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Synthesis, characterization and properties of the polysiloxane-based episulfide resin

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ABSTRACT

The polysiloxane episulfide resin (PSER) was synthesized through replacement of the oxygen atoms in 1,3,5,7-tetra-(3-glycidoxypropyl) tetramethylcyclotetrasiloxane (TGCS) with sulfur atoms using potassium thiocyanate (KSCN). It was characterized by FT-IR, ^{1}H NMR, MS and elemental analysis. The PSER resin was a low viscosity liquid, stable at room temperature. The polysiloxane episulfide resin was very reactive: a mixture of PSER and isophorondiamine gelated in a few seconds at room temperature. When *m*-phenylenediamine (*m*-PDA) or 2-ethyl-4-methylimidazole (2E4MZ) was used as curing agent, PSER exhibited higher reactivity compared with the parent polysiloxane epoxy resin. The reaction heat of the PSER resin was much lower in comparison with TGCS. The cured polysiloxane episulfide resin showed higher glass transition temperature and much lower water absorption, while the thermal stability was lower. It was found that methylhexahydrophthalic anhydride (MeHHPA) is not effective for curing the episulfide resin, although it is commonly used for curing epoxy resins.

1. Introduction

Polysiloxanes are widely used in various areas for their outstanding performance of high temperature resistance, weathering stability, excellent dielectric properties, as well as chemical and biological inertness [1–4]. It is therefore interesting to implant polysiloxane to other polymer systems [5–9]. Great efforts have been made in developing polysiloxane-modified epoxy resins, which are important in electronic and microelectronic encapsulation for excellent adhesive strength, good mechanical properties, easy to process and low cost [10–15]. For transparent optical packaging materials, silicone epoxy resin systems are being developed to overcome problems of macroscopic phase separation and bleeding of the silicone component [16–19].

Episulfide resins are the analogues of epoxy resins, in which the oxygen atoms are replaced by sulfur atoms. They have several advantages over epoxy resins: higher curing reactivity, higher refractive index, good adhesion to copper, higher glass transition temperature and lower water absorption [20–22]. These advantages make them very promising in a wide range of applications including optical resin, adhesives, microelectronic packaging, etc. [23–26].

This work is to communicate our recent studies on the polysiloxane-based episulfide resin. Polysiloxane episulfide resin (PSER) was synthesized through substitution of 1,3,5,7-tetra-(3-glycidoxypropyl) tetramethylcyclotetrasiloxane with potassium thiocyanate (KSCN). The structure of PSER was characterized by FT-IR, ^{1}H NMR, MS and elemental analysis. Reactivity with different curing agents, including *m*-PDA, 2E4MZ and MeHHPA, was studied by differential scanning calorimetric measurements (DSC), and the activation energies for these reactions were estimated using Ozawa's method. Thermal properties and water absorption of the cured polysiloxane episulfide were studied in comparison with those of the parent polysiloxane epoxy resin.

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2. Experimental

2.1. Materials

Allyl glycidyl ether and 1,3,5,7-tetramethylcyclotetrasiloxane (D4H) were industrial products and purified by distillation before use. Lamoreaux platinum catalyst (Pt catalyst) was a commercial product of Degussa. Thiourea and potassium thiocyanate (KSCN) were chemical reagents purchased from Beijing Chemical Reagents Co. and Sinopharm Chemical Reagent Co., Ltd., respectively, and used as received. *M*-phenylenediamine (*m*-PDA), isophorondiamine (IPDA), 2-ethyl-4-methylimidazole (2E4MZ) and tetrabutylammonium bromide ($N(C_4H_9)_4Br$) were supplied by Beijing Xingjin Chemical Reagents Co., Tianjin Chemical Reagents Co., Ltd., Acros Organics and Beijing Xingfu Institute of Fine Chemicals, respectively, and used as received. Methylhexahydrophthalic anhydride (MeHPPA) was a commercially available product of Lonza (Italy).

2.2. Synthesis of 1,3,5,7-tetra-(3-glycidoxypropyl) tetramethylcyclotetrasiloxane (TGCS)

To a 250 ml three-necked round bottom flask equipped with a reflux condenser, a thermometer, a nitrogen inlet and a magnetic stirrer, allyl glycidyl ether (35.7 g, 0.31 mol), toluene (50 ml) and platinum catalyst (0.44 mg, 1.1×10^{-6} mol) were loaded. Then the temperature of the reaction mixture was raised to 65 °C, D_4H (15 g, 0.0625 mol) was added in about 30 min and the reaction continued for a further 2 h. The reaction mixture was cooled to room temperature; the solvent and the excess reactant were removed under 80 °C/1 mm Hg to give TGCS product, a colorless liquid. Yield: 41.5 g (95.4%). ^1H NMR ($CDCl_3$, δ, ppm): 0.05 (s, 12H); 0.46–0.52 (t, 8H); 1.55–1.63 (m, 8H); 2.56–2.58 (d, 4H); 2.75–2.77 (d, 4H); 3.10–3.11 (m, 4H); 3.32–3.43 (m, 12H); 3.65–3.69 (q, 4H). FT-IR (cm^{-1}): 2997, 2933, 1260, 1077, 909. MS: *m*/*e* 696.6 (719.5–23). Elem. Anal. Calcd. for $C_{28}H_{56}O_{12}Si_4$: C, 48.28%; H, 8.04%. Found: C, 47.34%; H, 7.94%.

