

# Intermolecular Force and Thermal Properties of the Sulfonyl Epoxy Blends Cured with DGEBA Epoxy

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**ABSTRACT:** The sulfonyl epoxy monomer (SEP) was synthesized and further to blend with the diglycidyl ether of bisphenol A (DGEBA). The glass transition temperature ( $T_g$ ) of the SEP/DGEBA blended materials increased from 103.7 to 163.8°C. The cross-linking density and polymer chain self-association intra-molecular action affected more than that the polymer-polymer intermolecular action (hydrogen bonding) in the SEP blended with the DGEBA materials. The excess stabilization energy in the overall stabilization was only 0.00145% (14.5 ppm), which indicated that the polymer-polymer intermolecular action was weak. The ther-

mal degradation of the SEP segments could form various sulfate derivatives at lower temperature and analyzed by the TGA/GC/Mass. The sulfate derivatives could generate the thermal stable chars, which provided the "shielding effect" and antioxidation property. Additionally, these chars could also improve the protective effect and inhibit the thermal-oxidation decomposition under the air atmosphere. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 2165–2175, 2010

**Key words:** sulfonyl epoxy; thermal properties; intermolecular force; polymer blends

## INTRODUCTION

Epoxy resins are easy to cure with various curing agents,<sup>1,2</sup> and the epoxy resins possessed excellent heat and solvent resistance, good mechanical and electrical properties, good adhesion of many substrates.<sup>3–6</sup> Recently, various modified and novel synthesized epoxy resins were reported, such as the liquid crystalline epoxy resin,<sup>7</sup> the UV-curable epoxy resin,<sup>8</sup> the cycloaliphatic epoxy resin,<sup>9</sup> the benzoxazine type epoxy material,<sup>10</sup> naphthyl/dicyclopentadiene,<sup>11</sup> etc. However, the poor thermal stabilities of the epoxy resins limited its applications. To improve the thermal stabilities, the phosphorus moieties<sup>12,13</sup> or the silicon compounds<sup>14–16</sup> were introduced into the epoxy resins.

The sulfone materials have been applied to various high-performance engineering materials, such as fuel cell membranes,<sup>17–19</sup> gas separation membranes,<sup>20,21</sup> optical or photo materials,<sup>22,23</sup> etc. Because of the sulfonyl materials incorporated with the polymer materials, which could improve the thermal and oxidative stability, chemical resistance, and the glass transition temperature ( $T_g$ ).<sup>24–29</sup> The epoxy resins can be modified by physical blending

or chemical synthesis with various sulfonyl compounds. However, the epoxy resins blended with high molecular weight sulfonyl compounds could generate the phase separation and reduce the curing reactivity.<sup>30</sup>

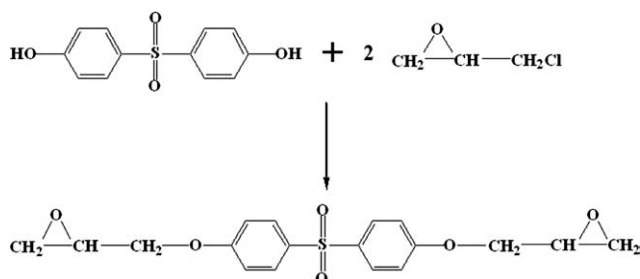
In our previous investigation,<sup>31</sup> the diglycidylether bisphenol sulfonyl monomer (sulfonyl epoxy, SEP) was synthesized by the bis(4-hydroxyphenyl)sulfone (SDOL) and the epichlorohydrin (ECH). In this work, various weight ratios of the SEP blended with the DGEBA epoxy resin. The SEP possessed the sulfonyl group ( $-\text{SO}_2-$ ) and two epoxy groups (showed as Scheme 1), this will without any phase separation be occurred. And it could increase the glass transition temperature ( $T_g$ ) by introduction of the SEP. The polymer-polymer intermolecular force of the SEP/DGEBA blended materials was estimated by the Gordon-Taylor and the Kwei equations. The activation energies of thermal degradation were calculated from the Horowitz-Metzger integral method. Furthermore, the thermal degradation of the cured epoxy material was investigated by the TGA/GC/Mass.

## EXPERIMENTAL

### Materials

Bis(4-hydroxyphenyl)sulfone (SDOL) was received from the TCI, Tokyo, Japan. Epichlorohydrin (ECH) and Tetrahydrofuran (THF) were obtained from the

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

Tedia, OH. Benzyltrimethylammonium chloride (BTAC) and 4,4-Methylenedianiline (DDM) were obtained from the Acros, Belgium. The diglycidyl ether of bisphenol A (DGEBA) epoxy was supplied by the Nan Ya Plastics, Taiwan, which contained the epoxide equivalent weight (EEW) of 180 g/equiv.

### Instrumental analysis and measurements

Differential scanning calorimetric (DSC) thermograms were performed with the Thermal analyzer (TA) DSC-2910 and by a heating rate of 10°C/min under the nitrogen atmosphere. Thermogravimetric analysis (TGA) was performed with a Thermal Analysis TGA-951 thermogravimetric analyzer, at 10°C/min heating rate and the gas flow rate was 100 mL/min under the nitrogen and air atmospheres. Analysis of evolved gas was performed by the 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, 120V).

### Synthesis of diglycidylether sulfonyl monomer (sulfonyl epoxy, SEP)<sup>31</sup>

A mixture of 2.5 g bis(4-hydroxyphenyl) sulfone (0.01 mol, SDOL), 18.5 g epichlorohydrin (0.2 mol, ECH) and 0.929 g benzyltrimethylammonium chloride (0.005 mol, BTAC) were stirred at room temperature. The homogeneous mixture was heated from room temperature to 70°C for 4 h. And the mixture cooled to room temperature; the excess ECH removed by vacuum system. The mixture was washed by distilled water and filtered. The solid product was dried in a vacuum oven at room temperature for 24 h. The SEP was a white powder, and the yield was 93%, the melting point (m.p.) of SEP was in the range of 139–143°C. Scheme 1 presents the preparation of the SEP.

EA for C<sub>18</sub>H<sub>18</sub>O<sub>6</sub>S—Calculated: C 59.67%; H 4.97%; S 8.84%, Found: C 57.92%; H 4.99%; S 8.11%, MS for C<sub>18</sub>H<sub>18</sub>O<sub>6</sub>S—Calculated: 362.0, Found: 362.0. FTIR (KBr, cm<sup>-1</sup>): 3063, 2927, 1590, 1498, 1286, 1138, 914. <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ (ppm) 7.81 (2H,d), 6.95 (2H,d),

4.28 (2H,dd), 3.91 (2H,dd). <sup>13</sup>C-NMR (CDCl<sub>3</sub>): δ (ppm) 161.91 (s), 134.29 (s), 129.51 (d), 114.98 (d), 69.03 (t), 49.73 (d), 44.08 (t).

