

Preparation, Intermolecular Motion, and Thermal Properties of Thiodiphenyl Epoxy

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Received 9 June 2009; accepted 21 March 2010

DOI 10.1002/app.32602

Published online 11 June 2010 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The thiodiphenyl epoxy (THEP) was prepared by the 4,4'-thiodiphenol (THDOL) and the epichlorohydrin (ECH) without using any NaOH or KOH catalysts. The THEP possessed weak hydrogen bonding in the cured THEP/DGEBA system. The intermolecular motion parameters k and q were 0.26 and -168.5 , respectively, which determined by the Gordon-Taylor and Kwei equations. The soft sulfide linkage ($-S-$) of the THEP degraded at lower temperature than cured DGEBA material, and further to form various thermal stable sulfate derivative chars. The char yields increased from 11.43 to

25.94 wt % and from 0.65 to 1.04 wt % in the nitrogen and air, respectively. Introduction of the THEP into the DGEBA could provide the antioxidation thermal property and improve the thermal stability of the DGEBA epoxy in the air. In the air atmosphere, the activation energies of the second thermal degradation were increased from 66.67 to 103.42 kJ/mol. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 2116–2125, 2010

Key words: epoxy; thermal properties; thermogravimetric analysis

INTRODUCTION

Epoxy resins are the thermosetting materials and widely used in various applications, such as the structural materials of the aerospace industry and encapsulating electronic components resins,^{1,2} which associated with their high-mechanical strength and modulus, good solvent resistance. Additionally, the cured epoxy resins possess satisfactory mechanical properties, such as minimum shrinkage, as cured epoxy resins can form the three-dimensional network structures through both thermosetting and photosealing processes. And cured epoxy resins possess excellent moisture resistance, good adhesive property and superior electrical resistance properties.^{3–6}

Recently, the thermosetting/thermoplastic materials blended modification were investigated. Various thermoplastic materials were modified,⁷ for instance, the polysulfone was modified or blended with epoxy resins.^{8–11} As the sulfone segments might decompose at low temperature and provide various thermal sulfate derivatives char,¹² which char could improve the thermal stability of the epoxy resins. However, the sulfone segments might cause phase separation,

whereas the epoxy resins blended or cured with the sulfone components.¹³

In our previous investigation,¹⁴ the sulfone-type epoxy monomer (SEP) was prepared and investigated. The SEP could be blended with the diglycidyl ether of bisphenol A epoxy (DGEBA) homogeneously, and the SEP could improve the thermal stability by generating various thermal sulfate derivative chars. Then, the organic thiodiphenyl group possesses sulfur element, which may generate various thermal sulfate derivative chars and improve the thermal stability of the DGEBA epoxy. In this work, the thiodiphenyl epoxy (THEP) was prepared by the 4,4'-thiodiphenol (THDOL) and epichlorohydrin (ECH). The THEP was prepared without any basic catalysts. FTIR, NMR, and mass analytic instrument were used to characterize the chemical structure of the THEP. Furthermore, the THEP was introduced into the DGEBA resin and blended homogeneously to study the thermal stability. The thermal properties of various THEP/DGEBA blended materials were investigated by the thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Both Gordon-Taylor and Kwei equations were used to predict the intermolecular force of various THEP/DGEBA materials. The statistic heat-resistant index temperature (T_s), the integral procedure decomposition temperature (IPDT) and the activation energies of thermal decomposition (E_a) was calculated by the

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Horowitz–Metzger integral method) of the thermal degradation properties of various THEP/DGEBA materials were studied.

EXPERIMENT

Materials

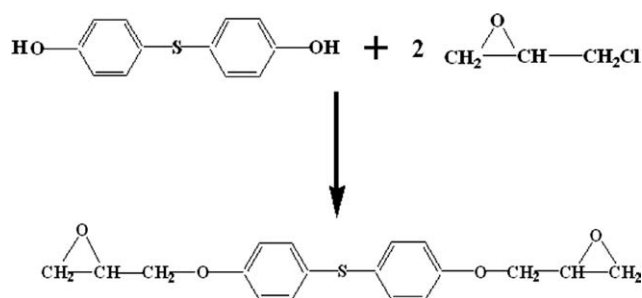
Bis(4-hydroxyphenyl)sulfide (THDOL) was received from TCI, Tokyo, Japan. ECH and Tetrahydrofuran (THF) were obtained from Tedia, OH, USA. Benzyltrimethylammonium chloride (BTAC) and 4,4-Methylenedianiline (DDM) were obtained from Acros, Belgium. The diglycidyl ether of bisphenol A (DGEBA) epoxy was obtained from Nan Ya Plastics, Taiwan, and contained the epoxide equivalent weight (EEW) of 180 g/equiv.

Instrumental analysis and measurements

Infrared spectra (FTIR) were recorded on the Perkin Elmer Spectrum One FT-IR (Massachusetts, USA); the KBr plate was used and measured in the nitrogen atmosphere. The $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra were measured by the Varian Unitynova 500 NMR Spectrometer (CA, USA) with CDCl_3 as the D-solvent. The molecular weight was measured by the JEOL JMS-SX102A (Tokyo, Japan) gas chromatograph liquid chromatograph mass spectrometer (GC/LC/Mass). Differential scanning calorimetric (DSC) thermograms were measured by the Thermal analyzer (TA) DSC-2910 at a heating rate of $10^\circ\text{C}/\text{min}$ under the nitrogen atmosphere and the weight of sample was 5.0 mg. Thermogravimetric analysis (TGA) was performed with the Thermal Analysis TGA-951 thermogravimetric analyzer at a heating rate of $10^\circ\text{C}/\text{min}$ and the weight of sample was 10.0 mg, which studied atmospheres were under the nitrogen and air atmosphere, respectively, the gas flow rate was 100 mL/min. The DSC and TGA were provided from Waters, (MA, USA). Analysis of evolved gas was performed by the TGA and an automatic thermal desorption instrument (Perkin-Elmer ATD 400, Massachusetts, USA). The collected gases were transferred to a hyphenated GC-MS (Clarus 500 GC, Clarus 500 MASS with ionization, 120V, Massachusetts, USA).