2.3. Synthesis of the polysiloxane episulfide resin (PSER)

KSCN (9.72 g, 0.1 mol) and water (15 ml) were loaded into a 100 ml three-necked round bottom flask equipped with a mechanical stirrer and a thermometer. After the dissolution of KSCN, the mixture of TGCS (8.74 g, 0.0125 mol) and ethanol (30 ml) was added in 5 min. The reaction mixture was stirred for 24 h at 30 °C and then poured into a 250 ml separating funnel, 40 ml $CHCl_3$ was added. The upper layer of aqueous solution was removed; the organic phase was washed with deionized water to the neutral pH and dried over anhydrous sodium sulfate. Then the solvent was removed under 45 °C/1 mm Hg to give the product PSER, a light-yellow liquid. Yield: 8.59 g (90.0%). ^1H NMR ($CDCl_3$, δ, ppm): 0.07 (s, 12H); 0.49–0.53 (t, 8H); 1.58–1.62 (m, 8H); 2.18–2.19 (d, 4H); 2.49–2.50 (d, 4H); 3.01–3.07 (m, 4H); 3.38–3.44 (m, 12H); 3.65–3.69 (q, 4H). FT-IR (cm^{-1}): 2933, 2864, 1260, 1087, 617. MS: *m*/*e* 760.6 (783.6–23) Elem. Anal. Calcd. for $C_{28}H_{56}O_8S_4Si_4$: C, 44.21%; H, 7.37; S, 16.84%. Found: C, 43.54%; H, 7.28%; S, 15.73%.

2.4. Curing procedure of the episulfide resin

M-PDA, 2E4MZ and MeHHPA, were used to cure the polysiloxane episulfide resin and the parent polysiloxane epoxy resin. The concentration of the curing agents was calculated according to the stoichiometry when *m*-PDA or MeHHPA was used; 1 weight part of $N(C_4H_9)_4Br$ was added as accelerator per 50 weight parts of MeHHPA. Five parts of 2E4MZ was used for curing 100 parts of the resins. Curing regime is given in Table 1.

2.5. Characterization of PSER

FT-IR spectra were obtained using a Perkin-Elmer 782 Fourier transform infrared spectrometer. ^1H NMR spectra were recorded with a Bruker MSL-400 MHz NMR spectrometer using $CDCl_3$ as solvent. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were obtained using a Bruker Biflex III MALDI-TOF mass spectrometer. Refractive index was measured at 25 °C by WZS-1 refractometer from Shanghai Optical Instrument Factory. Viscosity was measured by Brookfield DV-II Pro Viscometer. Differential scanning calorimetry (DSC) was performed on a SII EXSTAR6000-DSC6220 and the thermal gravimetric analysis (TGA) was carried out on a SII EXSTAR6000-TGA6300 in nitrogen at a heating rate of 10 °C min^{-1}. For equilibrium water absorptions, samples of Φ50 mm × 3 mm were used; weight changes were recorded after water saturation at 25 °C.

3. Results and discussions

3.1. Synthesis and characterization of the polysiloxane episulfide resin (PSER)

Polysiloxane episulfide resin can be obtained through hydrolytic condensation of epoxide-bearing silane and replacement of oxygen atoms of the epoxide with sulfur

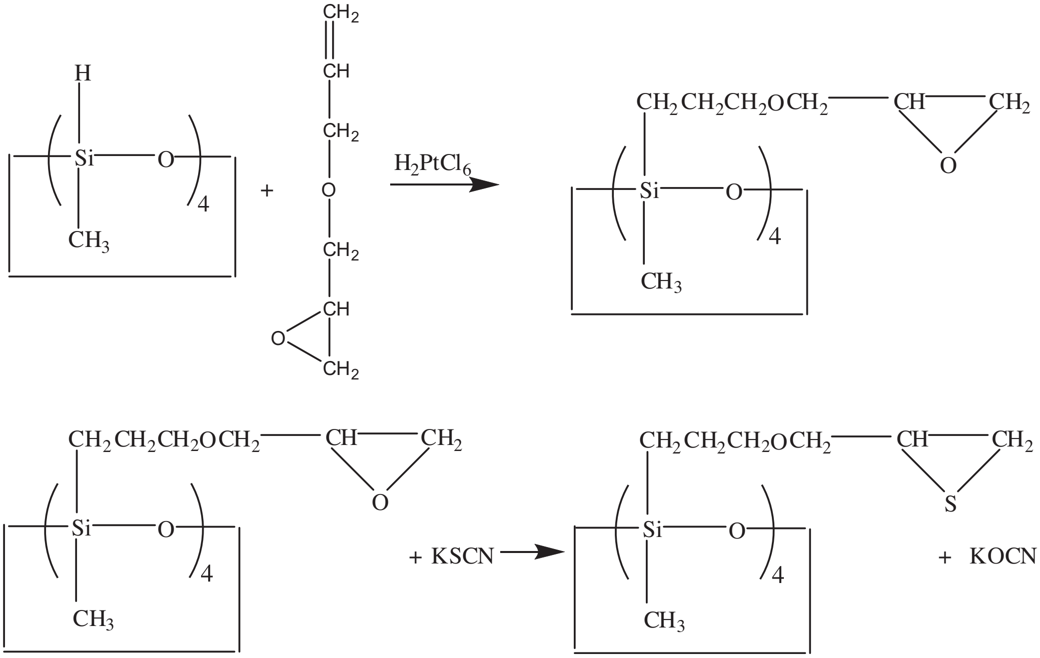
Table 1
Curing regime for the polysiloxane episulfide resin and the polysiloxane epoxy resin.

Curing system	Curing temperature (°C)	Curing time (h)	Post cure temperature (°C)	Post cure time (h)
PSER/*m*-PDA	120	3	150	4
TGCS/*m*-PDA	150	3	180	4
PSER/2E4MZ	120	3	150	4
TGCS/2E4MZ	150	3	180	4

atoms, such as the process described in the patent [27]. However, the structure of the resin was not well defined.

In this study we start from commercially available tetramethylcyclotetrasiloxane. First, 1,3,5,7-tetra-(3-glycidoxypropyl) tetramethylcyclotetrasiloxane (TGCS) was prepared through platinum-catalyzed hydrosilylation. Then the oxygen atoms in TGCS were replaced by sulfur atoms (Scheme 1). In this way polysiloxane episulfide resin (PSER) of well defined structure was obtained.

The reactant allyl glycidyl ether was used in excess to ensure complete consumption of Si–H bonds, residues of which may lead to gelation in the subsequent episulfidation reaction. Completion of the hydrosilylation reaction was indicated by disappearance of the FT-IR band at 2155 cm^{-1} and the ^1H NMR signals at 4.7 ppm. The characteristic absorption of the oxirane ring in the FT-IR spectra was found at 908 cm^{-1} (Fig. 1). The ^1H NMR spectrum with peak assignments is presented in Fig. 2.