### Preparation of the cured epoxy resins

All of the preparation of the SEP/DGEBA blended materials was prepared in the 2 : 1.1 molar ratio of the epoxy resin to the DDM curing agent. And the mixture reactants were soluble in the THF at room temperature. The weight ratios of the SEP to the DGEBA are 100 : 0, 90 : 10, 70 : 30, 50 : 50, 30 : 70, 10 : 90, and 0 : 100, respectively. In this study, the cured epoxy material (5S5D) was the abbreviation of the SEP/DGEBA blended material containing the DGEBA and SEP with the weight ratio of 50% to 50%, and further to cure. The 10S0D is the pristine cured SEP/DDM material. The preparation of the SEP/DGEBA blended materials was proceeded by the following thermal cured stages: at 120°C for 1 hr, 160°C for 1.5 hr, 180°C for 1.5 hr, 200°C for 2 hr in the oven.

### The prediction of the polymer-polymer intermolecular action of the SEP/DGEBA blended materials

There are many equations that can be used to predict the glass transition temperature ( $T_g$ ) of the miscible system. Hu et al.<sup>32</sup> used the Gordon-Taylor equation<sup>33,34</sup> to predict the polymer-polymer intermolecular action of the epoxy blended systems. Kuo et al.<sup>35</sup> and Liu et al.<sup>36</sup> investigated the polymer-polymer intermolecular action of the copolymerization and cured epoxy systems by the Kwei equation.<sup>37,38</sup> For the polymer blended system, the Gordon-Taylor and the Kwei equations could directly and easy to predict the state of the hydrogen bonding by the glass transition temperature ( $T_g$ ) of the polymer blended materials. And the parameters of these equations could correctly provide the tendency of the hydrogen bonding of the polymer blended system. Consequently, both the Gordon-Taylor and the Kwei equations were utilized in this work.

Gordon-Taylor equation<sup>32–34,39,40</sup>

$$T_g = \frac{W_1 T_{g1} + k W_2 T_{g2}}{W_1 + k W_2} \quad (1)$$

In eq. (1),  $T_{g1}$  and  $T_{g2}$  are the glass transition temperatures ( $T_g$ ) of the pristine epoxy materials. Meanwhile,  $W_1$  and  $W_2$  are the weight fractions of epoxy material 1 and epoxy material 2 in the cured reaction systems. The  $T_g$  is the glass transition temperature of the blended epoxy. The parameter  $k$  is the degree of curvature between the  $T_g$  and composition curve. Additionally, the parameter  $k$  could provide not only the semi-quantitative prediction of the

miscibility but also the intensity of the polymer chain molecular motion in this work.

Kwei equation<sup>37,38,41</sup>

$$T_g = \frac{W_1 T_{g1} + kW_2 T_{g2}}{W_1 + kW_2} + qW_1 W_2 \quad (2)$$

In the eq. (2),  $T_{g1}$  and  $T_{g2}$  are the glass transition temperatures ( $T_g$ ) of the pristine epoxy materials.  $W_1$  and  $W_2$  are the weight fractions of the epoxy material 1 and epoxy material 2. The  $T_g$  is the glass transition temperature of the blended epoxy. The parameter  $k$  and  $q$  are fitting constants. The parameter  $k$  has the same meaning as in the Gordon-Taylor equation. The parameter  $q$  corresponded to the hydrogen bonding intensity. The high positive  $q$  value indicated that the presence of powerful hydrogen bonding.

The backbone stabilization<sup>42,43</sup>

The parameter  $q$  is related to the change in energies of the different mixture components system. The parameter  $q$  can be expressed as the following eq. (3):

$$q = \frac{2f}{3k_B} [E_{12} - 0.5(E_{11} + E_{22})] \quad (3)$$

$E_{12}$ ,  $E_{11}$ , and  $E_{22}$  are the energies contribution to backbone stabilization between the polymer 1 and polymer 2, polymer 1 and polymer 1, polymer 2 and polymer 2, respectively. The  $f$  is the dispersion factor, which may depend on the completeness of the intermixing of the two components and affect the connection of neighboring chains.  $k_B$  is the Boltzmann constant ( $1.3806503 \times 10^{-23}$ , J/K). Reiserand coworkers<sup>43</sup> provided three categories with various  $k$  and  $q$  values. Such as the following equations:

The case of  $k = 1, q = 0$ :

$$E_{12} = 0.5(E_{11} + E_{22}) \quad (4)$$

The case of  $k = 1, q > 0$ :

$$E_{12} > 0.5(E_{11} + E_{22}) \quad (5)$$

The case of  $k = 1, q < 0$ :

$$E_{12} < 0.5(E_{11} + E_{22}) \quad (6)$$

At the case of  $k = 1$  and  $q > 0$ , the excess stabilization could be calculated by the eq. (7)<sup>43</sup>:

$$\text{The excess stabilization (kcal/mol)} = R_q W_1 W_2 \quad (7)$$

In eq. (7),  $R$  is the ideal gas constant (0.002 kcal/g).  $W_1$  and  $W_2$  are the weight fractions of the epoxy

material 1 and epoxy material 2, respectively. The parameter  $q$  has the same meaning as in the Kwei equation. And the stabilization of the overall backbone of polymer was calculated by the eq. (8):

$$\text{The overall backbone stabilization (kcal/mol)} = R \times T_g \quad (8)$$

$R$  is the ideal gas constant, and  $T_g$  is the glass transition temperature of various blended epoxy materials.

