46 (s, 12H).

Preparation of BP-SiH-EP 2

1,2-Epoxy-4-vinylcyclohexane (2.79 g, 22.6 mmol) and Karstedt's catalyst solution (3 μ L) were added in a three-necked round-bottom flask equipped with a reflux condenser under nitrogen protection. The mixture was stirred and heated to 90 °C for 1 h. After that, BP-SiH 1 (2.9 g, 10.7 mmol) was added slowly with stirring for 1.5 h. Then the mixture was purified by column chromatography to afford 4.21 g BP-SiH-EP 2 in the yield of 76.4%. MP: 59.7 °C. Viscosity: 0.39 Pa·s at 70 °C. ¹H-NMR (500 MHz, CDCl₃, δ): 7.54–7.58 (m, 8H), 3.10–3.13 (m, 4H), 1.08–2.20 (m, 18H), 0.72 (m, 4H), 0.26 (s, 12H).

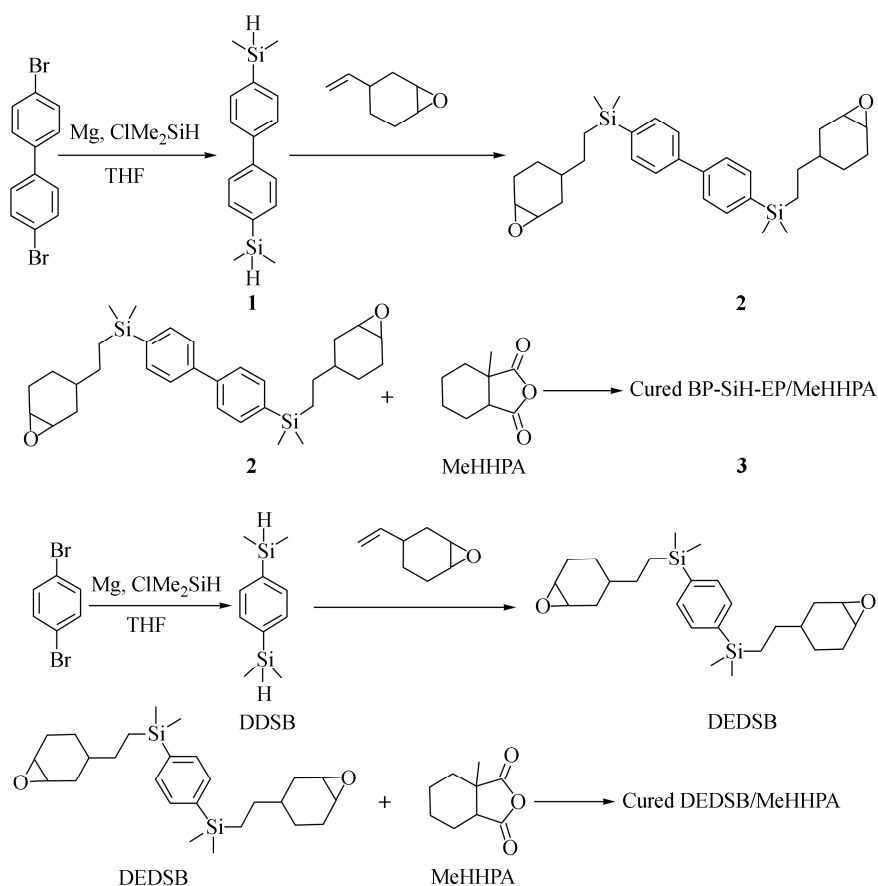
Preparation of thermosetting resins

For curing reaction, the epoxy (BP-SiH-EP **2** and DEDSB) was mixed with MeHHPA as a hardener with 0.85 equivalents of anhydride per equivalent of epoxy. Besides, 1 wt% of 2E4MZ-CN was added as an accelerator. Then the mixture was poured into a glass mold. After degassing in a vacuum oven at 130 °C for 1 h, the mold was then heated at 150 °C for 2 h, then at 180 and 200 °C for 1 h, respectively. After cooled to room temperature, the thermosetting resin was polished as rectangular bars with a size of 30 mm × 13 mm × 1.5 mm for DMA test.