Scheme 1. Synthesis of the polysiloxane episulfide resin (PSER).

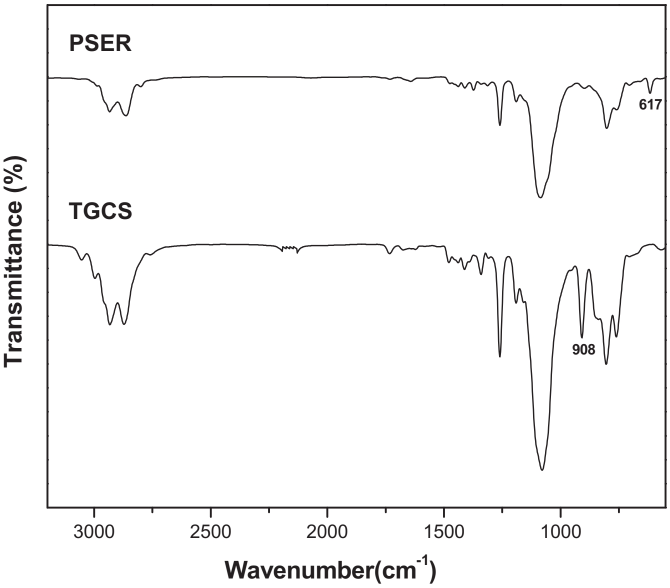


Fig. 1. FT-IR spectra for PSER and TGCS.

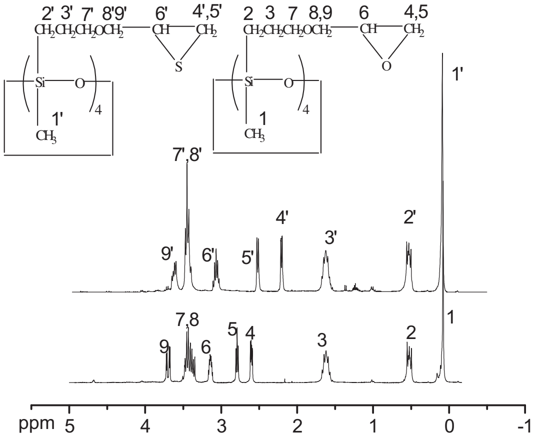


Fig. 2. ^1H NMR spectra for PSER and TGCS.

For converting epoxides to episulfides, thiourea and potassium thiocyanates have been used [28,29]. It was found that KSCN is preferable for the synthesis of PSER. When thiourea was used, gelation took place more easily.

In the FT-IR spectra of PSER shown in Fig. 1, the characteristic peak at 617 cm^{-1} due to the asymmetric deformation of episulfide ring [20] was observed. At the same time, the peak for the epoxide at 908 cm^{-1} disappeared. These results indicate the complete replacement of oxygen atoms by sulfur atoms. Comparing the ^1H NMR spectrum of PSER with that of the parent epoxide, it is clear that the chemical shifts of protons in the episulfide group are less than that of the protons in the epoxy group. It is reasonable on account of the difference in electronegativity of the elements. Sulfur is less electronegative compared with oxygen; therefore the protons in episulfide groups are electronically better shielded.

The PSER resin obtained was a liquid of low viscosity (1250 mPa s at 25 °C); this is advantageous for application. Refractive index (RI) of PSER was 1.51 at 25 °C, significantly higher than that of the parent epoxy resin (RI 1.46). This is just as expected, because the atomic refractive constant of sulfur is higher than that of oxygen.

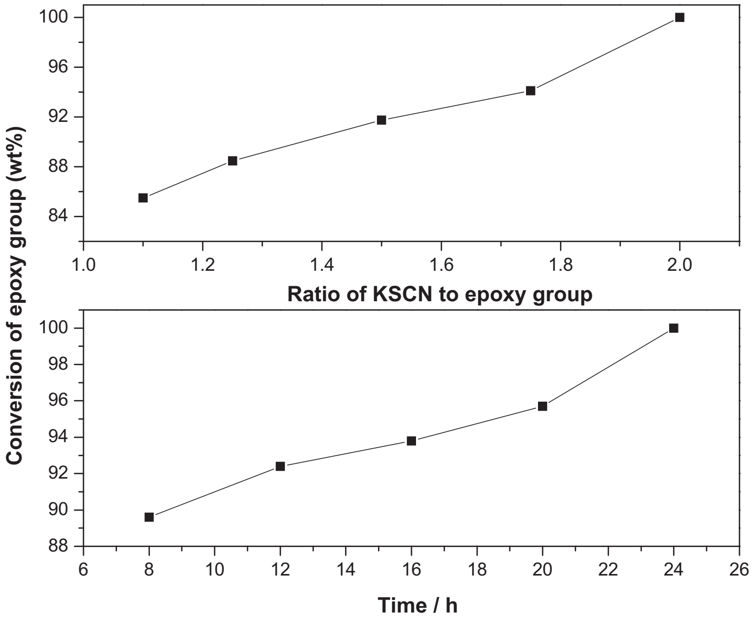
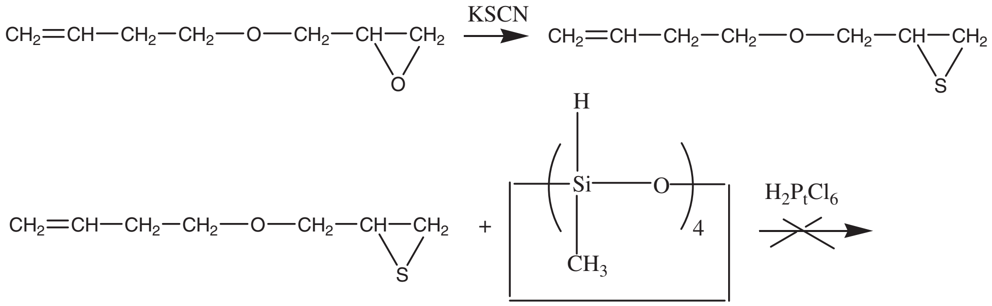


Fig. 3. Effect of reaction time and the molar ratio of KSCN to epoxy group on the conversion.