### The activation energies of thermal degradation (ea)<sup>44-46</sup>

The activation energies of thermal degradation are calculated by the Horowitz-Metzger integral method [eq. (9)]:

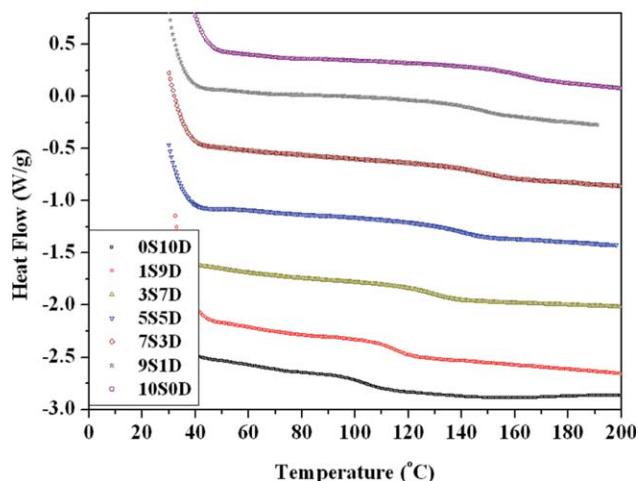
$$\ln[\ln(1 - \alpha)^{-1}] = \frac{E_a \times \theta}{R \times T_{\max}^2} \quad (9)$$

$E_a$  is the activation energies of the thermal degradation, and  $\alpha$  is the fraction of thermal degradation.  $T_{\max}$  is defined as the temperature at the maximum rate of thermal degradation weight loss.  $\theta$  and  $R$  are the values of  $T - T_{\max}$  and the gas constant, respectively. Furthermore,  $E_a$  is determined from the slop of the straight line corresponding to the plot of  $\ln\{\ln(1 - \alpha)^{-1}\}$  versus  $\theta$ .

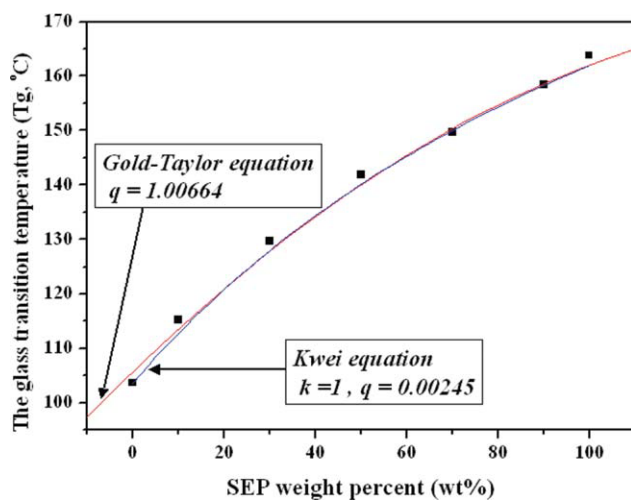
## RESULTS AND DISCUSSION

### The glass transition temperature ( $T_g$ )

Figure 1 presents the DSC thermograms of various SEP/DGEBA blended materials, and reveals a single  $T_g$ . The single  $T_g$  or the shift in the  $T_g$  of the parent



**Figure 1** The DSC thermograms of various SEP/DGEBA blended materials. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



**Figure 2** The Gordon-Taylor equation and the Kwei equation were utilized to predict the molecular interaction behavior of the SEP/DGEBA blended materials. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

polymers was used to estimate the miscibility of the copolymers. Notably, the characteristic single  $T_g$  of various SEP/DGEBA blended materials revealed completely miscibility in the amorphous state and without any phase separation. The  $T_g$  of various blended cured epoxy materials increased with SEP content. The increase of  $T_g$  resulted from the cross-linking density and the polymer-polymer intermolecular action (such as hydrogen bonding).

Several empirical equations can be used to correlate and predict the effect of the polymer-polymer intermolecular action of the polymer composites. In this work, both the Gordon-Taylor and the Kwei equations were employed to predict the polymer-polymer intermolecular action of the SEP/DGEBA blended materials. Figure 2 plots the best fit. For the predictive Gordon-Taylor model, the semi-quantitatively measured miscibility by the polymer-polymer intermolecular action parameter ( $k$ ) was 1.00664. At  $k$  value range from 0.8 to 1.2, the Gordon-Taylor equation indicates that the copolymer is a miscible

blend.<sup>43</sup> Additionally, the variation of the  $k$  value with the structure of the polymers, such as when the isopropyl group of the DGEBA is replaced with the sulfonyl group of the SEP, further to influences the interaction between the different polymer chains.<sup>32</sup> When the polymer inter- and intra-molecular actions of the SEP/DGEBA blended materials occurred,<sup>32,39,40</sup>  $k$  exceeded unity.

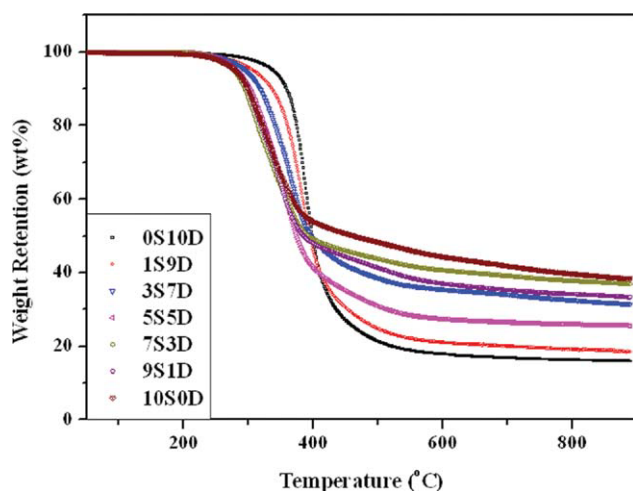
The parameter  $q$  in the Kwei equation could predicts the hydrogen bonding (molecular action) variation of the SEP/DGEBA blended materials. A higher positive  $q$  generally suggests a greater intermolecular hydrogen bonding strength than polymer chain intra-molecular action. In this work, however, the parameter  $q$  was a small positive value of close to zero (0.00245). For the polymer main chain, the formation of secondary hydroxyl group in the epoxy ring opening reaction, this phenomenon promoted polymer chain intra-molecular hydrogen bonding with the sulfonyl group of the SEP and to form the polymer chain intra-molecular hydrogen bonding of the SEP/DGEBA blended materials. Polymer-polymer intermolecular action was weak when the cured epoxy had a high cross-linking density. Lú et al.<sup>39</sup> found that the cross-linking structure (the three-dimensional network) might inhibit the polymer-polymer intermolecular hydrogen bonding and which structure possessed both shielding and screening effects. The sulfonyl group of the SEP was a strong electron-withdrawing functional group, which could promote the opening reaction of oxirane ring. Moreover, the alkyl group of the curing agent (DDM) exhibited strongly electron-donating property and improved the epoxy/amine curing reactivity. Consequently, the high degree of cross-linking was associated with high SEP contents in the SEP/DGEBA blended system, and observed a low  $q$  value.