Synthesis of the thiodiphenyl epoxy

Scheme 1 illustrates the synthesis of the thiodiphenyl epoxy (THEP). A mixture of the bis(4-hydroxyphenyl) sulfide (THDOL, 2.18 g, 0.01 mole), the ECH (18.5 g, 0.2 mole) and the benzyltrimethylammonium chloride (BTAC, 0.929 g, 0.005 mole) were stirred at room temperature. Then, the homogeneous reactants were heated to 70°C . After the reactants cooling at room temperature, the excess ECH was removed by



Scheme 1 The preparation of the THEP.

reducing pressure. The mixture was washed by distilled water at room temperature and then filtered. The product was dried in the vacuum oven at room temperature for 24 h. The thiodiphenyl epoxy (THEP) was a light yellow liquid and the yield of the THEP was 90%.

Preparation of the cured epoxy resins

In this study, the cured 5DG5THEP material was the abbreviation of the reaction system, which contained the DGEBA (DG) and the THEP with a weight ratio of 50 to 50%, respectively. Then, the DGEBA, 5DG5THEP, and THEP epoxy resins were cured with the DDM. All reaction systems were prepared in a 2:1.1 molar ratio of the epoxy resin to the DDM curing agent and resolved in the THF solvent at room temperature, further to obtain an excellent cross-linking architecture of the cured epoxy materials. The preparation of the cured epoxy samples were proceeded by following thermal cured cycles: 120°C for 1 h, 160°C for 1.5 h, 180°C for 1.5 h, 200°C for 2 h in the oven.

Kinetic studies of the curing reaction

Ozawa's method^{15,16}

The Ozawa's method expressed as Eq. (1):

$$E_a = \frac{-G}{1.052} \frac{d \ln \beta}{d(1/T_p)} \quad (1)$$

where E_a is the activation energy of curing, G is the ideal gas constant, β is the heating rate, T_p is the maximum temperature of the exothermic peak of the curing reaction. The activation energy of curing can be obtained by the plot of $\ln \beta$ versus $1/T_p$.

Kissinger's method^{17,18}

The Kissinger's method was also used to calculate the activation energy of curing (E_a) by Eq. (2):

$$\frac{d \left[\ln \left(\beta / T_p^2 \right) \right]}{d(1/T_p)} = - \frac{E_a}{G} \quad (2)$$

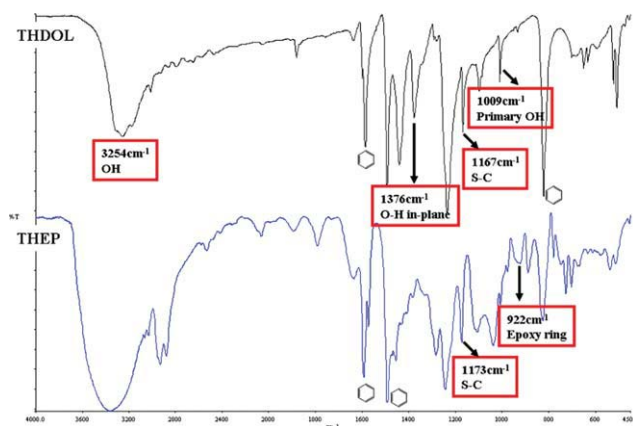


Figure 1 The FTIR spectra of the bis(4-hydroxyphenyl)-sulfide (THDOL) and the thiodiphenyl epoxy (THEP). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

where β is the heating rate, T_p is the maximum temperature of the exothermic peak of the curing reaction, and G is the ideal gas constant. Therefore, the activation energy of curing can be determined by the plot of $\ln(\beta/T_p^2)$ versus $1/T_p$.

The intermolecular force prediction of the THEP/DGEBA cured system

There are many equations can be used to predict the glass transition temperature (T_g) of the polymer miscible system. Hu et al.¹⁹ used the Gordon-Taylor equation^{20,21} to predict the intermolecular force of the cured blend epoxy system. Kuo et al.²² and Liu et al.²³ investigated the intermolecular motion of the polymer by Kwei equation, and the polymer prepared by the copolymerization or curing reaction.^{24,25} Consequently, both the Gordon-Taylor and Kwei equations were used.

Gordon-Taylor equation^{19,20,26,27}

$$T_g = \frac{W_1 T_{g1} + kW_2 T_{g2}}{W_1 + kW_2} \quad (3)$$

In the Eq. (3), the T_{g1} and T_{g2} are the glass transition temperatures (T_g s) of the pristine cured epoxy

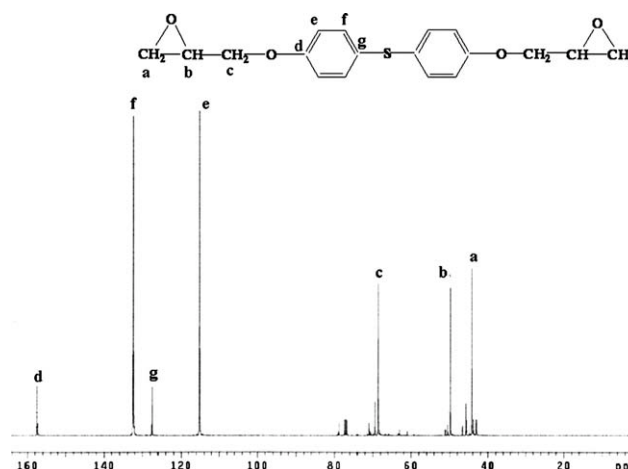


Figure 2 The ^{13}C -NMR spectra of the thiodiphenyl epoxy (THEP).