Scheme 2. The failed route for synthesis of PSER.

Influences of the reaction temperature, the reaction time and the molar ratio of KSCN to epoxy group on the episulfidation reaction were investigated. The reaction temperature along 30 °C is optimal. At temperatures lower than 20 °C, a long reaction time is needed to achieve complete conversion of epoxide into episulfide. This may bring in a risk of gelation, as the formed episulfide is not stable in the alkaline reaction medium [30]. If the reaction is carried out at temperatures higher than 45 °C, polymerization of the formed episulfide also becomes remarkable, although the time required for episulfidation is shortened.

The conversion of epoxy monomer into episulfide monomer was estimated by the ^{1}H NMR spectra of the product. A conversion curve is given in Fig. 3 for the reaction at 30 °C and molar ratio of KSCN to epoxy group at 2:1. It is seen that conversion was completed after ca. 24 h. In this case polymerization of the formed episulfide was insignificant. However, partial polymerization of episulfide was noted when

Table 2
Curing of the polysiloxane episulfide resin and the polysiloxane epoxy resin with *m*-PDA and 2E4MZ studied by DSC.

Composition	T_{onset}[a] (°C)	T_p[b] (°C)	T_f[c] (°C)	ΔH[d] (J/g)
PSER/*m*-PDA	75.9	134.7	238.3	153.0
TGCS/*m*-PDA	130.0	169.1	254.3	354.0
PSER/2E4MZ	125.6	136.4	172.7	204.0
TGCS/2E4MZ	106.6	165.1	277.2	408.0

[a] Onset temperature in DSC thermograph.
[b] Exothermal peak temperature.
[c] Exotherm ending temperature.
[d] Heat of reaction.

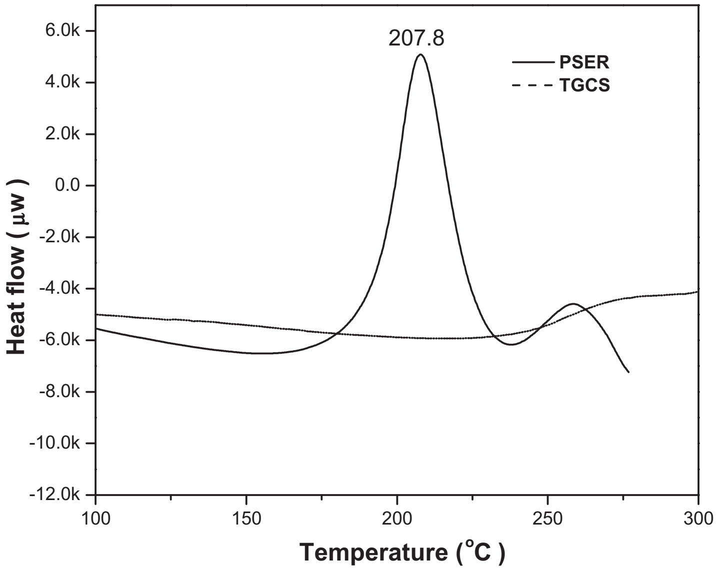


Fig. 4. DSC thermographs for TGCS and PSER.

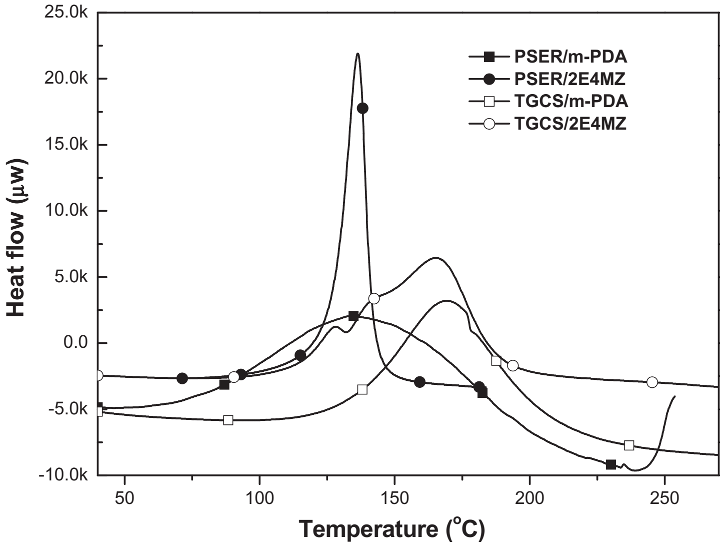
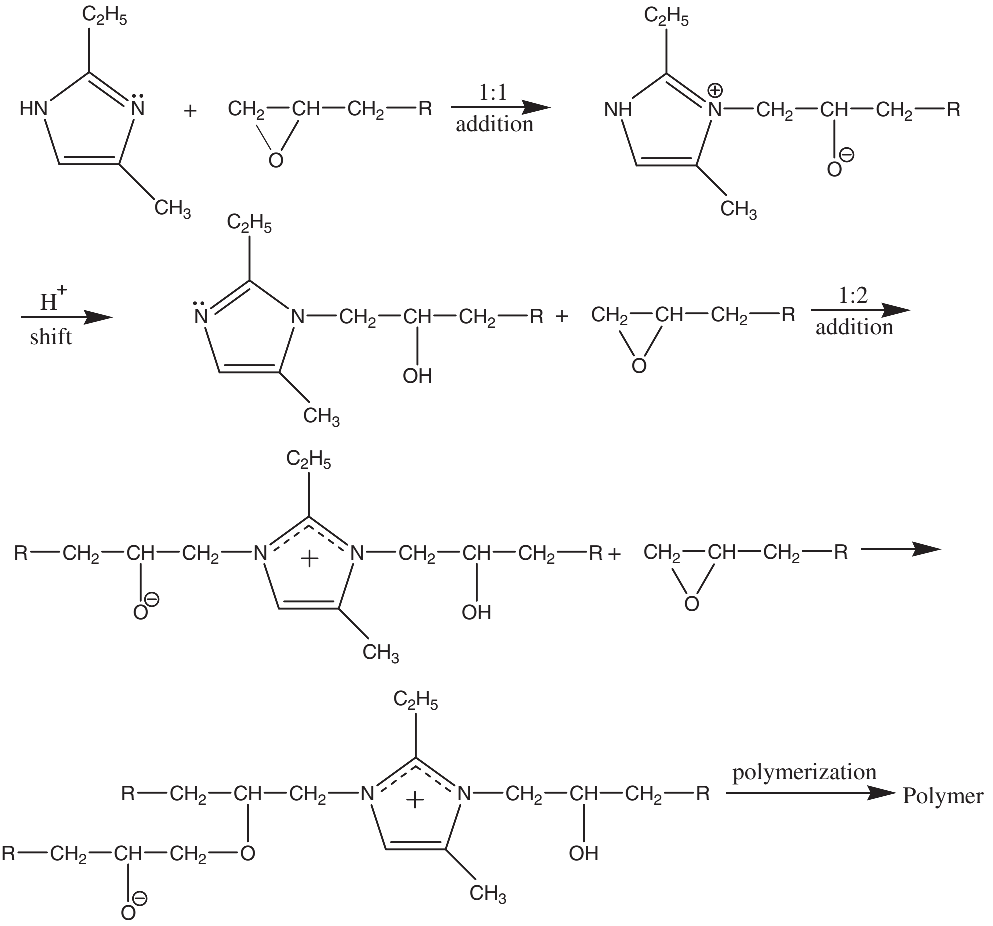