Reiser and coworkers<sup>43</sup> predicted the stailization of the polymer chain, which is the backbone of all molecular interaction. Table I presents the calculated backbone stabilization energies of various SEP/DGEBA blended materials. In this study, the case of  $k = 1$ ,  $q > 0$  (this work  $k = 1$ ,  $q = 0.00245$ ) was

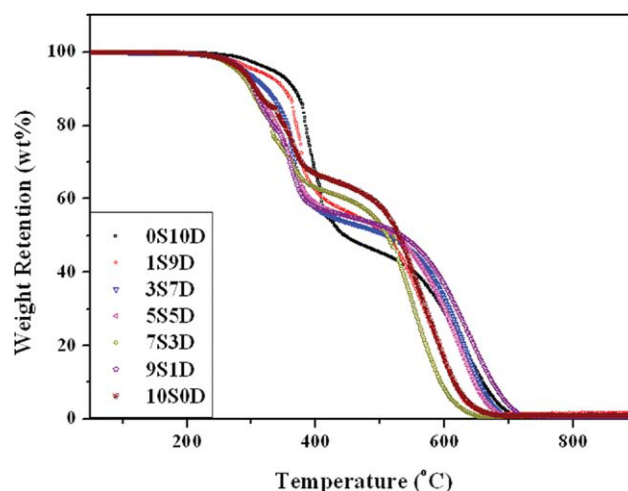
**TABLE I**  
The  $T_g$  and Polymer Chain Intermolecular Action Calculation of the Various SEP/DGEBA Blended Materials

Code	$T_g$ (°C)	RTg (kcal/mol)	$RqW_1W_2$ (kcal/mol)	Ratio ( $RqW_1W_s/RTg$ , %)
10S0D	163.8	$8.74 \times 10^{-1}$	a	a
9S1D	158.4	$8.63 \times 10^{-1}$	$4.32 \times 10^{-7}$	$5.00 \times 10^{-5}$
7S3D	149.7	$8.46 \times 10^{-1}$	$1.01 \times 10^{-6}$	$1.19 \times 10^{-4}$
5S5D	141.8	$8.30 \times 10^{-1}$	$1.20 \times 10^{-6}$	$1.45 \times 10^{-4}$
3S7D	129.6	$8.06 \times 10^{-1}$	$1.01 \times 10^{-6}$	$1.25 \times 10^{-4}$
1S9D	115.3	$7.77 \times 10^{-1}$	$4.32 \times 10^{-7}$	$5.60 \times 10^{-5}$
0S10D	103.7	$7.54 \times 10^{-1}$	a	a

a No values of calculation.



**Figure 3** The thermal degradation curves of various SEP/DGEBA blended materials in the nitrogen atmosphere. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



**Figure 4** The thermal degradation curves of various SEP/DGEBA blended materials in the air atmosphere. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

considered. For the 5S5D system, the product of  $W_1$  and  $W_2$ , and the excess backbone stabilization energy, were higher than those of other samples. The excess backbone stabilization energy of the 5S5D system was  $1.2 \times 10^{-6}$  kcal/mol. The overall backbone stabilization energy of the 5S5D system was 0.82996 kcal/mol. The fraction of the overall excess stabilization energy in the overall stabilization was very small, being only 0.00145% (14.5 ppm) of the overall stabilization. This phenomenon suggested that the increase of  $T_g$  resulted from the fact that the cross-linking density and the reactivity of the SEP/DGEBA blended system. Hence, the influence of the backbone stabilization energy was weaker than the influence of the cross-linking density and the reactivity of the SEP/DGEBA blended system. The change of  $T_g$  was a very sensitive to the change of the polymer main chain. The main chain of the cured SEP segments possessed numerous sulfonyl groups, which more strongly influenced the  $T_g$  than did the main chain of the cured DGEBA. Therefore, introducing the SEP component substantially increased  $T_g$ .

### The thermal degradation properties

The thermal degradation properties of various SEP/DGEBA blended materials were investigated by the TGA in the nitrogen and air atmospheres. Figures 3 and 4 and Table II present the TGA data.  $Td_3$  and  $Td_{10}$  decreased as the SEP contents increased, but the char formation increased with the SEP contents. The sulfonyl groups of the SEP decomposed at lower temperature than the DGEBA and to form the sulfate char, which char could provide the “shielding effect” and improve the thermal stability.<sup>31,45,47</sup> Therefore, the sulfate-derived char improved the thermal stability of the SEP/DGEBA blended materials.

### Kinetics of thermal degradation and the TGA/GC/mass analysis

The kinetics of thermal degradation were calculated by the Horowitz-Metzger equation and the results are summarized in Table III. Horowitz et al.<sup>46</sup> indicated that the thermal degradation activation energies calculated by the Horowitz-Metzger integral equation

**TABLE II**  
The Thermal Properties of the Various SEP/DGEBA Blended Materials

Code	$Td_3^a$	$Td_{10}^a$	$T_{max}^a$	Char <sub>800</sub> <sup>a</sup>	$Td_3^b$	$Td_{10}^b$	$T_{max1}^b$	$T_{max2}^b$	Char <sub>800</sub> <sup>b</sup>
0S10D	318.80	359.44	389.62	16.25	305.00	366.57	384.49	636.70	0.32
1S9D	285.05	336.88	379.19	18.96	280.50	350.65	373.39	582.22	0.44
3S7D	278.73	317.75	351.71	32.59	270.14	322.27	363.30	631.66	0.68
5S5D	266.51	302.28	343.18	25.94	264.60	307.01	359.27	625.60	1.03
7S3D	264.30	294.63	320.43	37.82	262.37	299.44	333.03	550.95	0.96
9S1D	267.90	299.83	330.86	34.16	273.79	303.80	362.29	639.73	1.08
10S0D	260.91	298.61	325.17	39.67	268.78	305.84	365.32	564.06	1.12

<sup>a</sup> The TGA was tested in the nitrogen atmosphere.

<sup>b</sup> The TGA was tested in the air atmosphere.