RESULTS AND DISCUSSION

Synthesis and Characterization of Monomer

Synthetic routes to monomers and the curing reaction with MeHHPA are shown in Scheme 1. BP-SiH **1** was firstly synthesized by Grignard reaction in the presence of magnesium powders, ClMe₂SiH and PPDBr. Then BP-SiH-EP **2** with double epoxy groups was prepared by hydrosilylation reaction of BP-SiH and 1,2-epoxy-4-vinylcyclohexane with Karstedt's catalyst. Another monomer (DEDSB) was obtained by the same procedure. After that, BP-SiH-EP and DEDSB were cured by MeHHPA as a hardener and 2E4MZ-CN as an accelerator, respectively.



Scheme 1 Synthetic routes to monomers and curing reaction with MeHHPA

¹H-NMR spectra of BP-SiH **1** and BP-SiH-EP **2** are shown in Fig. 1. For BP-SiH **1**, the peaks at $\delta = 7.49$ – 7.71 were ascribed to the protons of biphenyl. The proton of Si–H and the protons of Si–CH₃ appeared at $\delta = 4.58$ and 0.46 , respectively. As for BP-SiH-EP **2**, the protons of biphenyl showed at $\delta = 7.54$ – 7.58 (m, 8H),

the peak at $\delta = 0.26$ was ascribed to the protons of Si—CH₃, and the proton of Si—H bond at $\delta = 4.58$ disappeared, indicating the complete hydrosilylation reaction of Si—H bond with the double bond of 1,2-epoxy-4-vinylcyclohexane. The protons of epoxy groups emerged at $\delta = 3.10$ – 3.13 , which further evidenced the hydrosilylation reaction, while the protons on cyclohexane groups showed the severe split and overlapped peaks due to the effect of chiral carbon on cyclohexane groups and similar chemical environment. These peaks were difficult to be assigned. However, overall the percentage of integral values (peak area) for each range of chemical shift supported the formation of BP-SiH-EP 2.

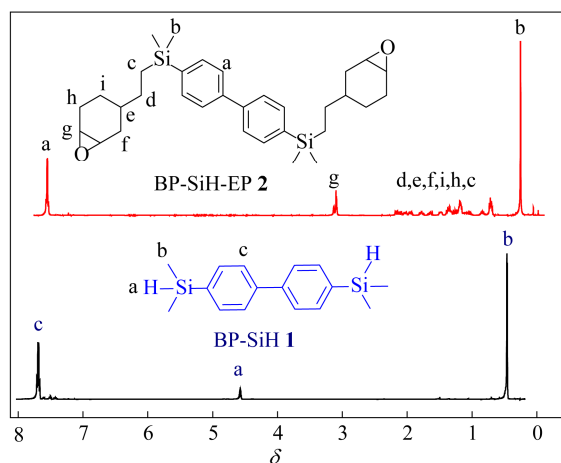


Fig. 1 ^1H -NMR spectra of BP-SiH 1 and BP-SiH-EP 2

^{13}C -NMR spectrum of BP-SiH-EP 2 is shown in Fig. 2. The peaks at $\delta = 141.4$ – 126.1 and $\delta = 53.2$ – 51.7 were attributed to the symmetric biphenyl ring and the epoxy groups, respectively. The peak at $\delta = -3.0$ belonged to the carbon of CH₃—Si. All the peaks referred to the corresponding carbons in the monomer, which evidenced the chemical structure of BP-SiH-EP 2.