Fig. 5. DSC thermographs for PSER and TGCS cured with *m*-PDA and 2E4MZ.

the reaction time was extended to 36 h, and gelation took place at 48 h.

The effect of the molar ratio of KSCN to epoxy group is also shown in Fig. 3 where the temperature was set at



Scheme 3. Reactions of epoxide with 2E4MZ upon curing.

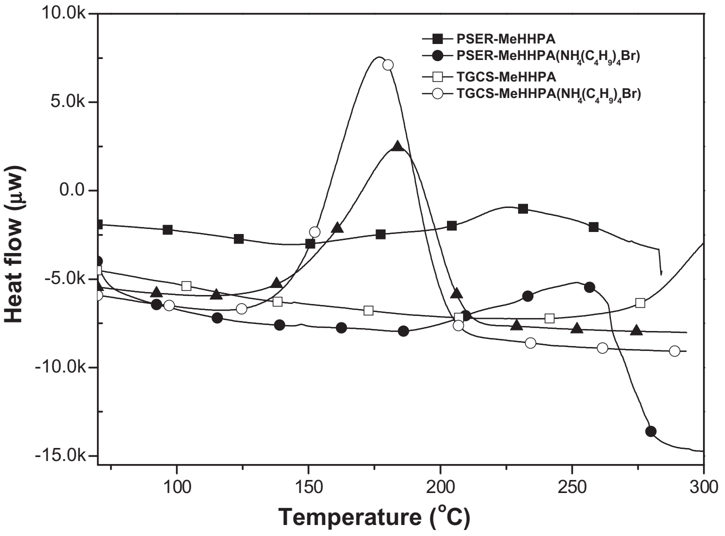


Fig. 6. DSC thermographs for PSER and TGCS cured with MeHHPA.

30 °C and reaction time 24 h. It is seen that complete conversion was achieved when a molar ratio of 2:1 was employed.

The alternative approach to the polysiloxane episulfide resin, in which episulfidation of allyl glycidyl ether was carried out first as illustrated in Scheme 2, has been tried. However, the followed platinum-catalyzed hydrosilylation of the episulfide was not successful because the platinum catalyst was poisoned by episulfide groups.

3.2. Reactivity of the polysiloxane episulfide resin

As the C–S bond is longer than the C–O bond, the episulfide ring is more stressed in comparison with the oxirane ring. As a result, episulfide compounds exhibited higher activity in ring-opening reactions. Fig. 4 shows the DSC curves for the polysiloxane episulfide resin and the parent polysiloxane epoxy resin, obtained at a heating rate of 10 °C/min under a flow of N_2 gas. An exothermal peak with onset temperature 191.0 °C and top temperature 207.8 °C is seen in the DSC curve for PSER. The peaks are undoubtedly ascribed to the thermal polymerization of the episulfide. No exothermal peak was observed for the polysiloxane epoxy resin till 300 °C.

Though the polysiloxane episulfide resin exhibited high reactivity in thermal polymerization, the resin was quite stable at room temperature: it can be easily cast after storage for two months without additive of stabilizer. Yet bisphenol A type episulfide resins are unstable at room temperature, and weak acids are usually added as stabi-

