

Preparation and thermal properties of diglycidylether sulfone epoxy

Yie-Chan Chiu, I-Chen Chou, Wei-Chuan Tseng, Chen-Chi M. Ma*

Department of Chemical Engineering, National Tsing-Hua University, 101, Section 2, Kuang Fu Road, Hsinchu 30013, Taiwan, ROC

Received 26 October 2007; received in revised form 19 December 2007; accepted 21 December 2007

Available online 9 January 2008

Abstract

A diglycidylether sulfone monomer (sulfone type epoxy monomer, SEP) was prepared from bis(4-hydroxyphenyl) sulfone (SDOL) and epichlorohydrin without any NaOH or KOH as basic catalyst. FT-IR, ^1H NMR, ^{13}C NMR and mass spectroscopic instruments were utilized to determine the structure of the SEP monomer. The cured SEP epoxy material exhibited not only a higher T_g (163.81 °C) but also a higher T_d than pristine DGEBA (from 111.25 °C to 139.17 °C) when the SEP monomer moiety had been introduced into the DGEBA system. The thermal stability of cured epoxy herein was investigated by thermogravimetric analysis (TGA). The results demonstrated that the sulfone group of the cured SEP material decomposed at lower temperatures and formed thermally stable sulfate compounds, improving char yield and enhancing resistance against thermal oxidation. Additionally, the IPDT and char yield of the cured SEP epoxy (IPDT = 1455.75, char yield = 39.67%) exceeded those of conventional DGEBA epoxy (IPDT = 667.27, char yield = 16.25%).

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Keywords: Sulfone epoxy; DGEBA epoxy; Thermal decomposition; Thermal kinetics

1. Introduction

The epoxy materials are important industrial thermosetting materials and have been used in adhesion, coating, and electronic and electrical products [1,2]. The application of diglycidylether materials and novel epoxy materials that contain functional groups has been investigated, such as the diglycidylether materials with low dielectric constant [3], novel liquid crystalline type epoxy [4,5], the valuable crosslinker [6,7] and other progressed investigation of polymer chemistry [8,9]. However, the low thermal stability of diglycidylether materials limits their application at high temperature. The thermal stability can be improved by adding a toxic halogen promoter, but the constituent halogen may cause environmental problems.

Several thermally stable diglycidylether materials have been developed by introducing maleimide, imide functional

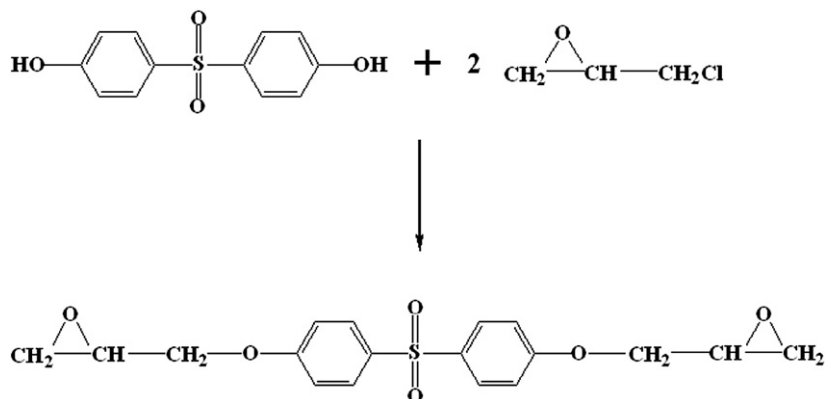
groups [10,11], phosphorus functional groups [12] and silicon functional groups [13] into an epoxy matrix or epoxy main chain. Liu et al. [14,15] investigated the phosphorus–silicon synergistic effect to improve the thermal stability of epoxy materials.

NaOH and KOH aqueous solvents have been adopted to prepare high-performance diglycidylether materials [3,5,16–19]. Basic aqueous solvents were used to catalyze the synthesis of epoxy materials [20]. However, this basic catalyst not only damages the environment but also increases the difficulty of purification of the synthesized diglycidylether monomer.

This work elucidates the synthesis of a diglycidylether sulfone monomer (sulfone type epoxy monomer, SEP) without any basic catalyst. FT-IR, NMR and mass spectrometries were utilized to characterize the chemical structure of the diglycidylether sulfone monomer. The glass transition temperatures (T_g s) of a cured sulfone-based monomer and DGEBA epoxy materials were investigated using DSC. The thermal stability of the cured epoxy was determined by TGA. Introduction of the SEP moiety into the DGEBA epoxy is anticipated to improve the thermal characteristics of cured epoxy resins.

* Corresponding author. Fax: +886 3 571 5408.

E-mail address: ccma@che.nthu.edu.tw (C.-C.M. Ma).



Scheme 1. Synthesis of diglycidylether sulfone monomer (SEP).

2. Experiment

2.1. Materials

Bis(4-hydroxyphenyl) sulfone (SDOL) was used as-received from TCI Co., Tokyo, Japan. Epichlorohydrin (ECH) and tetrahydrofuran (THF) were obtained from Tedia Co., OH, USA. Benzyltrimethylammonium chloride (BTAC) and 4,4-methylene-dianiline (DDM) from Acros Co., Belgium, were used as-received. The diglycidylether of bisphenol A (DGEBA) epoxy was supplied by the Nan Ya Plastics Co. Ltd., Taiwan, which contained an epoxide equivalent weight (EEW) of 180 g/equiv.