resins; meanwhile, W_1 and W_2 are the weight fractions of the epoxy resin 1 and epoxy resin 2 in the cured reaction system. The T_g is the glass transition temperature of the blended cured epoxy. The parameter k is related to the degree of curvature between the T_g and composition curve. Notably, the parameter k could not only provide the semiquantitative prediction of the miscibility but also the intensity of the molecular motion of the polymer blended system.

Kwei equation^{24,25,28}

$$T_g = \frac{W_1 T_{g1} + kW_2 T_{g2}}{W_1 + kW_2} + qW_1 W_2 \quad (4)$$

In the Eq. (4), the T_{g1} and T_{g2} are the glass transition temperatures (T_g s) of the pristine cured epoxy resins 1 and cured epoxy resins 2, respectively. W_1 and W_2 are the weight fractions of the epoxy resin 1 and epoxy resin 2 in the cured reaction system. The T_g is the glass transition temperature of the cured blended material. The parameter k and q are the fitting constants. The parameter k has the same meaning as in Gordon-Taylor equation. The parameter q corresponded to the hydrogen bonding intensity. The highly positive q value indicated that the presence of the powerful hydrogen bonding interaction.

TABLE I
The NMR Characteristic Chemical Shift Peaks of the Thiodiphenyl Epoxy (THEP)

	a	b	c	d	e	f	g
$^1\text{H-NMR}^a$	2.66, 2.81	3.26	3.81, 4.16	* ^b	6.77	7.18	* ^b
$^{13}\text{C-NMR}^a$	44.24	49.79	68.54	157.51	115.15	132.39	127.49

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

^b No characteristic peaks appeared.

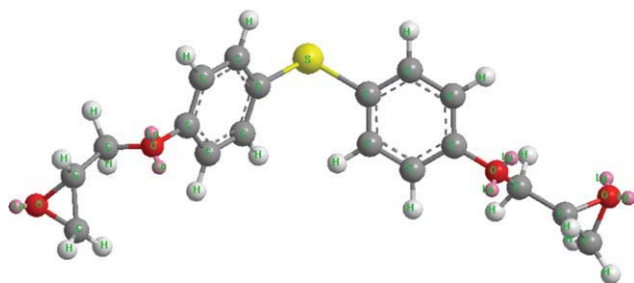


Figure 3 The minimum energy model of the thiodiphenyl epoxy (THEP) structure. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

The statistic heat-resistant index (T_s)

The statistic heat-resistant index temperature (T_s) was determined from the thermal degradation temperature of 5% weight loss (T_{d5}) and 30% weight loss (T_{d30}) of the cured blended materials by the TGA investigation. The statistic heat-resistant index temperature (T_s) was calculated by the Eq. (5)^{29–31}:

$$T_s = 0.49[T_{d5} + 0.6 \times (T_{d30} - T_{d5})] \quad (5)$$

The integral procedure decomposition temperature

The integral procedure decomposition temperature (IPDT) calculated from the Eq. (6) and proposed by previous investigations^{32–34}:

$$IPDT(^{\circ}C) = AK \cdot (T_f - T_i) + T_i \quad (6)$$

where parameters A and K are the area ratio of total experimental curve, which curve defined by the TGA thermal degradation traces. T_i is the initial experimental temperature, and T_f is the final experimental temperature. In this study, the T_i and T_f are 50 and 800 $^{\circ}C$, respectively. A and K can be calculated by the Eq. (7) and Eq. (8). The values of the S_1 , S_2 , and S_3 are determined by the previous studies.^{32–34}

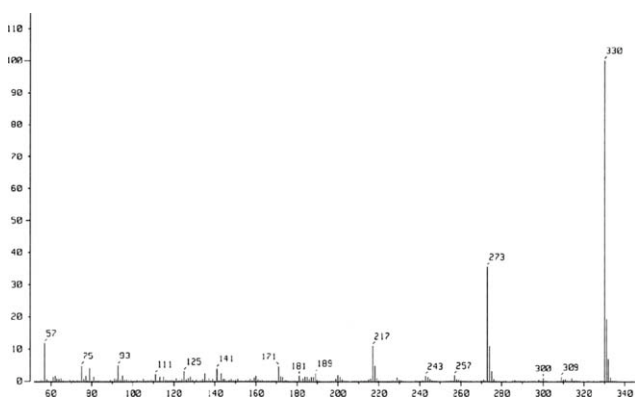


Figure 4 The mass spectrometry of the thiodiphenyl epoxy (THEP).