**TABLE III**  
The Thermal Degradation Activation Energies of Various SEP/DGEBA Blended Materials

Code	R-square	Ea <sup>a</sup> (kJ/mol)	R-square	Ea <sub>1</sub> <sup>b</sup> (kJ/mol)	R-square	Ea <sub>2</sub> <sup>c</sup> (kJ/mol)
0S10D	0.99	25.74	0.99	120.82	0.99	75.02
1S9D	0.99	18.49	0.99	123.72	0.98	84.55
3S7D	0.99	18.30	0.99	87.22	0.99	94.61
5S5D	0.98	18.05	0.99	63.84	0.99	92.00
7S3D	0.99	22.39	0.99	78.51	0.99	83.00
9S1D	0.99	21.15	0.99	60.76	0.99	78.29
10S0D	0.98	18.49	0.99	53.55	0.99	78.67

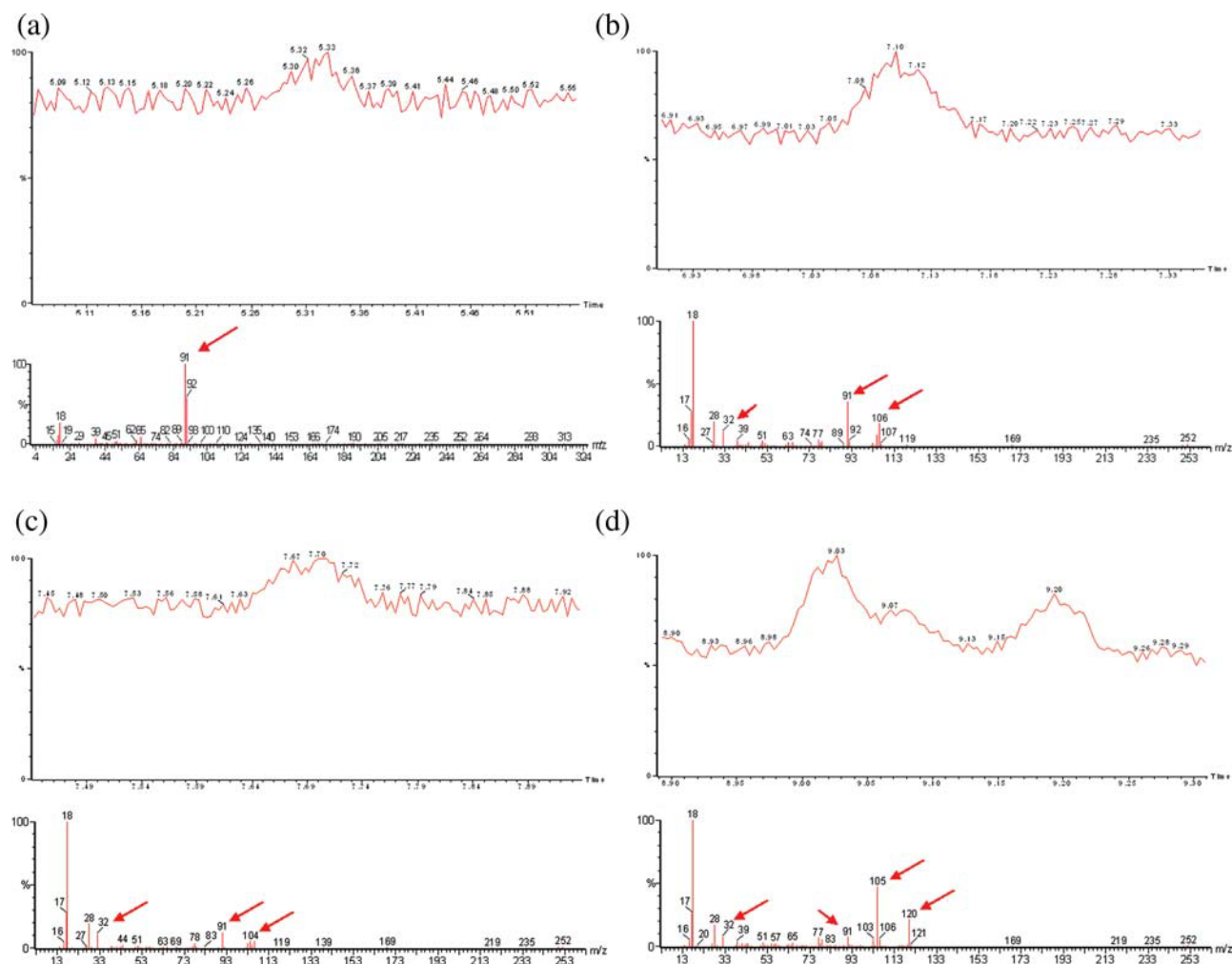
<sup>a</sup> Thermal degradation under the nitrogen atmosphere.

<sup>b</sup> The first thermal degradation under the air atmosphere.

<sup>c</sup> The second thermal degradation under the air atmosphere.

is easy to compare the relative thermal stabilities of materials. And this equation is best applied when the temperature range is narrow, as the thermal degradation such the nature of the reaction. The reaction order, activation energies, and frequency factor do not change over the temperature range study. Addi-

tionally, the Horowitz-Metzger integral equation could not only particularly for quick analyses but also suitable for thermal degradation activation energies calculation at high temperature.<sup>46</sup> Under the nitrogen atmosphere, the tendency of the thermal degradation activation energies of the SEP/DGEBA



**Figure 5** The evolved gas analysis by the GC and the mass fragmentations spectrum at (a) 5.334 min, (b) 7.106 min, (c) 7.692 min, (d) 9.029 min, (e) 9.196 min, (f) 9.456 min, (g) 9.880 min, and (h) 10.593 min under the nitrogen atmosphere. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