2.2. Instrumental analysis and measurements

Infrared spectra (FT-IR) were recorded on a Perkin Elmer Spectrum One FTIR (USA), using a KBr plate and measured in atmosphere. The ^1H NMR and ^{13}C NMR spectra were obtained from a Varian UnityInova 500 NMR Spectrometer (USA) with CDCl_3 as a D-solvent. The molecular weight was measured on a JEOL JMS-SX102A (Japan) gas chromatograph–liquid chromatograph mass spectrometer. Differential scanning calorimetric (DSC) thermograms were recorded with a Thermal Analyzer (TA) DSC-2910 (USA) at a heating rate of $10\text{ }^\circ\text{C}/\text{min}$ under nitrogen atmosphere. Thermogravimetric analysis (TGA) was performed with a Thermal

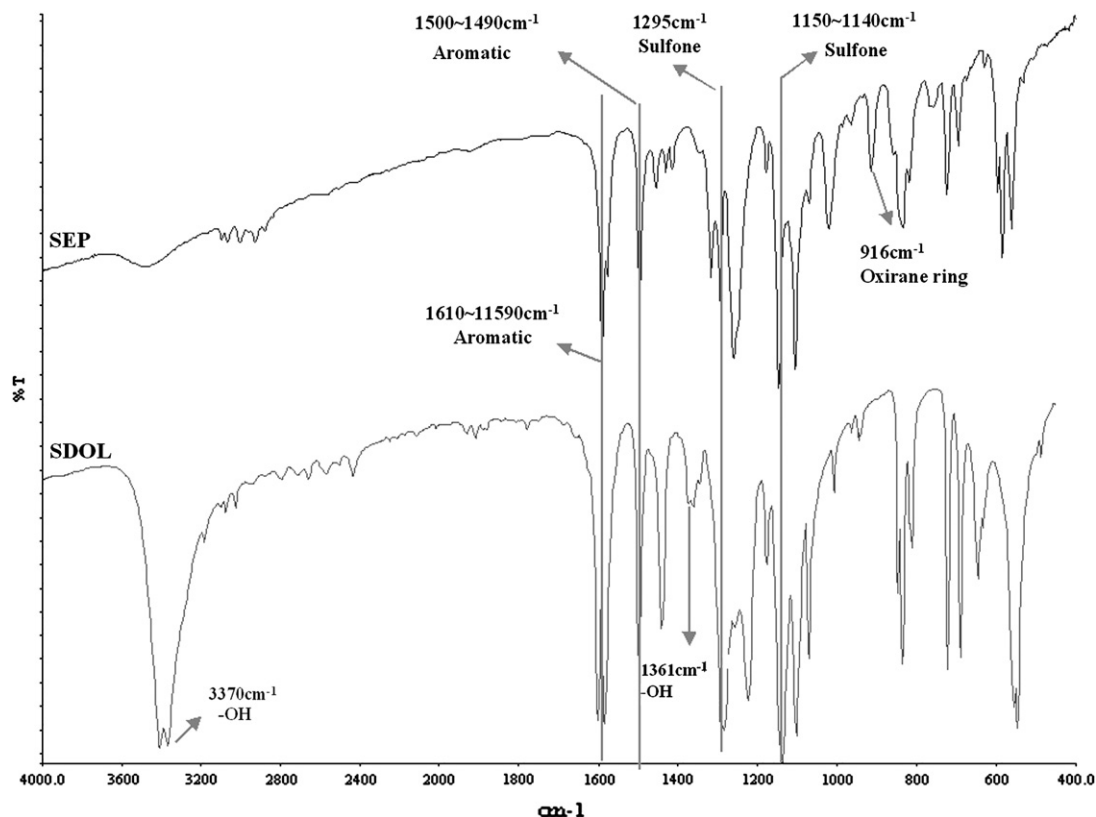


Fig. 1. The comparability of FT-IR spectra of the diglycidylether sulfone monomer (SEP) and bis(4-hydroxyphenyl) sulfone (SDOL).