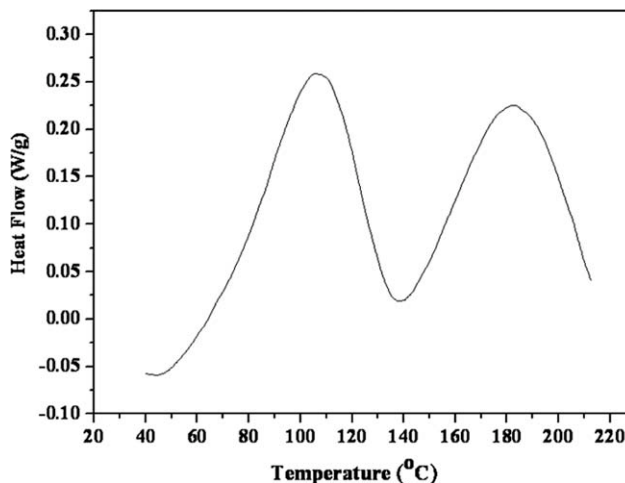


Figure 5 The DSC trace of the THEP/DDM curing reaction.

$$A = \frac{S_1 + S_2}{S_1 + S_2 + S_3} \quad (7)$$

$$K = \frac{S_1 + S_2}{S_1} \quad (8)$$

The activation energies of thermal degradation (E_a)^{33–35}

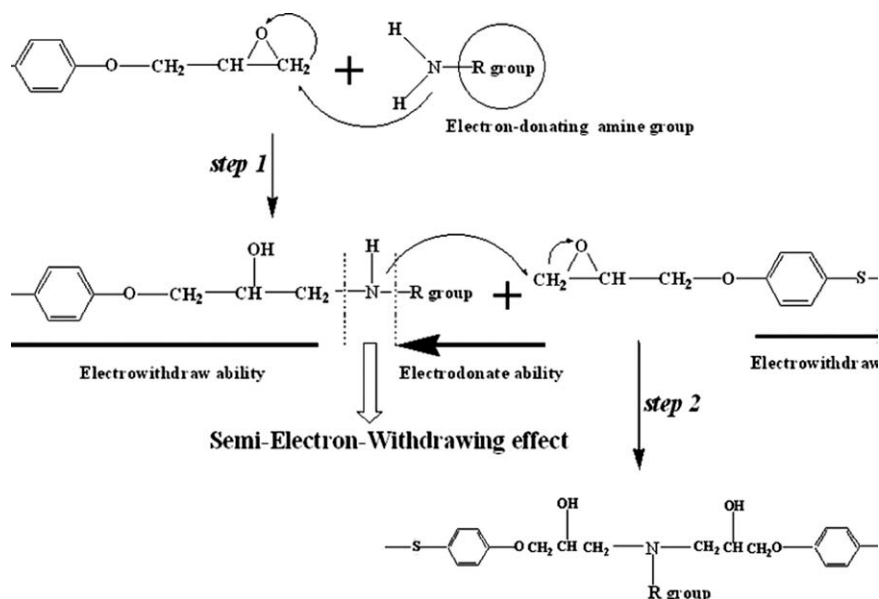
The activation energies of thermal degradation (E_a) were obtained from the TGA decomposed trace and calculated by the Horowitz-Metzger integral method (the Eq. (9)):

$$\ln[\ln(1 - \alpha)^{-1}] = \frac{E_a \times \theta}{R \times T_{max}^2} \quad (9)$$

In the Eq. (9), E_a is the activation energy of thermal degradation, and α is the thermal decomposition fraction. T_{max} is defined as the temperature at the thermal decomposition maximum rate. θ and R are

TABLE II
The Curing Kinetics of the Thiodiphenyl Epoxy (THEP)/DDM System

		Ozawa Method	
		First stage	Second stage
Slope	-6575.7	Slope	-11378
G	8.314	G	8.314
E_{a1} (kJ/mol)	51.97	E_{a2} (kJ/mol)	89.92
R^2	0.99	R^2	0.99
		Kissinger Method	
		First stage	Second stage
Slope	10816	Slope	31715
G	8.314	G	8.314
E_{a1} (kJ/mol)	89.92	E_{a2} (kJ/mol)	263.68
R^2	0.99	R^2	0.99



Scheme 2 Electrophilic reaction of epoxy curing with electron donating amine group.

the $T - T_{\max}$ and the gas constant, respectively. The E_a is determined from the slope of the straight line corresponding to the plot of $\ln\{\ln(1 - \alpha)^{-1}\}$ versus θ .

RESULTS AND DISCUSSION

Preparation the thiodiphenyl epoxy

Generally, the basic catalysts (such as NaOH or KOH) must be used in the preparation of the epoxy resins, which type catalyst is utilized not only to neutralize the halogen acid but also to accelerate the chemical synthesis. However, introduction of these basic catalysts may generate epoxy oligomers. And the basic catalyst could reduce the epoxy purity and pollute the environment. In this work, the thiodiphenyl epoxy (THEP) is a sulfide-type epoxy, which prepared by the bis(4-hydroxy-phenyl) sulfide (THDOL) and ECH without any basic catalysts. The structures of the THEP and THDOL were determined by the FTIR. Figure 1 illustrated that the dehydrochloro reaction was revealed by the disappearance of the hydroxyl group ($-\text{OH}$) in aromatic ring of the THDOL at 1376 cm^{-1} (OH in-plane) and 1009 cm^{-1} (Primary OH). The absorption peaks around 2933 , 1586 , 1492 , and 826 cm^{-1} were associated with the aromatic ring. The characteristic peak of the sulfide structure ($\text{S}-\text{C}$) was around 1167 cm^{-1} . The characteristic peak of the THEP at 922 cm^{-1} is the epoxy group.