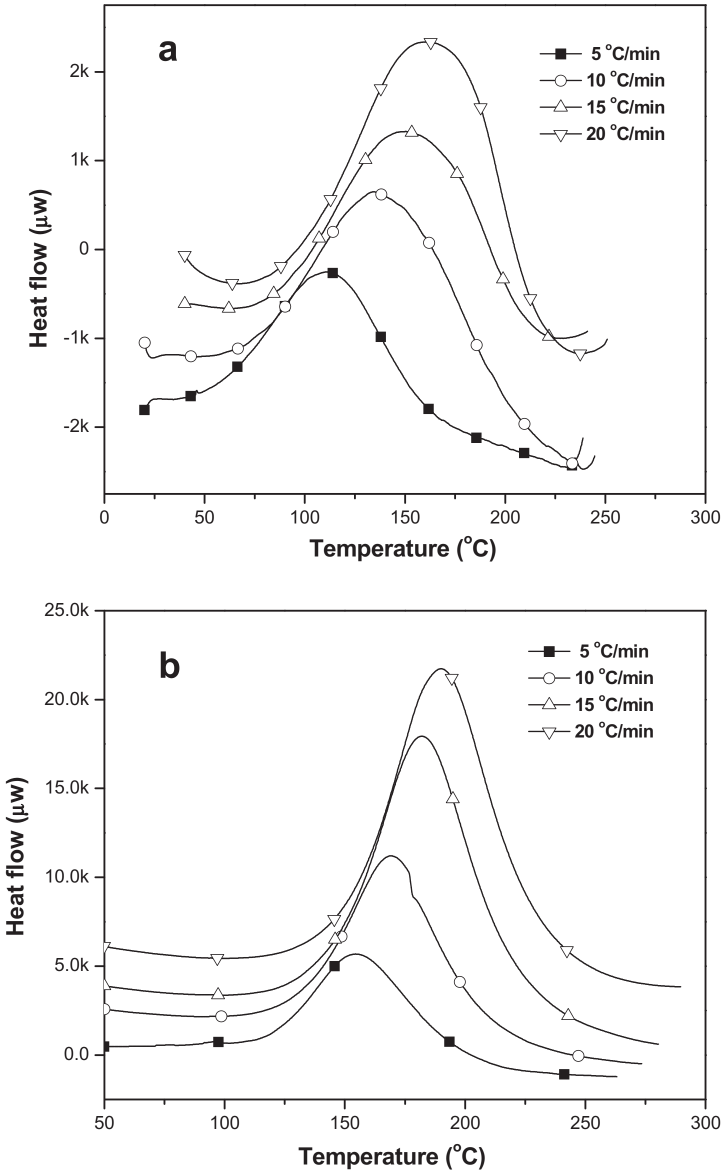


Fig. 7. DSC curves for (a) PSER/*m*-PDA and (b) TGCS/*m*-PDA at different heating rate.

lizer upon storage [31]. Good storage stability of PSER may be related with high purity. The polysiloxane episulfide resin was a liquid of low viscosity; therefore alkaline impurities from the reaction mixture could be easily removed by washing with water.

The episulfide resin showed very high reactivity with amines, especially aliphatic and alicyclic amines. The blends of PSER with isophorondiamine (IPDA) gelated in a few seconds at room temperature. Even at 0 °C, the gel time of the mixture was less than 5 min. High curing reactivity at low temperature is an outstanding advantage of the episulfide resin, which make it widely applicable in the fields such as rapid-cure implants and instant adhesives [32].

Aromatic amine *m*-phenylenediamine (*m*-PDA) is less reactive compared with IPDA; the gel time of the PSER/*m*-PDA system was ca. 4 h at 25 °C. The DSC thermograph for the PSER/*m*-PDA system is shown in Fig. 5, with the TGCS/*m*-PDA system for comparison; the results are summarized in Table 2. It is seen that the exothermal peak temperature for PSER/*m*-PDA was about 35 °C lower than that for TGCS/*m*-PDA. Obviously the episulfide resin is more reactive with aromatic amine compared with the parent epoxide.

2E4MZ is a commonly used curing agent for epoxy resins; the mechanism of curing is illustrated in Scheme 3 [33,34]. For the TGCS/2E4MZ system, three exothermal peaks at 126.7 °C, 135.9 °C and 165.1 °C, respectively, can be seen in the DSC curve (Fig. 5). The former two peaks can be attributed to the addition reactions and the third peak can be attributed to homopolymerization of epoxide

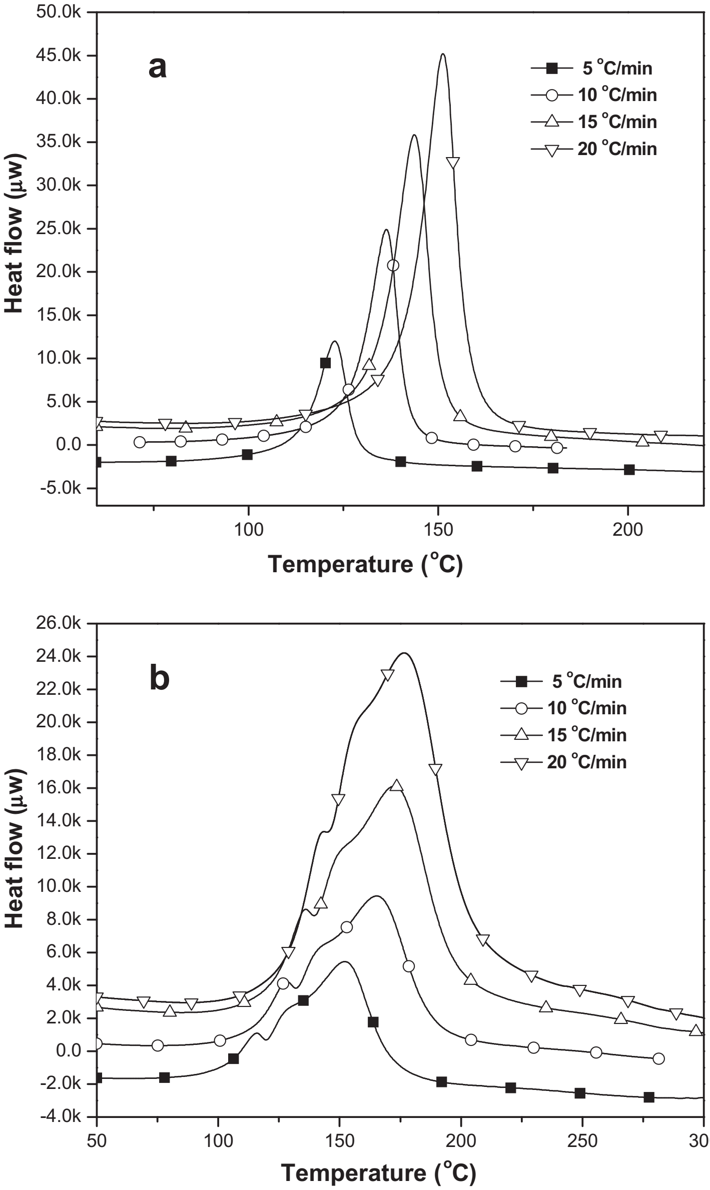


Fig. 8. DSC curves of (a) PSER/2E4MZ and (b) TGCS/2E4MZ at different heating rate.

initiated by the oxygen anion. However, in the case of PSER/2E4MZ, only one sharp exothermal peak at 136.4 °C was observed. The curing of episulfide/2E4MZ might proceed through the reactions similar to that shown in Scheme 3, but the anionic homopolymerization of episulfide took place at much lower temperatures. Therefore, the exothermal peaks for the addition and the homopolymerization were merged in the DSC curve.