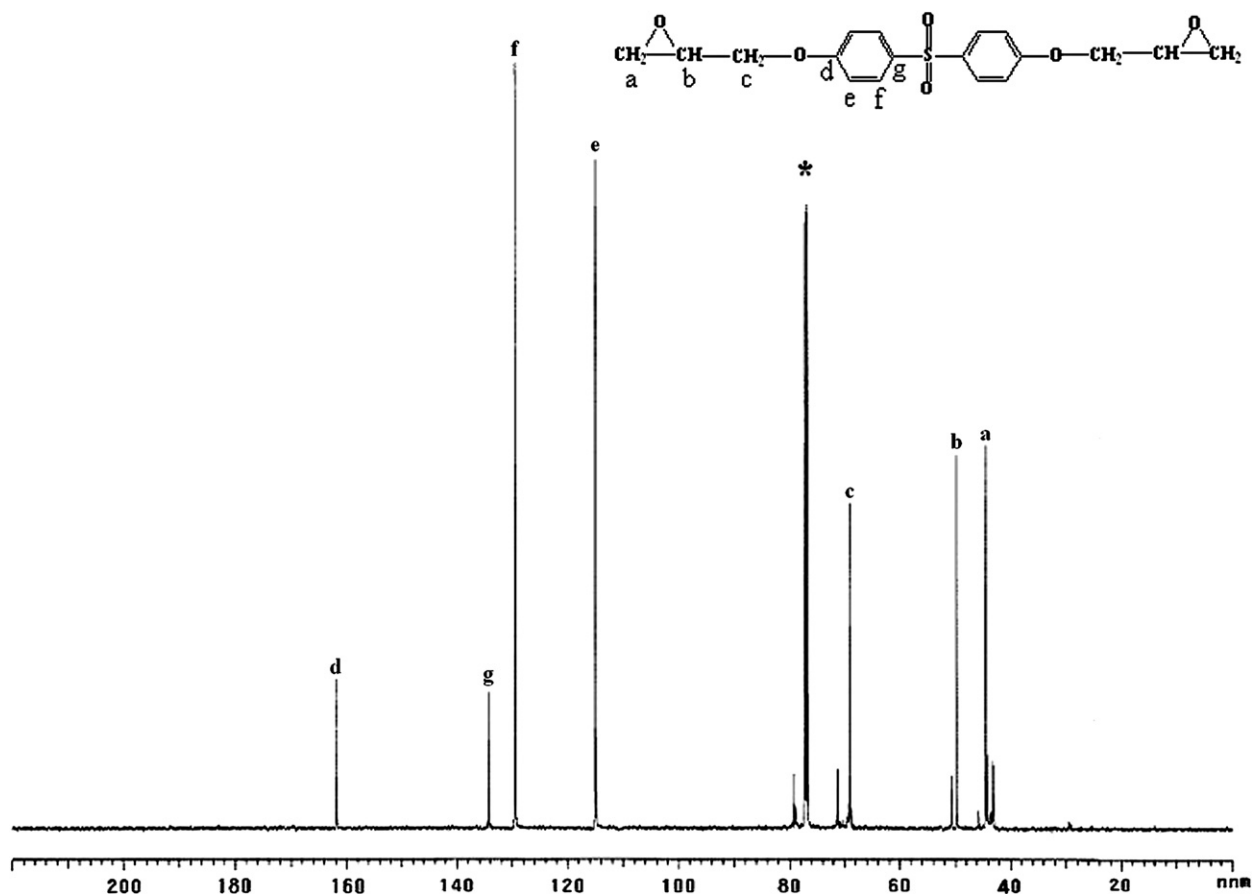


Fig. 2. The ^{13}C NMR spectra of the diglycidylether sulfone monomer (SEP).

Analysis TGA-951 thermogravimetric analyzer at a heating rate of $10\text{ }^\circ\text{C}/\text{min}$, under nitrogen and air atmosphere, and the gas flow rate was $100\text{ mL}/\text{min}$. Analysis of evolved gas was performed by a TGA and an automatic thermal desorption instrument (Perkin–Elmer ATD 400). The collected gases were transferred to a hyphenated GC–MS (Clarus 500 GC, Clarus 500 MASS with ionization, 120 V).

2.3. Synthesis of diglycidylether sulfone monomer (SEP)

Scheme 1 illustrates the synthesis of diglycidylether sulfone monomer (SEP). A mixture of 2.5 g (0.01 mol) of bis(4-hydroxyphenyl) sulfone, 18.5 g (0.2 mol) of epichlorohydrin and 0.929 g (0.005 mol) of benzyltrimethylammonium chloride

was stirred at room temperature. Then, the homogeneous mixture was heated to $70\text{ }^\circ\text{C}$. After cooling at room temperature, the excess epichlorohydrin was removed at a reduced pressure. The mixture was washed by distilled water at room temperature and then filtered. The solid product was dried in a vacuum oven at room temperature for 24 h . The diglycidylether of bisphenol sulfone monomer (SEP) was a white powder and the yield was 93% .

2.4. Preparation of the cured epoxy resins

In this study, the cured sample of 5DG–5SE was the abbreviation of the reaction system containing DGEBA and SEP with a weight ratio of $50:50$. Then, the DGEBA, 5DG–5SE and SEP epoxy resins were cured with DDM. All the reaction

Table 1

The NMR characteristic chemical shift peaks of the diglycidylether sulfone monomer (SEP)

	a	b	c	d	e	f	g
$^1\text{H NMR}^a$	2.70, 2.89	3.30	3.89, 4.25	b	6.95	7.81	b
$^{13}\text{C NMR}^a$	43.24	49.73	69.03	161.91	114.98	129.51	134.29

^a The D-solvent was CDCl_3 and the chemical shift unit was ppm.

^b No characteristic peaks appeared.