Figure 2 displayed the NMR absorption peaks of the THEP, and the data summarized in Table I. The $^1\text{H-NMR}$ absorption peaks of the THEP around $2.66\text{--}3.26\text{ ppm}$ were the epoxy ring protons. And the absorption peaks at $\delta = 3.81 \sim 4.16\text{ ppm}$ were the $\text{AR}-\text{O}-\text{CH}_2-$ characteristic peaks of the THEP. The

characteristic peaks at $\delta = 6.77 \sim 7.18\text{ ppm}$ attributed to the aromatic protons. The chemical structure of the THEP was also determined by the $^{13}\text{C-NMR}$ (Fig. 2). The chemical shifts at $115.15 \sim 157.51\text{ ppm}$ were associated with the aromatic ring. The chemical shifts of the epoxy groups were around 69.03 , 49.73 , and 43.03 ppm . Figure 3 presents the architecture of the THEP, which determined by using the minimum energy model³⁶ and displayed the ball and stick structure model. Figure 4 presents the mass spectrum of the THEP, which illustrates that the molecular structure of the THEP is the monomer structure. Consequently, the thiodiphenyl epoxy (THEP) was synthesized without any basic catalyst.

The Figure 5 illustrates that the THEP cured with the DDM curing agent and two exothermic peaks (two curing stages) can be appeared. The activation

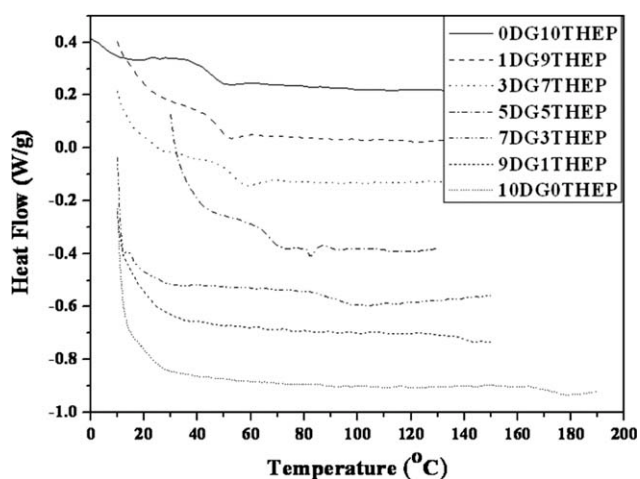


Figure 6 The DSC thermograms of various cured THEP/DGEBA materials.

TABLE III
Thermal Properties of the Various Cured Thiodiphenyl Epoxy (THEP)/DGEBA Materials

Code	T_g (°C)	T_{d5}^a	T_{d5}^b	T_s^a	T_s^b	Char (780°C) ^a	Char (780°C) ^b
0DG10THEP	43.35	223.91	222.13	136.66	133.03	25.94	1.04
1DG9THEP	49.09	217.00	226.27	129.66	133.60	25.04	0.95
3DG7THEP	54.08	225.11	230.83	134.81	135.26	20.18	0.57
5DG5THEP	67.54	241.14	241.89	144.94	140.70	16.6	0.81
7DG3THEP	94.49	262.08	264.21	153.43	152.68	13.79	0.62
9DG1THEP	140.00	307.17	298.11	168.28	166.52	12.35	0.83
10DG0THEP	166.56	354.00	314.17	182.30	170.05	11.43	0.65

^a Under the nitrogen atmosphere.

^b Under the air atmosphere.

energies (E_{a1}) of the THEP/DDM curing reaction were 51.97 ~ 89.92 kJ/mol and 89.92 ~ 263.68 kJ/mol, which E_{a1} calculated by Ozawa's^{15,16} and Kissinger's methods,^{17,18} respectively (summarized in Table II). The activation energy of the curing reaction of the second curing stage (E_{a2}) was higher than the first curing stage (E_{a1}). Generally, the epoxy/amine curing reaction was initiated by the epoxy ring reacting with the primary amine and to generate the secondary amine; then, the other epoxy groups further to react with the secondary amine.³⁷ For the DDM/THEP curing reaction, the first curing stage associated with the electron donating primary amine of the DDM cured with the THEP, and transferred to the semielectron-withdrawing secondary amine of the DDM. The second curing stage was the semielectron-withdrawing secondary amine of the DDM further to cure with the THEP and finish the DDM/THEP curing reaction (showed as Scheme 2). The E_{a1} is the activation energy of the THEP cured with the electron-donating primary amine of the DDM (first curing stage). The E_{a2} is the activation energy of the THEP cured with the semielectron-withdrawing secondary amine of the DDM (second curing stage).

However, the semielectron-withdrawing secondary amine cured with the THEP was more difficult than the electron-donating primary amine. As the electron effect of the amine curing agent could interfere with the epoxy/amine curing reaction. Jang et al.³⁸ found that the increment of the proton donor curing-agents could facilitate the curing reaction through donor-acceptor complex. This phenomenon leads to improve not only the cross-linking density but also the viscosity of the substance, and increase the activation energy of the epoxy/amine curing reaction.³⁹ For the second curing stage, the cross-linking architectures and viscosity of the reaction system could improve the maximum exothermic peak temperatures. Hence, the activation energies of the second curing stage (E_{a2}) were higher than the first curing stage (E_{a1}). Meanwhile, the maximum exothermic peak temperatures (T_p) increased with

the heating rate, as the polymer chain propagated rapidly and improved the system viscosity. The improvement of T_p values could cause the sharper slope in the Kissinger's model than in Ozawa's model. Consequently, the activation energies of curing reaction calculated by the Kissinger's model were higher than the Ozawa's model.