Heat release upon curing was calculated by integration. It was found that the reaction heat of PSER was much lower than that of TGCS, whether *m*-PDA or 2E4MZ was employed as curing agent. Low heat release on curing of episulfide is advantageous for avoiding excessive stress in the cured products.

Fig. 6 shows the DSC thermographs for the PSER/MeHHPA and TGCS/MeHHPA systems. For curing of the polysiloxane epoxy resin with anhydride, an accelerator is needed. No exothermal peak was observed up to 300 °C for TGCS/MeHHPA without accelerator. An exothermal peak appeared at 176.9 °C with the addition of $N(C_4H_9)_4Br$ as accelerator.

For the episulfide/MeHHPA system without accelerator, an exothermal peak was observed at 226.2 °C in the DSC thermograph, which is 18 °C above the exothermal peak temperature of PSER alone. It is likely that MeHHPA did not react with episulfide at all; or rather it hindered the homopolymerization of episulfide. It is also interesting to note that the exothermal peak shifted to even higher temperature with the addition of $N(C_4H_9)_4Br$.

3.3. Curing kinetics of the polysiloxane episulfide resin

The apparent kinetics of curing was investigated by DSC scans at a series of heating rate. Fig. 7 shows the DSC scans for PSER/*m*-PDA and TGCS/*m*-PDA. The peak temperature raised with increasing heating rate as expected. Similar results are shown in Fig. 8 when 2E4MZ was applied as curing agent.

Table 3
Activation energy for the curing of the polysiloxane episulfide resin and the polysiloxane epoxy resin.

Composition	Activation energy (kJ/mol)
PSER	71.01
PSER/*m*-PDA	36.4
TGCS/*m*-PDA	60.2
PSER/2E4MZ	65.1
TGCS/2E4MZ	83.3

Table 4
Thermal properties of the cured polysiloxane episulfide resin and the cured polysiloxane epoxy resin.

Materials	T_g (°C)	T_d [a] (°C)	T_5 [b] (°C)	Char [c] (%)
PSER/*m*-PDA	179.4	289.0	276.0	27.0
TGCS/*m*-PDA	160.5	413.2	395.1	29.7
PSER/2E4MZ	120.7	296.4	302.9	21.5
TGCS/2E4MZ	102.9	395.0	377.0	24.6

[a] Decomposition temperature.
[b] Temperature at 5% weight loss.
[c] Residual char at 600 °C.

Assuming that (1) the peak exothermic (T_p) represents a point of constant conversion, (2) the curing reaction follows the first order kinetics, (3) the temperature dependence of the reaction rate constant obeys Arrhenius equation, apparent activation energies (E_a) of curing can be calculated using Ozawa's method [35,36]:

$$E_a = \frac{R\Delta \log \beta}{0.4567\Delta(1/T_p)}$$

where, E_a, activation energy (kJ/mol); R, gas constant (8.314 J/mol K); β, heating rate (°C/min); T_p, peak temperature (K).

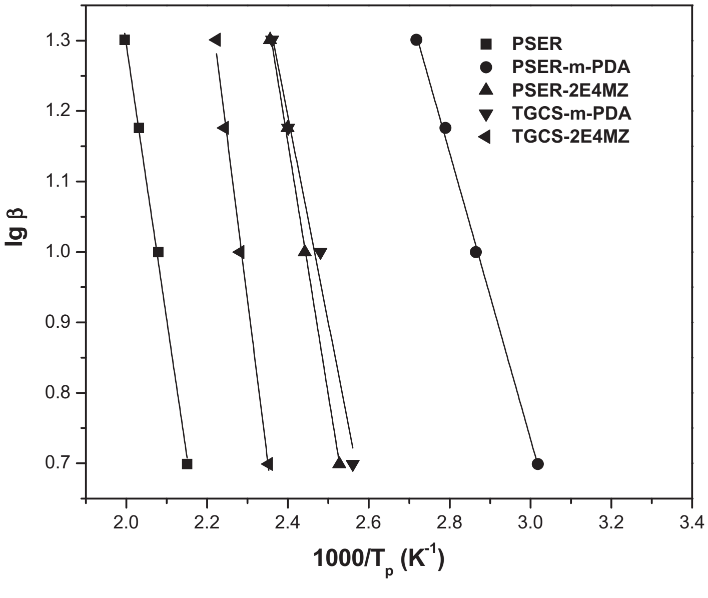


Fig. 9. Plot of log β vs. $1000/T_p$ for PSER and TGCS.

Fig. 9 shows the plots of log β vs. $1000/T_p$ for the curing of episulfide and epoxide with different agents, and for the polymerization of the episulfide resin without curing agent. For the TGCS/2E4MZ system, the peak temperature of homopolymerization of epoxide was adopted. E_a values calculated from the slope of the lines are listed in Table 3.

It is seen that E_a for curing of the polysiloxane episulfide resin is much lower than that for the polysiloxane epoxy resin with *m*-PDA and 2E4MZ as curing agent. In other word, the polysiloxane episulfide resin shows a much higher reactivity with these curing agents. For both PSER and TGCS, E_a of the curing reaction with *m*-PDA was much lower than that of curing reaction with 2E4MZ, i.e., the addition of N–H to episulfide or epoxide takes place more easily, compared with homopolymerization of episulfide or epoxide.