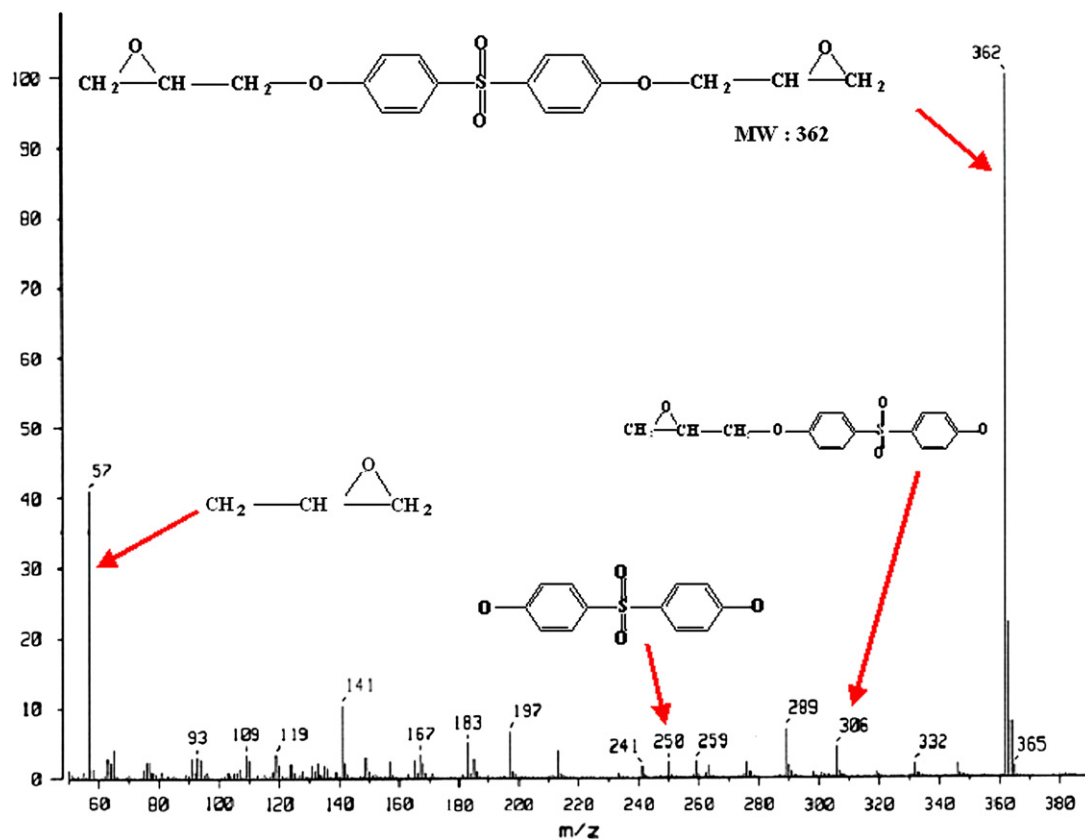


Fig. 3. The mass spectrometry of the diglycidylether sulfone monomer (SEP).

systems were prepared in a 2:1.1 molar ratio of epoxy resin to DDM curing agent to obtain an excellent cross-linking architecture of cured epoxy materials. Furthermore, all the mixture reactants were soluble in the THF solvent at room temperature. The preparation of cured epoxy samples was proceeded by the following thermal cured stages: at 120 °C for 1 h, 160 °C for 1.5 h, 180 °C for 1.5 h, and 200 °C for 2 h in the oven.

2.5. The statistic heat-resistant index (T_s)

The statistic heat-resistant index temperature (T_s) was determined from the temperature of 5% weight loss (T_{d5}) and of 30% weight loss (T_{d30}) of the sample by thermogravimetric analysis (TGA). The statistic heat-resistant index temperature (T_s) was calculated by Eq. (1) [21–23].

$$T_s = 0.49[T_{d5} + 0.6 \times (T_{d30} - T_{d5})] \quad (1)$$

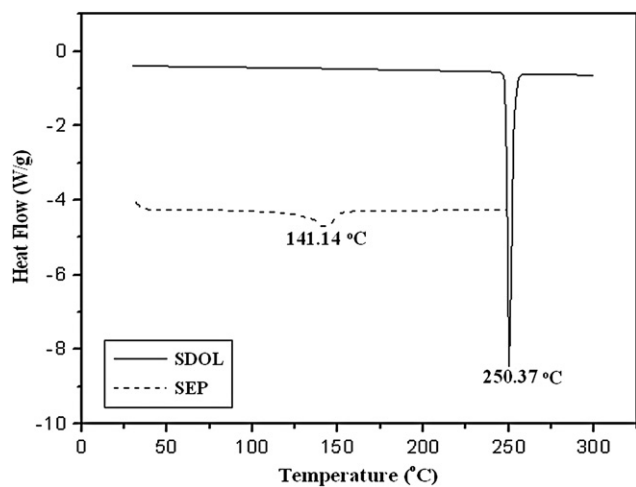


Fig. 4. The measurement of melting point of the diglycidylether sulfone monomer (SEP) and bis(4-hydroxyphenyl) sulfone (SDOL).

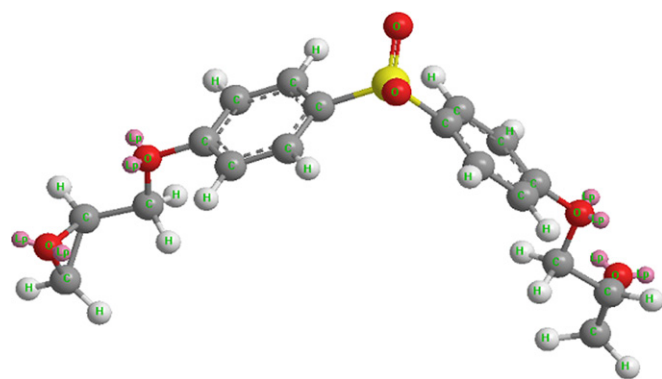


Fig. 5. The minimum energy model of the diglycidylether sulfone monomer (SEP) structure.

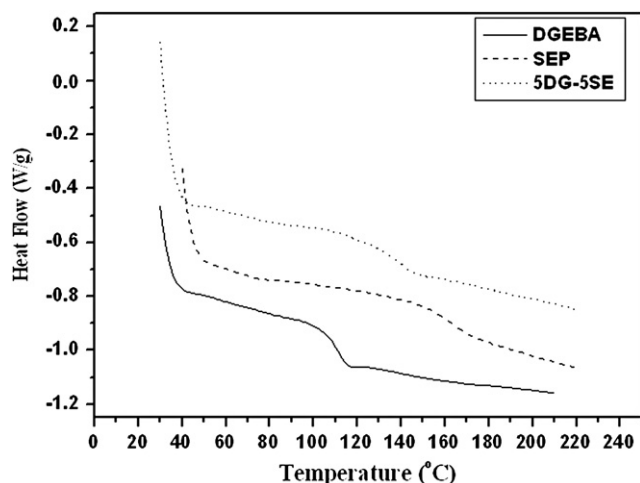


Fig. 6. The glass transition temperature (T_g) of various cured epoxy resins.

2.6. The integral procedure decomposition temperature (IPDT)

The integral procedure decomposition temperature (IPDT) was calculated from the method proposed by previous investigation [24–26].

$$\text{IPDT} (^{\circ}\text{C}) = AK \times (T_f - T_i) + T_i \quad (2)$$

where A is the area ratio of total experimental curve defined by the total TGA thermogram traces. T_i was the initial experimental temperature and T_f was the final experimental temperature. In this study, the T_i and T_f were 50 °C and 800 °C, respectively. A and K can be calculated by Eqs. (3) and (4). The values of S_1 , S_2 and S_3 were determined by previous studies [24–26].

$$A = \frac{S_1 + S_2}{S_1 + S_2 + S_3} \quad (3)$$

$$K = \frac{S_1 + S_2}{S_1} \quad (4)$$

2.7. The activation energies (E_a) of thermal decomposition

The activation energies of thermal decomposition were obtained from the TGA decomposed trace and calculated from the Horowitz–Metzger integral method [25–27] by Eq. (5).