The glass transition temperature (T_g) of the cured THEP/DGEBA materials

Figure 6 and Table III present the DSC investigations of various cured THEP/DGEBA materials. The characteristic single T_g of various cured THEP/DGEBA materials associated with these materials completely miscible in the amorphous state without any phase separation. The T_g values decreased with the THEP content, since the sulfide linkage (—S—) was a soft-linkage. Additionally, the sulfide linkage (—S—) possessed weaker intermolecular force (hydrogen bonding) than the sulfone (—SO₂—) linkage. Chiu et al.¹⁴ found that the introduction of the sulfone type epoxy into the DGEBA could improve the T_g , as of the

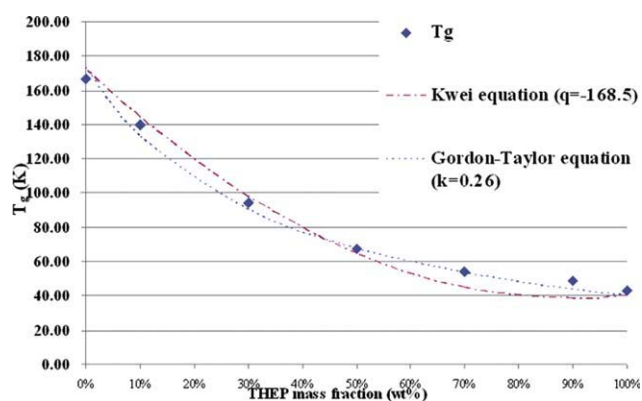


Figure 7 The Gordon-Taylor equation and Kwei equation were utilized to predict the molecular interaction behavior of the various cured THEP/DGEBA materials. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

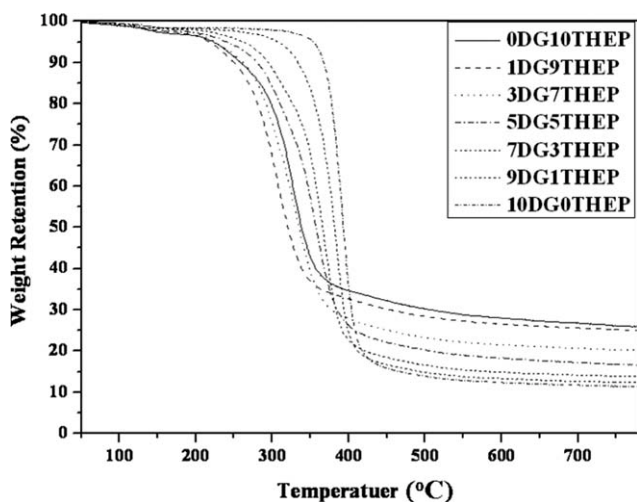


Figure 8 The thermal degradation curves of various cured THEP/DGEBA materials in nitrogen atmosphere.

physical cross-linking (the generation of the hydrogen bonding) could improve the T_g values.

Figure 7 presents the prediction of intermolecular force by Gordon-Taylor and Kwei equations and plots with the best fit method. From the Gordon-Taylor model, the intermolecular motion parameter (k) was estimated as 0.26. The low k value is attributed to the weak intermolecular force between the sulfide linkage ($-S-$) and the DGEBA main chain. The parameter q in the Kwei equation could predict the variation in the hydrogen bonding intensity. The high q value indicated that the copolymer possesses the excellent intermolecular hydrogen bonding strength.⁴⁰ It is notably that the parameter q was a high negative value (-168.5), this associated with the weak hydrogen bonding existed in the THEP/DGEBA curing system. Park et al.^{41,42} indicated that the hydrogen bonding could improve the T_g values of the cured epoxy materials. Consequently, the soft sulfide linkage ($-S-$)

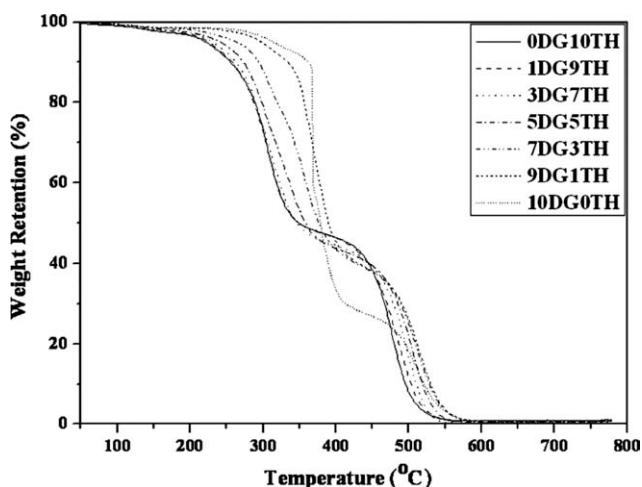


Figure 9 The thermal degradation curves of various cured THEP/DGEBA materials in air atmosphere.

TABLE IV
The Thermal Degradation Parameters of the Various Cured Thiodiphenyl Epoxy (THEP)/DGEBA Materials

Code	E_a (kJ/ mol) ^{a,c}	E_{a1} (kJ/ mol) ^{b,c}	E_{a2} (kJ/ mol) ^{b,c}	IPDT ^a	IPDT ^b
0DG10THEP	78.08	67.68	88.75	796.12	388.06
1DG9THEP	78.53	69.46	86.35	772.81	387.44
3DG7THEP	75.58	68.52	103.42	681.30	387.42
5DG5THEP	78.26	54.19	95.67	596.00	395.79
7DG3THEP	99.18	66.25	86.87	548.83	408.95
9DG1THEP	143.99	123.62	82.21	539.79	422.42
10DG0THEP	216.64	133.62	66.67	543.20	412.70

^a Under the nitrogen atmosphere.

^b Under the air atmosphere.

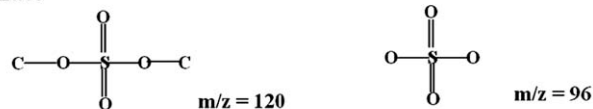
^c Calculated by Horowitz-Metzger integral method.

and the weak intermolecular action (hydrogen bonding) resulted in the T_g decreased. Additionally, the secondary hydroxyl group formation of the curing reaction might promote the intramolecular hydrogen bonding. Consequently, the T_g values of various cured THEP/DGEBA materials decreased with the introduction of the THEP.