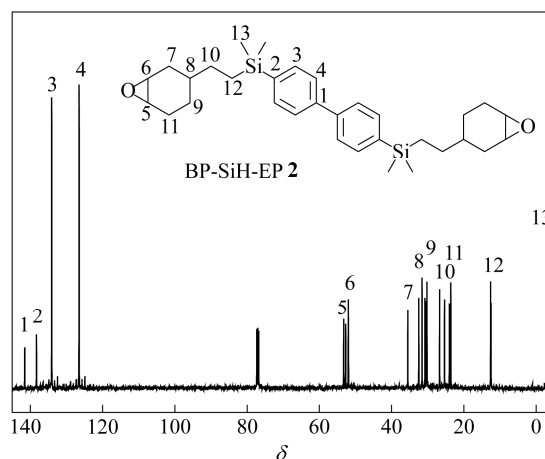


Fig. 2 ^{13}C -NMR spectrum of BP-SiH-EP 2

Figure 3 shows the FTIR spectra of BP-SiH 1, BP-SiH-EP 2 and cured BP-SiH-EP/MeHHPA 3. It could be seen that, for BP-SiH 1, the Si—H groups located at 2117 cm^{-1} . The characteristic absorption of Si—CH₃ groups was observed at 1249 cm^{-1} [17]. The strong and weak absorptions at 1596 cm^{-1} and 1423 – 1457 cm^{-1} belonged to the Si-biphenylene groups. The peaks at 2844 – 2958 cm^{-1} were assigned to C—H stretching vibration of saturated alkyl. Compared with SiH-BCB 1, the characteristic Si—H peak of BP-SiH-EP 2 at 2117 cm^{-1}

disappeared because of the hydrosilylation. Besides, the characteristic cycloaliphatic epoxy peak was observed at 885 cm^{-1} [15].

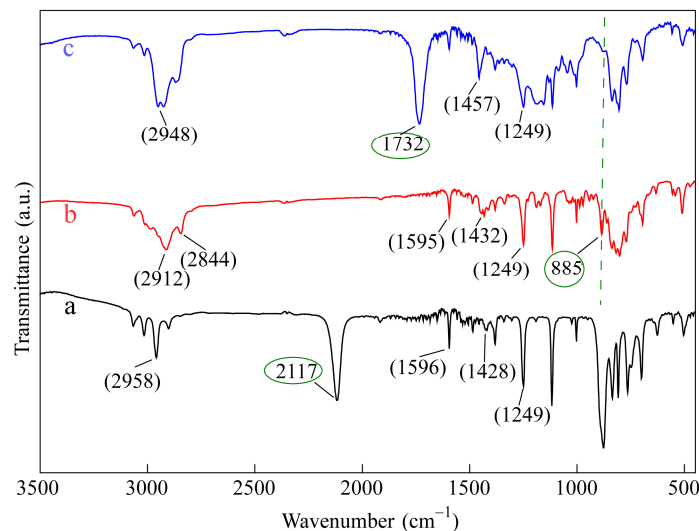


Fig. 3 FTIR spectra of BP-SiH **1** (a), BP-SiH-EP **2** (b) and cured BP-SiH-EP/MeHHPA **3** (c)

Synthesis and Characterization of the Cured Resin

The FTIR spectrum of cured BP-SiH-EP/MeHHPA **3** is shown in Fig. 3. The new peak at 1732 cm^{-1} was attributed to the stretching vibration of $\text{C}=\text{O}$ of carboxylic ester groups in MeHHPA. Besides, the characteristic cycloaliphatic epoxy peak at 885 cm^{-1} almost disappeared, indicating that nearly complete cure was achieved with the cure conditions employed in this work[15].