Table 2
The thermal properties of various cured epoxy resins

Sample	T_g	T_{d5}^a	T_{d5}^b	Char ₈₀₀ ^a	Char ₈₀₀ ^b
DGEBA	111.25	338.33	332.89	16.25	0.32
SEP	163.81	278.29	284.93	39.67	1.12
5DG-5SE	139.17	281.32	280.99	25.94	1.03

^a Under the nitrogen atmosphere.

^b Under the air atmosphere.

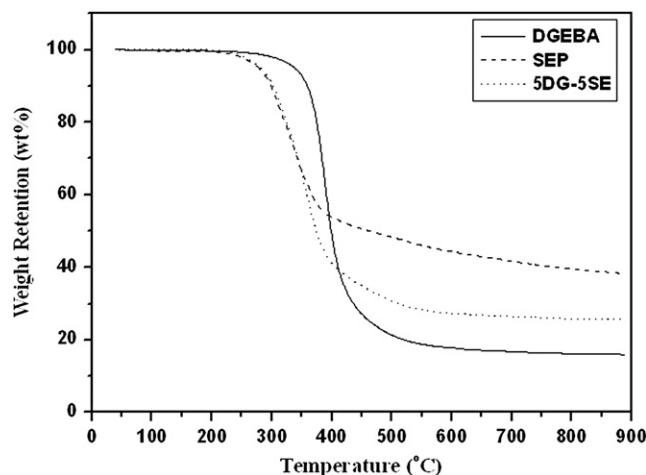


Fig. 7. The thermogravimetric analysis (TGA) traces of various cured epoxy resins in nitrogen atmosphere.

$$\ln[\ln(1 - \alpha)^{-1}] = \frac{E_a \times \theta}{R \times T_{\max}^2} \quad (5)$$

where E_a is the activation energy of the thermal decomposition and α is the thermal decomposition fraction. T_{\max} is defined as the temperature at the maximum rate of weight loss of thermal decomposition, θ and R are the $T - T_{\max}$ and gas constant, respectively. Furthermore, E_a was determined from the slope of the straight line corresponding to the plot of $\ln\{\ln(1 - \alpha)^{-1}\}$ versus θ .

3. Results and discussion

3.1. Synthesis of diglycidylether sulfone monomer (SEP)

Epoxy resins are generally prepared from the halohydrin with aliphatic or aromatic hydroxyl compounds. Basic catalysts (such as NaOH or KOH) must be used in stoichiometric concentrations not only to neutralize the halogen acid but also to accelerate the chemical synthesis. Additionally, the basic

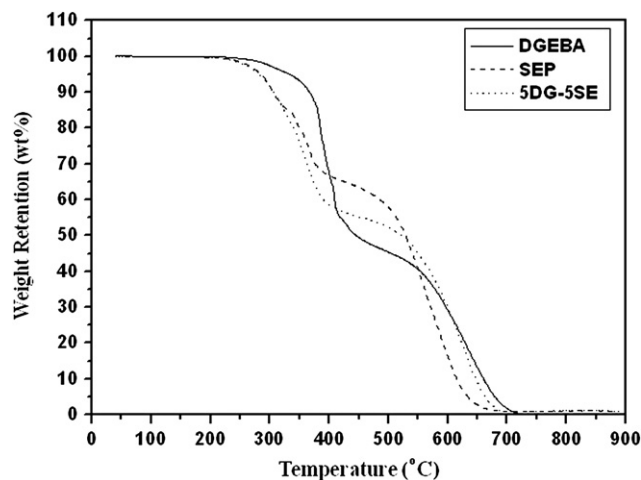


Fig. 8. The thermogravimetric analysis (TGA) traces of various cured epoxy resins in air atmosphere.

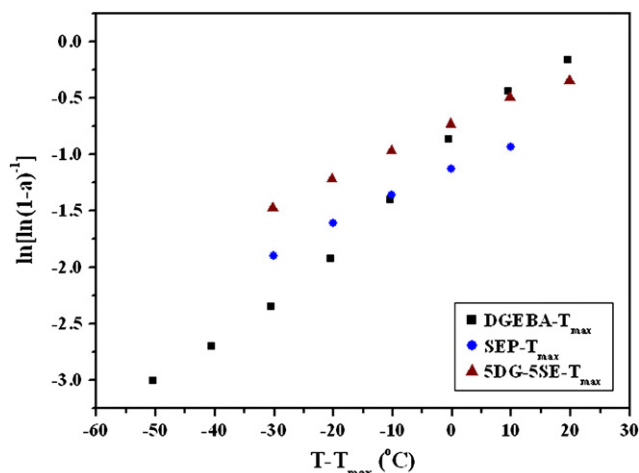


Fig. 9. The plots of activation energies (E_a s) of thermal decomposition of various cured epoxy resins in nitrogen atmosphere.

catalyst may form an epoxy oligomer, reducing the purity of the epoxy product and contaminating the environment. Bis(4-hydroxyphenyl) sulfone which possesses an H_2O moiety may decrease the solubility of bis(4-hydroxyphenyl) sulfone into the epichlorohydrin solution or cause phase separation of the reactant, consequently decreasing the reactivity and product yield of the synthesized epoxy. Hence, benzyltrimethylammonium chloride (BTAC) is a tetra-alkylammonium salt, and is shown as a phase-transfer catalyst and was added into the reaction system. The sulfone-containing epoxy monomer is a functional-type epoxy monomer, which was herein obtained by reacting bis(4-hydroxyphenyl) sulfone (SDOL) with epichlorohydrin without any basic catalyst. The structures of SEP and SDOL were elucidated by FT-IR, as presented in Fig. 1. The proceeding of the dehydrochloro reaction was revealed by the disappearance of the peaks associated with the hydroxyl group ($-\text{OH}$) of SDOL at 3410 cm^{-1} and 1361 cm^{-1} ($-\text{OH}$ in plane). However, the broad peak at