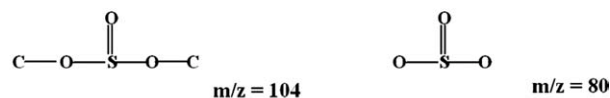
The thermal degradation properties of the cured THEP/DGEBA materials

Figures 8 and 9 illustrate the TGA investigation under the nitrogen and air atmospheres, respectively. The thermal degradation parameters were summarized in Tables III and IV. It is notably, T_{d5} and T_s values decreased with the THEP content, as the soft sulfide linkage ($-S-$) in the THEP might decompose at low temperature and further to form the sulfate derivative chars. Huang et al.¹² found that the sulfone group of the epoxy could provide the "shielding effect" when various sulfate derivative chars were formed, which chars could further to retard the thermal decomposition of the epoxy. It

Sulfate



Sulfite



Sulfonate

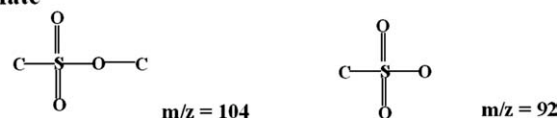


Figure 10 The structures of various sulfate derivative chars.

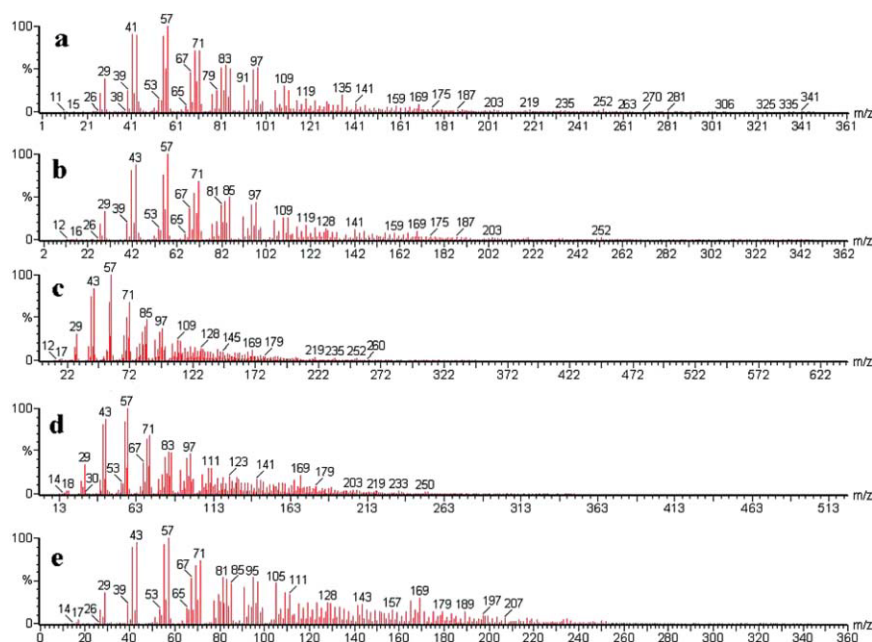
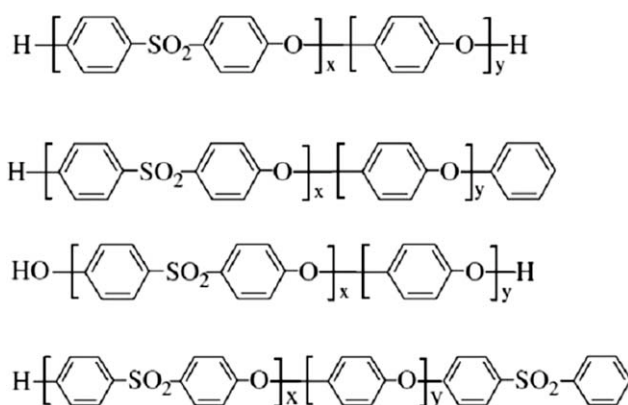


Figure 11 The mass fragmentations spectrum of the THEP/DDM material thermal degradation at (a) 250°C, (b) 300°C, (c) 350°C, (d) 400°C, (e) 450°C (in the air atmosphere). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

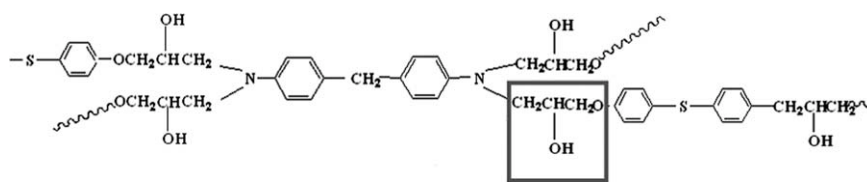
suggested that the thermal degradation of the soft sulfide linkage ($-\text{S}-$) of the THEP might decompose at low temperature to catch the oxygen and generate the various sulfate derivative chars (showed as Fig. 10), which phenomenon could decrease the oxygen contents while the thermal degradation of the epoxy. Then, the thermal stable sulfate derivative chars are more difficult to thermal decompose than cured epoxy. During the thermal degradation, additionally, the various sulfate derivative chars were formed and dispersed into the cured epoxy. This phenomenon such the epoxy cured and blended with various thermal stable sulfate derivative fillers. Consequently, the char yield increased from 11.43 to 25.94% and 0.65 to 1.04% under the nitrogen and air atmospheres, respectively. And the sulfate derivative chars formation could inhibit the thermal degradation and improve the thermal stability of the epoxy.¹⁴