The epoxy BP-SiH-EP **2** and DEDSB were cured with MeHHPA as a hardener and 2E4MZ-CN as an accelerator, respectively. The curing behavior was studied by DSC from room temperature to $250\text{ }^{\circ}\text{C}$ at a ramping rate of 10 K/min . The results are shown in Fig. 4. For BP-SiH-EP/MeHHPA, the exotherm showed that the initial exothermal temperature began at $121\text{ }^{\circ}\text{C}$, achieved maximum at $174\text{ }^{\circ}\text{C}$ with a shoulder peak at $148\text{ }^{\circ}\text{C}$, and ended at $200\text{ }^{\circ}\text{C}$, while for DEDSB/MeHHPA, the initial exothermal temperature began at $122\text{ }^{\circ}\text{C}$, reached maximum at $169\text{ }^{\circ}\text{C}$ with a shoulder peak at $151\text{ }^{\circ}\text{C}$, and ended at $201\text{ }^{\circ}\text{C}$.

Figure 4 gives the T_g of cured resins obtained by DSC. The curve of cured BP-SiH-EP/MeHHPA **3** showed a glass transition with the extrapolated onset temperature at $176\text{ }^{\circ}\text{C}$ and extrapolation end temperature at $191\text{ }^{\circ}\text{C}$. The T_g of cured BP-SiH-EP/MeHHPA **3** was $184\text{ }^{\circ}\text{C}$, which was $22\text{ }^{\circ}\text{C}$ higher than that of cured DEDSB/MeHHPA.

DMA was carried out to investigate the thermal mechanical properties of the cured epoxy resins. Figure 5 shows the storage modulus and $\tan\delta$ with temperature changes for the MeHHPA-cured BP-SiH-EP and DEDSB. The initial storage modulus of cured BP-SiH-EP/MeHHPA was as high as 2.2 GPa at room temperature, which was the same as that of cured DEDSB/MeHHPA. The high storage modulus suggests the high stiffness of cured BP-SiH-EP/MeHHPA. Additionally, cured BP-SiH-EP/MeHHPA could also maintain high storage modulus ($>1\text{ GPa}$) in a wide temperature range (from room temperature up to $176\text{ }^{\circ}\text{C}$). As determined by $\tan\delta$ versus temperature curve, T_g of cured BP-SiH-EP/MeHHPA was $192\text{ }^{\circ}\text{C}$, which was $20\text{ }^{\circ}\text{C}$ higher than cured DEDSB/MeHHPA with the T_g of $172\text{ }^{\circ}\text{C}$. The high T_g is due to the incorporation of rigid biphenyl group.

In order to further study the structure of the cured resin, the crosslinking density of the two epoxy resins is calculated according to the Eq. (1)[18–20]

$$\rho = E' / 3RT \quad (1)$$

where ρ is the crosslinking density expressed in moles of elastically effective network chains per cubic meter of

the sample, E' is the storage modulus of the cured network at a temperature above T_g , R is the universal constant (8.314 J/(mol·K)) and T is the absolute temperature at which the experimental modulus is determined. The E' ($T_g + 40^\circ\text{C}$) of cured BP-SiH-EP/MeHHPA and cured DEDSB/MeHHPA are 20.88 and 15.59 MPa, respectively. The crosslinking density of cured BP-SiH-EP/MeHHPA calculated by the Eq. (1) is $1.65 \times 10^3 \text{ mol/m}^3$, which is higher than that of cured DEDSB/MeHHPA ($1.29 \times 10^3 \text{ mol/m}^3$).