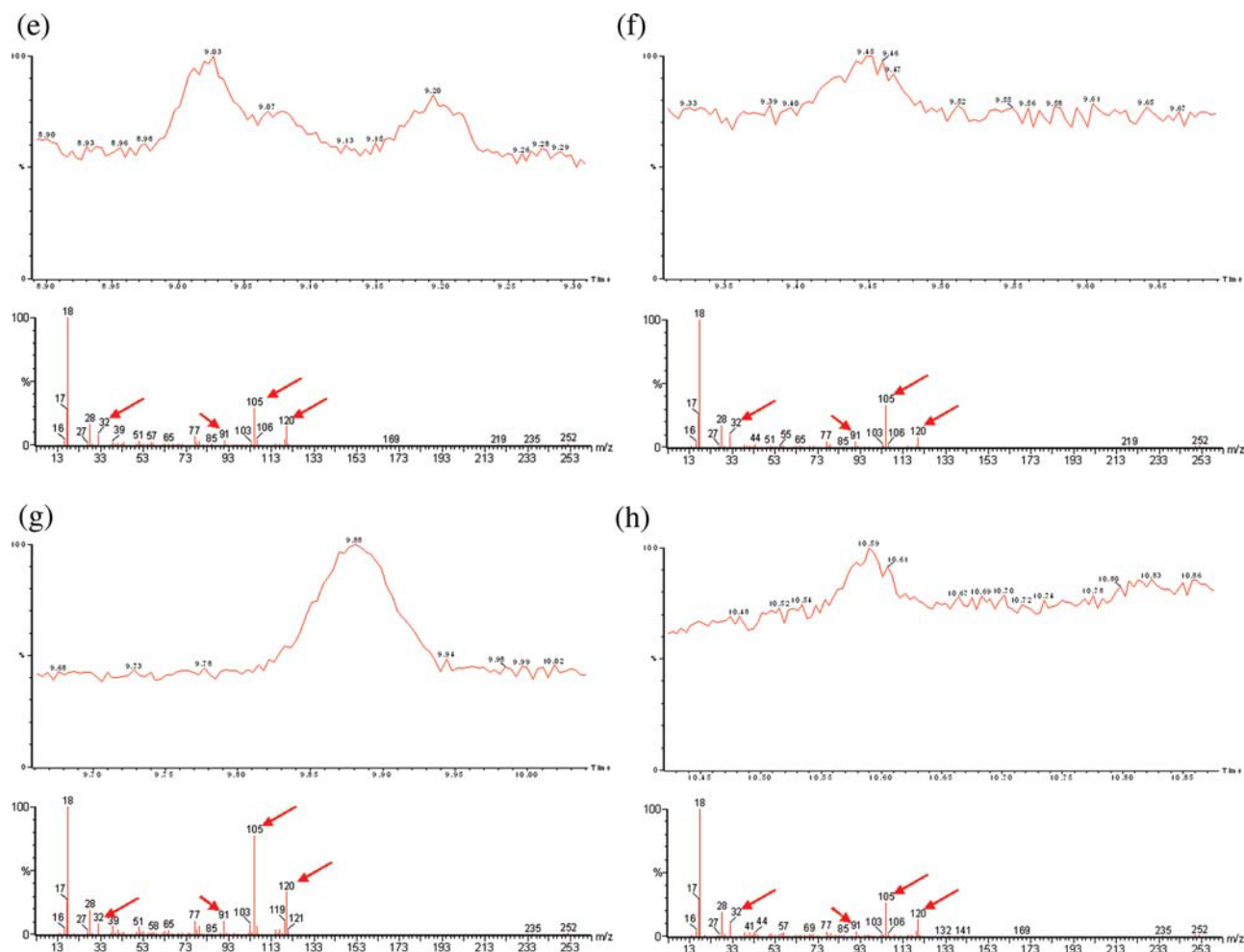


Figure 5 (Continued from the previous page)

blended materials were first decrease, then increase, and then decrease with the SEP contents increased. Which phenomenon associated with the sulfonyl groups of the SEP were more easily to decompose than the DGEBA, and further to generate the thermal stable sulfate derivatives char yields. These thermal stable sulfate derivatives char yields could improve the thermal stability of the SEP/DGEBA blended materials. Hence, the activation energies of thermal degradation were first decrease and then increase under the nitrogen atmosphere. However, the activation energies of thermal degradation of the SEP/DGEBA blended materials decreased again, since the thermal stable sulfate derivatives char yields might not prevent the numerous sulfonyl groups of the SEP from thermal decomposed at low temperature. The thermal degradation properties of the cured SEP (10S0D) were further analyzed by the TGA/GC/Mass<sup>48,49</sup> at the temperatures range between 300°C and 350°C in the nitrogen atmosphere. Figure 5(a,h) present the GC analysis of the evolved gas and the mass fragmentations spectra at 5.334, 7.106, 7.692, 9.029, 9.196, 9.456, 9.880, and

10.593 min. All of the spectra revealed not only the sulfur mass fragmentation (MW: 32), but also the mass fragmentations associated with various sulfate derivatives. Figure 6 presents the chemical structure and the molecular weight of various sulfate

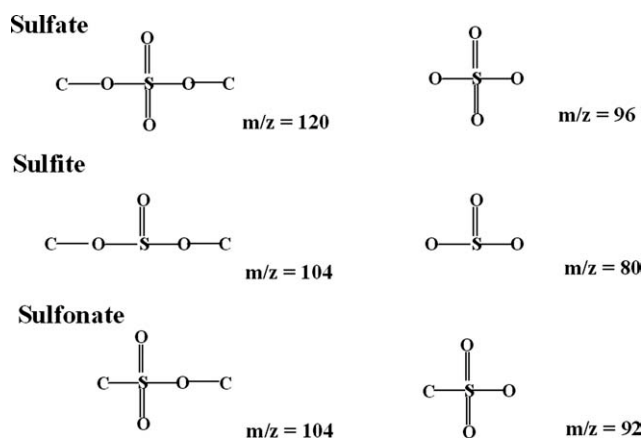
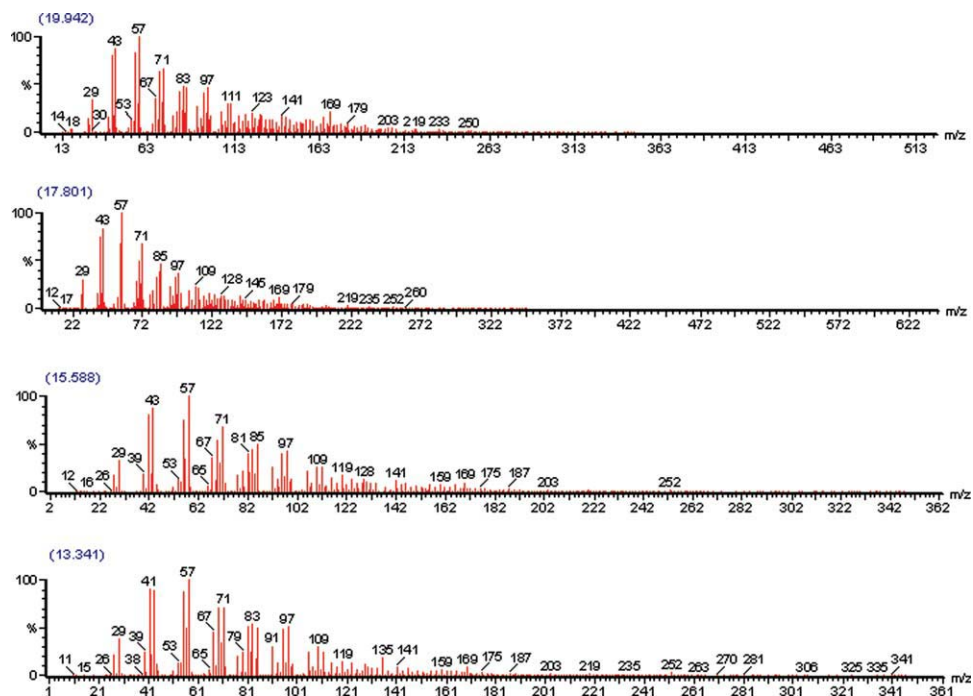