3435 cm^{-1} of SEP was associated with the hydroxyl group ($-\text{OH}$) in H_2O . Absorption peaks around 3010 cm^{-1} , 1600 cm^{-1} , 1499 cm^{-1} and 692 cm^{-1} were obtained from the aromatic ring group. The two absorption peaks around 1295 cm^{-1} and 1147 cm^{-1} were obtained from the asymmetric structure of SO_2 . Notably, the absorption peak from SEP at 916 cm^{-1} is characteristic of the oxirane ring.

The chemical structure of SEP was characterized using NMR, as presented in Fig. 2 and Table 1. The absorption peaks of ^1H NMR around $\delta = 2.70\text{--}3.31\text{ ppm}$ correspond to the oxirane ring protons [6,8,10]. The protons of $\text{AR}-\text{O}-\text{CH}_2-$ in SEP were associated with the absorption peaks at $\delta = 3.70\text{--}4.28\text{ ppm}$. The absorption peaks at $\delta = 6.93\text{--}7.81\text{ ppm}$ were attributed to the aromatic protons, verifying that SEP monomer with the expected chemical structure had been synthesized successfully.

The chemical structure of SEP was determined by ^{13}C NMR as shown in Fig. 2. The chemical shift at $114.98\text{--}161.91\text{ ppm}$ is associated with the aromatic ring and the chemical shifts at 69.03 ppm , 49.73 ppm and 43.03 ppm are associated with epoxide groups [8,13,18]. The mass spectrometric data verified the SEP structure (Fig. 3). The molecular ion peak appeared at $m/z = 362$ for SEP; this value equaled the predicted molecular weight of the SEP compound.

DSC was used to determine the melting point of SDOL and SEP. Fig. 4 reveals that SDOL yields an endothermic peak at $250.37\text{ }^\circ\text{C}$. The endothermic peak of SEP was at $141.14\text{ }^\circ\text{C}$. All the compounds yielded only one endothermic peak, suggesting that the product was very pure. Furthermore, the fragmentation segment of the mass spectrum included characteristic ion peaks that provided further evidence of the chemical structures of the prepared SEP compounds. The architecture of SEP was determined using the minimum energy model [28] and the ball and stick structure model. Fig. 5 depicts a postulated structure of SEP. Accordingly, the sulfone epoxy monomer was synthesized without any basic catalyst.

3.2. Thermal behavior of various cured epoxy resins

Fig. 6 and Table 2 present the glass transition temperatures (T_g s) of various cured epoxy resins. The T_g of cured SEP ($163.81\text{ }^\circ\text{C}$) exceeded that of the cured DGEBA ($111.25\text{ }^\circ\text{C}$). Since the sulfone group of the SEP moiety is hydrogen bonded with the hydroxyl group of the diglycidylether in the ring opening, the polymer chain interaction (hydrogen bonding) may have improved the cross-linking density, increasing the glass transition temperature of the cured SEP epoxy. The T_g of cured SDG–5SE epoxy exceeded that of the pristine cured DGEBA epoxy. This phenomenon was caused by the hydrogen bonding, which is associated with the sulfone group of SEP and the hydroxyl group of diglycidylether during ring opening, or with the hydroxyl group in the DGEBA main chain. The T_g of cured SDG–5SE was increased from $111.25\text{ }^\circ\text{C}$ to $139.17\text{ }^\circ\text{C}$. Park and Jin [19,29] demonstrated that hydrogen bonding improved the T_g of their epoxy system.

Figs. 7 and 8 plot the thermogravimetric analysis (TGA) traces, which were also referenced by Table 2. The 5% weight

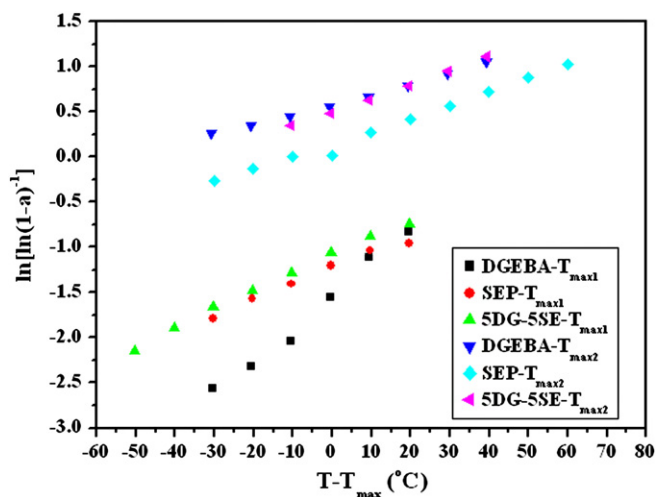


Fig. 10. The plots of activation energies (E_a s) of thermal decomposition of various cured epoxy resins in air atmosphere.

Table 3
The parameters of thermal stability and the kinetics of the thermal decomposition of various cured epoxy resins

Sample	IPDT ^a	IPDT ^b	T_s^a	T_s^b	E_a^a	E_{a1}^b	E_{a2}^b
DGEBA	667.27	403.77	179.14	181.77	878.18	130.88	78.64
SEP	1455.75	495.3	155.25	166.58	751.68	57.80	81.20
5DG–5SE	1535.23	500.28	156.05	161.66	797.01	66.93	95.15

^a Under the nitrogen atmosphere.