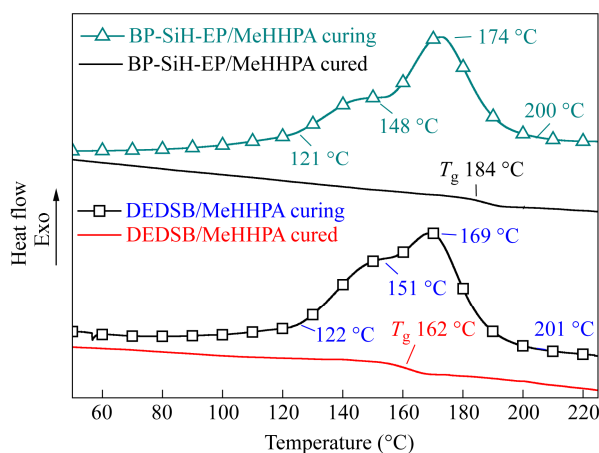


Fig. 4 DSC curves of MeHHPA-cured BP-SiH-EP and DEDSB

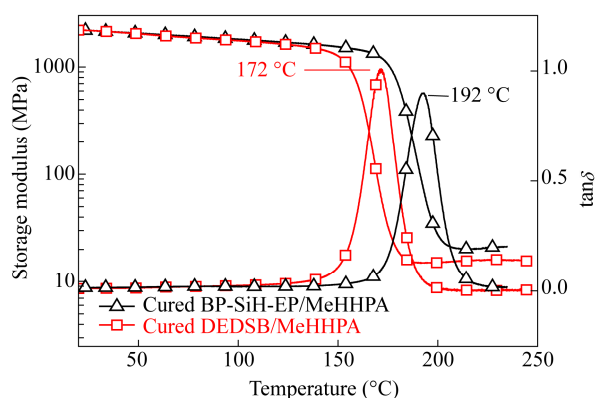
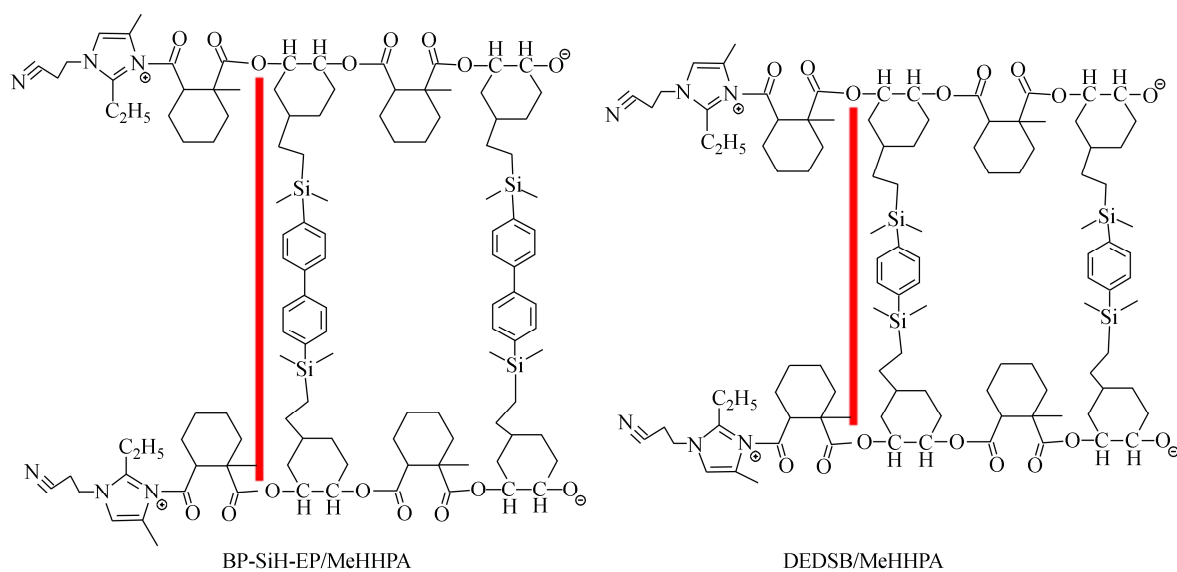


Fig. 5 DMA curves of the MeHHPA-cured BP-SiH-EP and DEDSB

As shown in Scheme 2, compared with phenyl groups, the introduction of biphenyl groups may enlarge the distance between the crosslinking points, resulting in the decrease of crosslinking density of polymers. This indicates that cured BP-SiH-EP/MeHHPA has a lower crosslinking density than cured DEDSB/MeHHPA, which conflicts with the calculation results above. The inconsistency may be ascribed to the differences in the rigidity of polymer chain and intermolecular interaction, which lead to the differences in the storage modulus above T_g . Therefore, it should be noted that the calculation of crosslinking density by Eq. (1) is not quantitatively accurate for highly crosslinked thermosets.