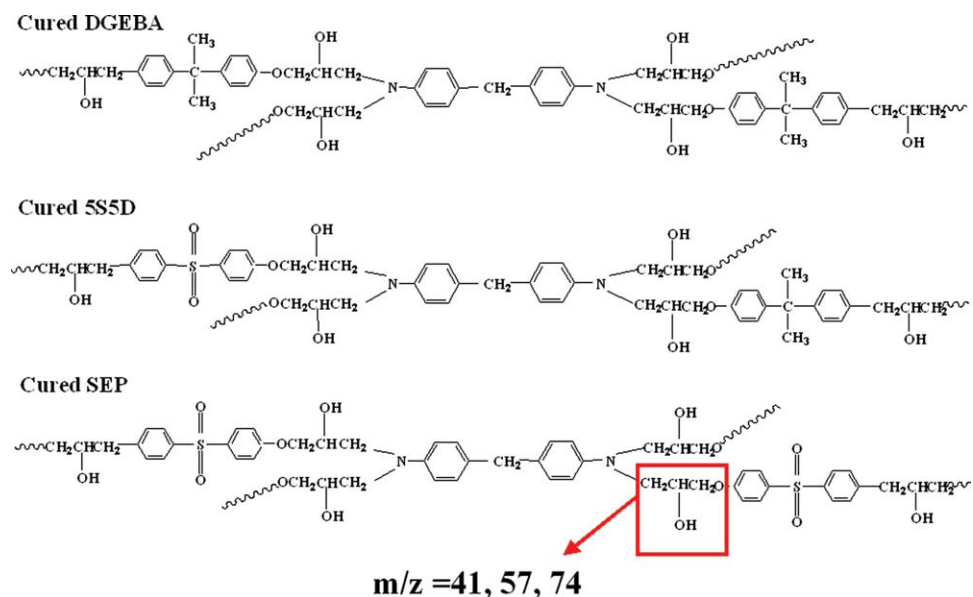
Figure 6 The chemical structure and molecular weight of various sulfate derivatives.



**Figure 7** The mass fragmentation spectra at 13.341 min, 15.588 min, 17.801 min, and 19.942 min under the nitrogen atmosphere. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

derivatives. Generally, the C—S bonding was easy to thermal decomposition than the C—C bonding, since the energy of the C—S bonding was lower than the C—C bonding.<sup>50</sup> Additionally, the degradation of the C—S bonding of the sulfonyl materials could further to form the SO<sub>2</sub> and some sulfate derivatives.<sup>51–53</sup> Samperi et al.<sup>54</sup> investigated the sulfonyl materials thermal decomposition oligomer products and found that various sulfate derivative chars' architectures by

the TGA/GC/Mass. In this study, the thermal degradation of the SEP/DGEBA blended materials was also investigated by the TGA/GC/Mass. The thermal degradation of the SEP/DGEBA blended materials could form the sulfate derivatives char yields, which char yields were like macromers (oligomers). Consequently, various sulfate derivatives char yields might be formed the short chemical fragments and showed as Figure 6. Then, the sulfate derivatives char yields



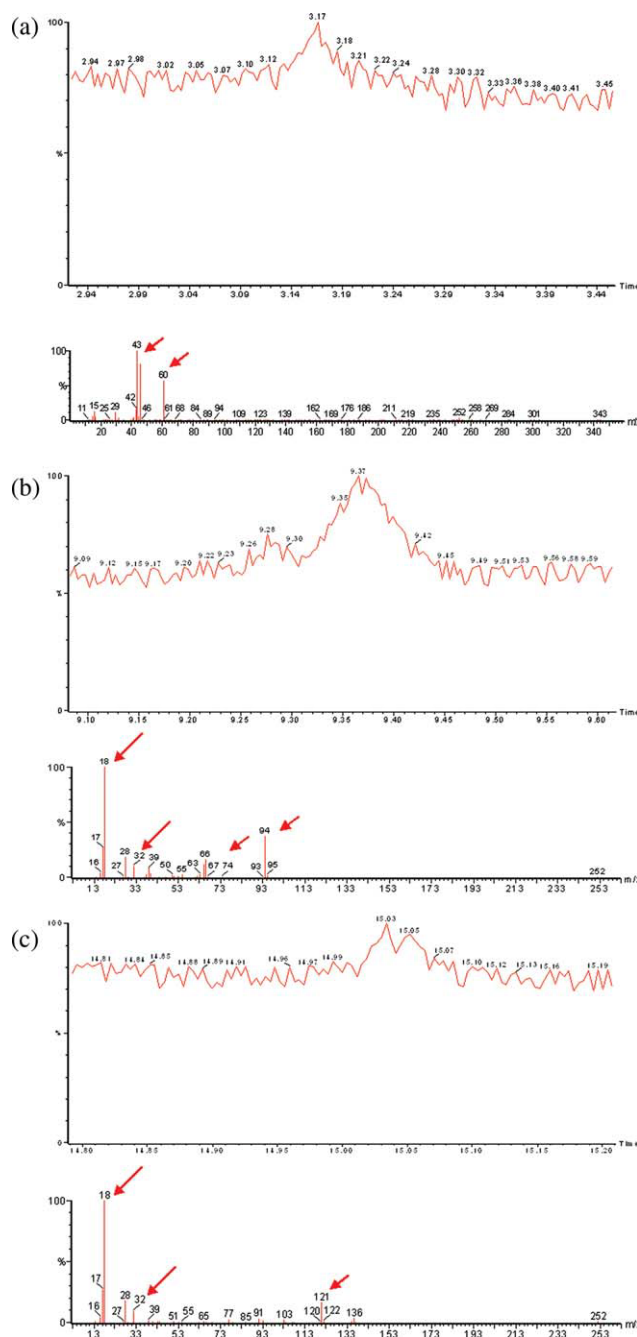
**Figure 8** The chemical structures of the alkyl derivatives occurred via thermal degradation. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



might decompose and further to form the mass characteristic fragments ( $m/z$ ) around 80, 92, 96, 104, and 120. Figure 5(a,h) identify various sulfate derivatives were formed upon initial thermal degradation and limited further to decompose. Figure 7 presents the mass fragmentation spectra at 13.341, 15.588, 17.801, and 19.942 min. Most of the mass fragmentations corresponded to the alkyl derivatives, these chemical structures are presented in Figure 8. Notably, the alkyl derivatives were generated after the sulfonyl groups decomposed. The thermal degradation of sulfonyl groups in cured SEP epoxy was favored over that of the alkyl groups, the sulfate derivatives thus formed markedly protected the cured epoxy from thermal degradation.