There are many studies found that the sulfone type materials could easy to decompose at low temperature, and to form several sulfate derivatives.^{43–46} As the energy of the C–S bonding is lower than the C–C bonding, meanwhile, the degradation of the C–S bonding could further to form SO_2 and some sulfate derivatives.^{45,46} Naylor et al.⁴⁷ and Wellisch et al.⁴⁸ indicated that the thermal degradation of the sulfone type materials exhibited four characteristic steps: initiation, propagation, transfer, and termination, and they suggested that the β -elimination is the rate-determining step of the thermal degradation. Samperi et al.⁴⁹ investigated the thermal decomposi-

tion products of the sulfone type material and found that various sulfate derivative chars' architectures by the TGA/GC/Mass. In this study, the thermal degradation of the THEP/DDM material was investigated by TGA/GC/Mass. Figure 11 presents the mass fragmentations spectrum of the THEP/DDM material at 250°C, 300°C, 350°C, 400°C, and 450°C, respectively, in the air atmosphere. From the Figure 11, the mass characteristic fragments (m/z) around 164, 180, 214, 234, 240, 250, 302, 310, and 326 suggested that the mass fragmentations spectrum of the possible chemical structure fragments and showed as Scheme 3. The x values of Scheme 3 were 0, 0.5, or 1, and the y values of Scheme 3 were 0, 0.5, or 1. Then, these sulfate derivatives char yields may decompose and further to form the mass



Scheme 3 The possible structures of the char yields.



Scheme 4 The aliphatic linkage chemical structure of the THEP/DDM Material.

characteristic fragments (m/z) around 80, 92, 96, 104, and 120. Consequently, various sulfate derivative char yields might be formed the short chemical fragments and showed as Figure 10. Additionally, the mass characteristic fragments (m/z) around 41, 57, and 71 were associated with the aliphatic linkage of the cured THEP/DDM material (see Scheme 4). Liu et al.^{5,16,50} indicated that the char formation could improve the thermal stability of the polymer materials. As the char improvement could not only decrease the combustible gases contents but also form the barrier to hinder heat transfer. The sulfate derivative chars might be formed during the THEP thermal degradation and served as the thermal stable segments; furthermore, which segments were further decomposed at high temperature and defended the cured THEP/DGEBA material.

The activation energies of the thermal degradation (E_a) and the integral procedure decomposition temperature (IPDT) are summarized in Table IV. In the nitrogen atmosphere, the E_a values decreased with the THEP content, as the soft sulfide linkage ($-S-$) of the THEP could be degraded at lower temperature than the cured pristine DGEBA epoxy, and to form various thermal stable sulfate derivative chars. Under the air atmosphere, two thermal degradation stages were observed. The activation energies of the first (E_{a1}) and second thermal degradation stages (E_{a2}) are summarized in Table IV. In the first thermal degradation stage, the E_{a1} values decreased with the THEP content. As the soft sulfide linkage ($-S-$) of the THEP might easy to decompose under the air atmosphere, and the oxygen served as the catalyst of the first thermal degradation stage. It is notably, the E_{a2} values increased with the THEP (from 66.67 kJ/mol to 103.42 kJ/mol). Because of various thermal stable sulfate derivative chars were formed in the first thermal degradation stage, these chars could further to provide the "antioxidation thermal property" or "shielding effect" and improve the thermal stability of the cured THEP/DGEBA material. The IPDT values increased with the THEP content under the nitrogen atmosphere. The increased IPDT values associated with the sulfide linkage ($-S-$) of the THEP may reduce the volatile fraction under the nitrogen atmosphere. In the air atmosphere, the DGEBA and THEP are the organic compounds, and the sulfide linkage ($-S-$) of the THEP could decompose at lower temperature than that of the DGEBA.

Consequently, the IPDT values decreased slightly with the THEP content in the air atmosphere.

CONCLUSIONS

The sulfide-type epoxy (thiodiphenyl epoxy, THEP) was prepared by the bis(4-hydroxyphenyl) sulfide (THDOL) and ECH without any basic catalysts (NaOH or KOH). The activation energies of the THEP/DDM curing reaction calculated by Ozawa's and Kissinger's methods, and the values were 51.97 ~ 89.92 kJ/mol and 89.92 ~ 263.68 kJ/mol, respectively. The first stage of the curing reaction associated with the electron donating primary amine of the DDM cured with the THEP and the DDM transferred to the semielectron-withdrawing secondary amine. The second stage of the curing reaction was the semielectron-withdrawing secondary amine further to cure with the other epoxy groups of the THEP (showed as Fig. 5 and Scheme 2). The intermolecular force parameters k and q were 0.26 and -168.5 estimated by Gordon-Taylor and Kwei equations, respectively. Which low parameters resulted from the weak hydrogen bonding existed in the THEP/DGEBA curing system, and this phenomenon also caused the T_g decreased with the introduction of the THEP. In the thermal degradation investigation, the soft sulfide linkage ($-S-$) of the THEP might decompose at low temperature and generate various thermal stable sulfate derivative chars. Consequently, the char formations of the THEP/DGEBA materials were increased from 11.43 to 25.94% and 0.65 to 1.04% under the nitrogen and air atmospheres, respectively. The thermal stable sulfate derivative chars could further to provide the antioxidation thermal property or shielding effect and improve the thermal stability of the of the THEP/DGEBA materials. Meanwhile, the sulfate derivative chars could improve the activation energies of the second thermal degradation stage (E_{a2}), which could increase from 66.67 to 103.42 kJ/mol under the air atmosphere.

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