The difference between E_a for the PSER/2E4MZ system and E_a for the neat PSER resin is marginal, ca. 6 kJ/mol. It is likely that polymerization in the neat PSER resin proceeds by a similar mechanism as in the PSER/2E4MZ system. In the PSER/2E4MZ system, anionic polymerization of episulfide is initiated by 2E4MZ, whereas in the neat PSER resin anionic polymerization is initiated by heat. Therefore, in the DSC thermograph the peak temperature appears about 71 °C earlier in the former case.

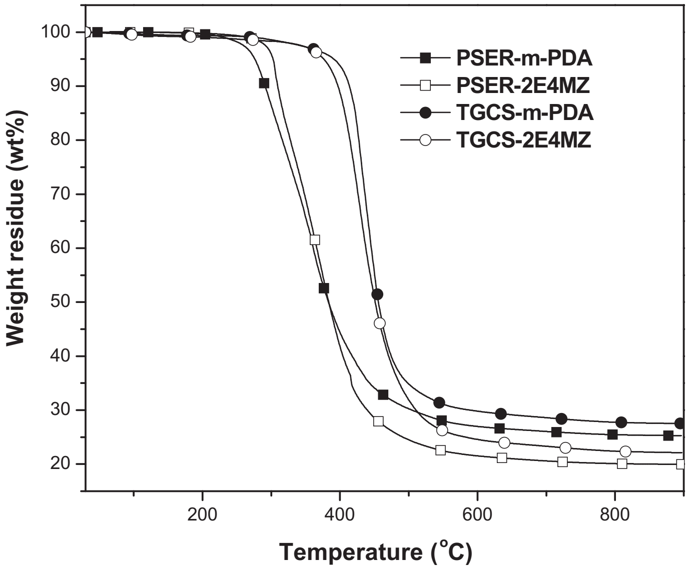


Fig. 10. TGA thermographs for TGCS and PSER cured with *m*-PDA and 2E4MZ.

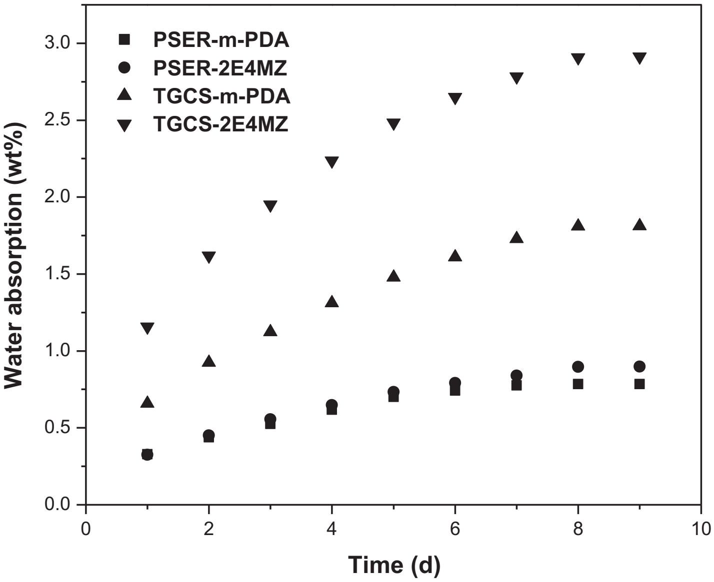


Fig. 11. Water absorption vs. time for cured resins.

3.4. Properties of cured polysiloxane episulfide resins

Cured polysiloxane episulfide resins were prepared with *m*-PDA and 2E4MZ as curing agent. The curing regimes are given in Table 1. The properties of the cured resins were studied to illustrate the merit and disadvantages of the episulfide resin.

Glass transmission temperatures (T_g) of the materials determined by DSC are listed in Table 4. In general, T_g of the cured episulfide resin was higher for about 20 °C compared with that of the corresponding epoxy resin when the same curing agent was used. Certainly the C–S bonds are more difficult to rotate compared with the C–O bonds; thus the polymer chain in the cured episulfide is more rigid.

Fig. 10 shows the TGA graphs for PSER and the parent epoxy resin cured with different agents. The decomposition temperature, the temperature for 5% weight loss and the residual char at 600 °C are summarized in Table 4. It is seen that the episulfide resin is less stable at high temperatures whichever *m*-PDA or 2E4MZ was used as curing agent. No wonder, the bonding energy of C–S (272 kJ/mol) is much lower than that of C–O (326 kJ/mol). Poor thermal stability of the C–S bond is disadvantageous for the resin to be used at high temperatures. On the other hand, however, it may be helpful for the materials such as reworkable underfill.

Fig. 11 shows the water absorption vs. time at 25 °C for the cured PSER and TGCS. For all the cured resins, water saturation reached in 7–8 days. The cured polysiloxane episulfide resins showed a much lower water absorption compared with the cured epoxy resin whichever *m*-PDA or 2E4MZ was used as curing agent. It was reasonable for that the C–S bond is less polar compared with the C–O bond. Low water absorption is very important for the materials used in microelectronic packaging.

4. Conclusions

Polysiloxane episulfide resin PSER of well defined structure was synthesized by replacement of oxygen atoms in the polysiloxane epoxy resin TGCS with sulfur atoms using potassium thiocyanate. Under the optimized reaction conditions, a complete conversion of epoxide into episulfide was achieved. The structure of the polysiloxane episulfide resin was confirmed by FT-IR, ^{1}H NMR, MS and elemental analysis. The polysiloxane episulfide resin was a liquid of low viscosity and it could keep stable for over two months at room temperature. When IPDA was blended with PSER resin, the gelation time of the mixture was only a few seconds. The reactivity of the episulfide resin and the parent epoxy resin with *m*-PDA, 2E4MZ and MeHHPA was studied by DSC measurements. The polysiloxane episulfide resin exhibited higher reactivity with *m*-PDA or 2E4MZ compared with the polysiloxane epoxy resin. The heat release of curing reaction for the polysiloxane episulfide was much less than that for the polysiloxane epoxy resin. MeHHPA did not react with episulfide effectively. Cured PSER exhibited higher T_g and much lower water absorption compared with the cured TGCS. However, the thermal stability of the cured PSER was much lower than that of the cured TGCS.

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