^b Under the air atmosphere.

loss temperatures (T_{d5S}) of cured SEP and cured 5DG–5SE materials were lower than those of cured DGEBA material in the nitrogen and air atmospheres. Since the sulfone group linkage of SEP may decompose at lower temperatures forming sulfate compounds, these sulfate compounds can dramatically retard the thermal decomposition (as presented in Figs. 7 and 8). Fig. 8 demonstrates that the sulfate compounds efficiently retard the thermal-oxidation stage, increasing the associated temperature from 350 °C to 500 °C in air. Huang et al. [30] established that the sulfone group in the epoxy provided a “shielding effect” when the sulfate (or sulfonate) compounds were formed. Therefore, the sulfate (or sulfonate) compounds of the SEP retarded the decomposition of the epoxy compounds. The char yields increased from 16.25% to 39.67% in an atmosphere of nitrogen and from 0.32% to 1.12% in an atmosphere of air. The increasing relationship between the char yield and the amount of sulfone groups of SEP was obvious. However, the sulfone group of SEP served as a promoter of char formation. Liu et al. [1,2,15,16,26] indicated that the formation of char might improve the flame retardancy, resulting from the decline in the amount of combustible gases and the formation of a barrier to heat transfer as the char was formed.

3.3. Thermal stability of various cured epoxy resins

In this study, two parameters were used to specify the thermal stability, the statistic heat-resistant index (T_s) [21–23] and

the integral procedure decomposition temperature (IPDT) [24–26]. Table 2 summarizes the data. The values of statistic heat-resistant index (T_s) of the cured SEP and 5DG–5SE materials were associated with 5% weight loss and 30% weight loss temperatures and lower than those of cured DGEBA material. Since the sulfone group in SEP was decomposed at a lower temperature further to form the sulfate (or sulfonate) compounds and increase the char yield. The integral procedure decomposition temperatures (IPDTs) of cured SEP and 5DG–5SE materials exceeded those of the cured DGEBA material. Notably, in nitrogen, the values of IPDT of cured SEP (1455.75) and 5DG–5SE (1535.23) materials were double those of cured DGEBA (667.27) material. The sulfone group of cured SEP forms the sulfate (or sulfonate) char, which not only retards the thermal decomposition, but also promotes the formation of the char. Therefore, the IPDT values increased significantly with the number of sulfone groups in the SEP moiety.

The activation energies (E_{as}) of thermal decomposition were calculated using the Horwitz–Metzger equation [25–27] and are plotted in Figs. 9 and 10 as well as Table 3. Figs. 9 and 10 reveal that all of the slopes of the curves of the cured epoxy resins were obtained, and the R^2 values exceed 0.99. In the nitrogen atmosphere, the E_a values of cured SEP and 5DG–5SE materials were lower than those of cured DGEBA. From Fig. 7 (TGA in nitrogen), the SEP and 5DG–5SE samples were decomposed at lower temperature in the range 300–420 °C, resulting from the decomposition of the sulfone group

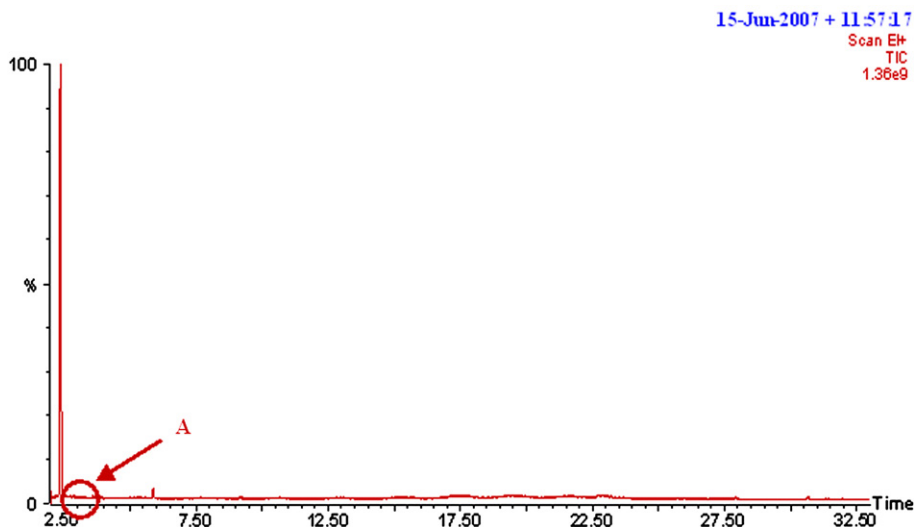


Fig. 11. Detection of the thermal volatiles of the cured SEP.

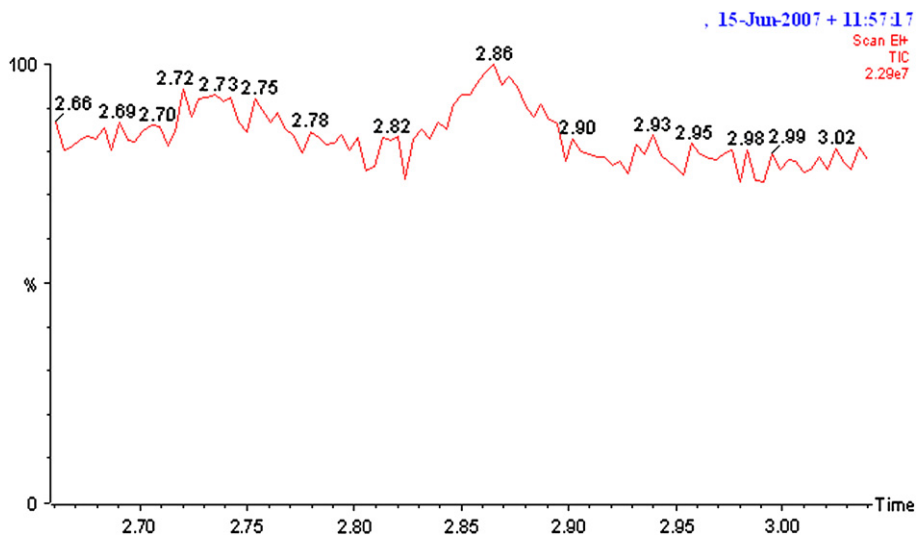


Fig. 12. Detection of the thermal volatiles of the cured SEP in the region A of Fig. 11.