Scheme 2 Models of the MeHHPA-cured BP-SiH-EP and DEDSB

TGA curves of the MeHHPA-cured BP-SiH-EP and DEDSB are shown in Fig. 6. It shows that there is almost no weight loss ($< 1\%$) as the temperature below $300\text{ }^{\circ}\text{C}$, meaning that cured BP-SiH-EP/MeHHPA and DEDSB/MeHHPA have better thermal stability. The temperature of 5% weight loss of cured BP-SiH-EP/MeHHPA ($T_{5\%} = 339\text{ }^{\circ}\text{C}$) is summarized in Table 1, which is higher than that of cured DEDSB/MeHHPA ($T_{5\%} = 330\text{ }^{\circ}\text{C}$). This signifies that the rigid biphenyl group contributes to the good thermal stability.

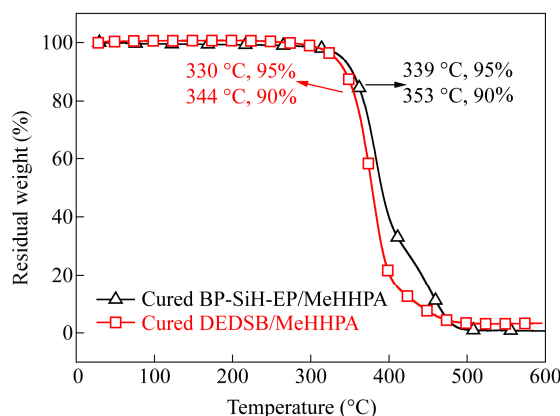


Fig. 6 TGA curves of the MeHHPA-cured BP-SiH-EP and DEDSB

Table 1 Thermal and mechanical properties of MeHHPA-cured BP-SiH-EP and DEDSB^[15]

	Monomer structure	E' ^a (GPa)	T_g ($^{\circ}\text{C}$)		$T_{5\%}$ ^c ($^{\circ}\text{C}$)
			DSC	$\tan\delta$ ^b	
Cured BP-SiH-EP/MeHHPA		2.2	184	192	339
Cured DEDSB/MeHHPA		2.2	162	172	330

^a Storage modulus at $25\text{ }^{\circ}\text{C}$; ^b Glass transition temperature according to $\tan\delta$; ^c 5% Weight loss temperature

CONCLUSIONS

In summary, epoxy monomer of BP-SiH-EP with biphenyl group has been successfully prepared by hydrosilylation reaction. $^1\text{H-NMR}$, $^{13}\text{C-NMR}$ and FTIR were used to characterize the structure of obtained monomer. The curing behavior of monomer with MeHHPA as a hardener and 2E4MZ-CN as an accelerator was tested by DSC. The cured BP-SiH-EP/MeHHPA shows a high T_g at $192\text{ }^{\circ}\text{C}$ according to $\tan\delta$ of DMA and high storage modulus which can be maintained in a wide temperature range up to $176\text{ }^{\circ}\text{C}$. The improvement of T_g can be ascribed to the introduction of rigid biphenyl group. The crosslinking density of cured BP-SiH-EP/MeHHPA is lower than that of cured DEDSB/MeHHPA estimated from their chemical structures, which conflicts with the calculated results based on the rubber elasticity equation. The inconsistency indicates that the calculated crosslinking densities are not comparable, possibly owing to their differences in the rigidity of polymer chains and intermolecular interaction. Moreover, it means that the calculation of crosslinking density from storage modulus above T_g is not always accurate and reliable for highly crosslinked thermosets. TGA study shows that the cured resins possess high thermal stability with $T_{5\%}$ at $339\text{ }^{\circ}\text{C}$. All the results demonstrate that the incorporation of rigid biphenyl group of BP-SiH-EP enhances the heat resistance of epoxy resin.

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