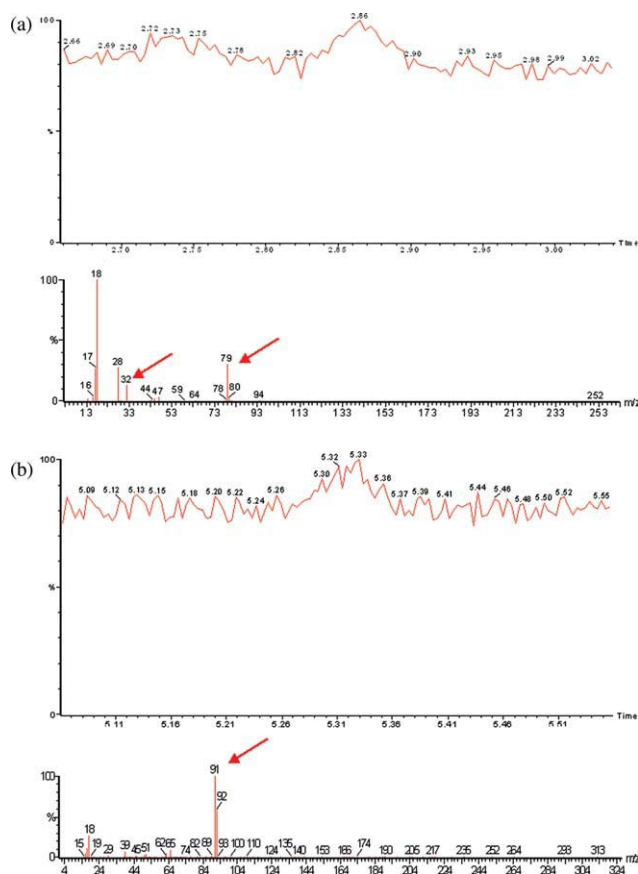
Figure 4 presents two-stage thermal degradation of the SEP/DGEBA blended materials in the air atmosphere. From Table III, the activation energies decreased with the SEP contents, since the oxygen not only promoted thermal degradation of the SEP/DGEBA blended materials but also easily destroyed the sulfonyl main-chain of the SEP. Figure 9(a,c) present the identified thermal volatiles and the mass fragmentation spectra during the first stage thermal degradation (at temperatures of 280–330°C) in the air atmosphere for 3.166, 9.367, and 15.030 min, respectively. The evolved gas and the analysis of the mass fragments demonstrated that various sulfate derivatives were formed. And the char was formed from various sulfate derivatives in this thermal degradation stage, and the alkyl groups of the cured epoxy main-chain were destroyed. Therefore, the activation energies of the first stage thermal degradation decreased sharply as the SEP contents increased.

For the activation energies of second stage thermal degradation, which tendency increased and then decreased as the SEP contents increased. Same as the thermal degradation under the nitrogen atmosphere, because the thermal stable sulfate derivatives char yields could provide the “shielding effect” to improve the thermal stability in the thermal oxidation stage (second thermal degradation stage) under the air atmosphere. However, the sulfonyl groups of the SEP is easy to thermal decompose and the energy of the S–C bonding is lower than the C–C bonding. Hence, the “shielding effect” of the sulfate derivatives char yields might not inhibit the thermal degradation of the numerous sulfonyl groups, additionally; the sulfate derivatives char yields possessed the S–C bonding. Consequently, the activation energies of second stage thermal degradation increased and then decreased with the SEP contents. However, the activation energies of the second stage of thermal degradation remained at 80 kJ/mol, since the sulfate-derived char could further to prevent thermal oxidation of the SEP/DGEBA blended materials, it may have the “shielding effect”<sup>47</sup> and antioxidation



**Figure 9** The thermal volatiles and the mass fragmentations of the first stage thermal degradation under the air atmosphere at (a) 3.166 min, (b) 9.367 min, and (c) 15.030 min. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

properties. The GC/Mass analysis of the thermal volatiles and the mass fragmentations spectra reveal that the second stage thermal degradation occurred at temperatures from 500 to 550°C at 2.861 and 5.334 min, as presented in Figure 10(a,b), respectively, which indicated that most of sulfate-derived char decomposed and provided protection in this thermal decomposition stage. The mass fragmentation in Figure 10(a,b) yielded the structure of the sulfate



**Figure 10** The thermal volatiles and mass fragmentations spectrum of the second stage thermal degradation under the air atmosphere at (a) 2.861 min and (b) 5.334 min. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

derivatives, presented in the right-hand of Figure 6 (low molecular weight sulfate derivatives). The thermally stable sulfate-derived char may limit the thermal degradation, and maintain the activation energy of the second stage thermal degradation.

## CONCLUSION

A thermal stable sulfone epoxy monomer (SEP) was synthesized and further to cure with various weight ratios of the DGEBA. The glass transition temperature ( $T_g$ ) of various SEP/DGEBA blended materials increased from 103.68 to 163.81°C. The polymer chain interaction was estimated by the Gordon-Taylor and the Kwei equations, the  $k$  and  $q$  value were obtained as 1.00664 and 0.00245, respectively. These results indicated that the most of polymer chain interaction was the intra-molecular action and the polymer chain intra-molecular action more influence than the polymer chain intermolecular action. And the excess stabilization energy in the overall stabilization observed was only 0.00145% (14.5 ppm). This

phenomenon indicated that the polymer chain intermolecular action was very weak. From the TGA/GC/Mass investigation, the SEP degraded at low temperature and provided various thermal stable sulfate derivative chars, which could prevent the SEP/DGEBA blended materials from thermal oxidation and generate the “shielding effect” to inhibit the thermal degradation. Consequently, the first stage thermal degradation activation energies decreased with the SEP contents, and the second stage thermal degradation activation energies retained 80 kJ/mol under the air atmosphere.

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