at lower temperature and the more extensive char formation. The E_a values of cured SEP and 5DG–5SE materials were thus lower. In the air atmosphere, all of the cured epoxy samples decomposed in two stages, as presented in Fig. 8. Accordingly, various cured epoxy resins were decomposed under two thermal conditions and the E_a values of the two stages of thermal decomposition in air were calculated. In the first stage of thermal decomposition in air, the E_{a1} values of the cured SEP and 5DG–5SE samples were lower than those of the cured DGEBA sample. They are the same as those of the cured epoxy resins that decomposed in nitrogen. The thermal decomposition stage was associated with the decomposition of the sulfone group of SEP at low temperature and the formation of the char. However, the E_{a2} values of cured SEP and 5DG–5SE materials substantially exceeded those of cured DGEBA. The second stage of thermal decomposition in air was a thermal-oxidation stage. The higher values of E_{a2} resulted from the formation of sulfate (or sulfonate) char of the sulfone group of the SEP moiety at a lower temperature. The sulfate (or sulfonate) char provided the anti-thermal-oxidation effect, like the “shielding effect” that was reported by Huang et al. [30]. In the thermal degradation study, the TGA/GC/MASS instruments were utilized to study the thermal decomposition and the

yield of sulfate (or sulfonate) moiety. The data are shown in Figs. 11–14. The total ion current from the thermal decomposition stage between 530 °C and 550 °C in the air atmosphere was separated into single ion current in the GC step and analyzed by the mass detector. The single ion current shown in Fig. 12 was from the separated section A of Fig. 11. From Figs. 11 and 12, it is clear to detect the sulfone fragments in this stage. Furthermore, the mass fragmentation spectrum (Fig. 13) illustrated that the $m/z = 32$ was the sulfur $-(S)-$ from the volatile of the thermal degradation. The $m/z = 64$ was the sulfone $-(SO_2)-$ mass fragmentation. It is notably the $m/z = 80$ was the mass fragmentation of the sulfonate compound $-(SO_3)-$ and the $m/z = 94$ was the mass fragmentation of the sulfate compound $-(SO_4)-$. Fig. 14 suggested the chemical structure of the sulfone compounds. Consequently, it was suggested the sulfate (sulfonate) compounds might be formed during the SEP thermal degradation and served as a thermal stable layer; furthermore, the sulfate (or sulfonate) compounds were further decomposed at higher temperature. Additionally, introducing the SEP moiety into the DGEBA epoxy improved not only the kinetics of thermal-oxidation decomposition (see Table 3) but also the thermal stability, in both nitrogen and air atmospheres.

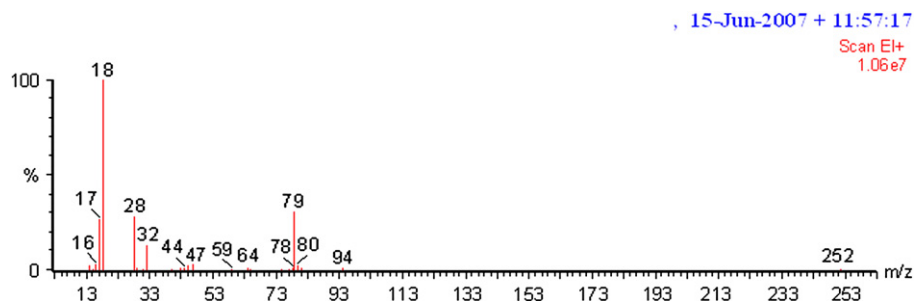


Fig. 13. The mass fragmentation spectrum of the SEP between the region A.

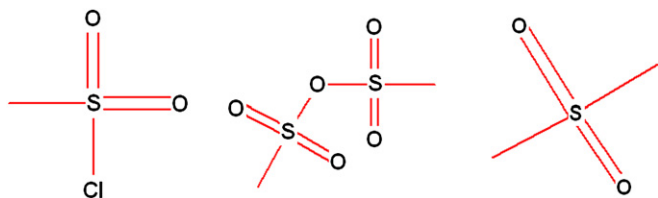


Fig. 14. The suggested mass fragmentation of volatiles in the thermal degradation.

4. Conclusion

In this investigation, a diglycidylether sulfone monomer (sulfone type epoxy monomer, SEP) was synthesized without the use of any basic catalyst. The molecular weight of SEP was obtained using a mass spectrometer. The cured SEP material has a high glass transition temperature (T_g) of 163.81 °C. Introducing the SEP moiety into the DGEBA epoxy resin increases T_g from 111.25 °C to 139.17 °C, by the formation of hydrogen bond between the sulfone group and the hydroxy group during the ring opening of the oxirane structure. The sulfone group in the cured SEP moiety decomposed at a lower temperature, forming the sulfate (or sulfonate) compounds, which had a shielding effect and reducing T_g . Moreover, the generation of sulfate (or sulfonate) compounds not only improved the char yield but also supported the anti-thermal-oxidation ability at a higher temperature. Accordingly, the values of IPDT and the char yield in nitrogen and air were increased.

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