

# Epoxy Toughening Using Low Viscosity Liquid Diglycidyl Ether of Ethoxylated Bisphenol-A

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**ABSTRACT:** Two new epoxy resins, diglycidyl ether of ethoxylated bisphenol-A (BPA) with two and six oxyethylene units (DGEBAEO-2 and DGEBAEO-6) were synthesized and characterized. DGEBAEO-6 was used to toughen the conventional epoxy resin diglycidyl ether of BPA (DGEBA). The blends of DGEBA with different amounts of DGEBAEO-6 were cured by 4,4'-diamino diphenylmethane (DDM), and their thermal and mechanical properties were examined. The DSC and DMA results presented that DGEBA/DGEBAEO-6 blends exhibited a homogenous phase, and the glass transition temperature of the blends was inversely proportional to the content of DGEBAEO-6. The impact strength of the cured blends was directly proportional to the content of DGEBAEO-6, and

reached five times higher than that of the neat DGEBA when 50 wt % DGEBAEO-6 was used; the same impact strength was achieved for DDM-cured DGEBAEO-2. The viscosities of the blends decreased with increasing the DGEBAEO-6 content, whereas the tensile and flexural strength and the thermal stabilities were not obviously affected. Scanning electron microscopic results confirmed that the plastic deformation inducing by the incorporated flexible oxyethylene units was responsible for the toughness improvement. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 1913–1921, 2012

**Key words:** toughening; epoxy resin; ethoxylated; impact strength

## INTRODUCTION

Owing to good comprehensive properties, such as high stiffness and mechanical strength, high chemical resistance and thermal stability, ease of processing, and high adhesive strength, epoxy resins are among the most widely applied thermosetting resins in various fields, including adhesives, coatings, electronic packaging, and composite matrix resins. However, due to high crosslink density, cured epoxy resins are intrinsically brittle with poor fatigue properties and damage tolerance.<sup>1</sup>

Many efforts have been devoted to increase the toughness of epoxy resins. The dominant strategy to date has been to add a second phase, such as rubbery elastomers,<sup>2–4</sup> rigid inorganic particles,<sup>5</sup> high-performance thermoplastic resins,<sup>6–8</sup> and hyperbranched polymers,<sup>9–11</sup> to produce a multiphase morphology or a semi-interpenetrating polymer network that is able to initiate a variety of toughening mechanisms. An important aspect in toughening needs to be considered is the variation of processability. Most of the above-mentioned toughening additives are high molecular weight polymers, and

they tend to be either solids or high-viscosity liquids, which cause large increases in the viscosity of the final formulation even with comparatively small amounts, and, thus, the processability is deteriorated. Increasing the toughness without compromising the desirable processing and product characteristics remains a leading challenge in the development of superior epoxy resins.

Besides adding toughening additives, modification of epoxy structure is also an effective method to improve toughness. The modification is usually achieved by two means, including chemical modification of epoxy resin from a rigid backbone structure to a more flexible backbone structure and decrease of the crosslink density of a cured epoxy resin.<sup>12,13</sup> For example, flexible siloxane segments are incorporated into diglycidyl ether of bisphenol-A (DGEBA) and greatly improve its impact strength;<sup>14</sup> Takao Iijima has synthesized some new aromatic epoxy resins, which are incorporated with oxyethylene units and finds that the new resins are more tough and show no decrease in strength and modulus compared to the unmodified resins;<sup>15,16</sup> Sue uses DGEBA coupled with bisphenol-A (BPA) as a chain extender to investigate the effect of crosslink density on the toughness and modulus.<sup>17,18</sup> In these studies, the modification of epoxy structure not only improves the toughness but also improves the processability of the epoxy resins.<sup>19,20</sup>

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In this study, DGEBA was modified by incorporating different amounts of oxyethylene units. Two BPA-type epoxy resins containing two and six oxyethylene units (DGEBAEO-2 and DGEBAEO-6) were synthesized through the reaction between ethoxylated BPA and epichlorohydrin. The effect of the incorporated oxyethylene unit amounts on the viscosity, thermal, and mechanical properties of epoxy resins was examined. Moreover, due to the elastomer characteristic of cured DGEBAEO-6, it was used as a toughening additive blending with DGEBA to investigate the toughening effect; the compatibility, impact strength, and fracture morphology of the blends were systematically studied.

## EXPERIMENTAL

### Materials

Epichlorohydrin, sodium hydroxide, toluene, and 4,4'-diamino diphenylmethane (DDM) were supplied by the Beijing Chemical Reagents, China, and used as received; BPA-type glycol with two oxyethylene units (BAEO-2) and with six oxyethylene units (BAEO-6) were purchased from the GPRO Jiangsu Zhongshan Chemical, China; DGEBA epoxy resin with an epoxy value of 0.51 (molecular weight: 390420) was supplied by WUXI DIAISH Epoxy, China.

### Synthesis of DGEBAEO-2 and DGEBAEO-6

BAEO-2 (97.2 g, 0.3 mol) and epichlorohydrin (277.6 g, 3 mol) were added to a 500 mL three-necked flask equipped with a mechanical stirrer, a thermometer, a water condenser, and a nitrogen inlet. The flask was heated to 70°C to completely dissolve BAEO-2, and solid sodium hydroxide (24 g, 0.6 mol) was added. The reaction mixture was stirred for 4 h and then an extra 6 g sodium hydroxide was added. After stirring for 6 h, the temperature was increased to 85°C and held for 1.5 h. After the reaction completed, 300 mL toluene was added, and the solution was washed with deionized water several times to the neutral pH. The organic phase was separated; toluene and excess epichlorohydrin were distilled off under reduced pressure to give the product DGEBAEO-2, a pale yellow liquid, in 80% yield. DGEBAEO-6, a light yellow liquid, was synthesized by the same procedure in 88% yield.

### Curing procedure and measurement

The neat epoxy resins and the blends according to the compositions in Table I were compounded stoichiometrically with the curing agent 4,4'-diaminodiphenylmethane (DDM): one epoxy group corre-

**TABLE I**  
Viscosities of the DGEBAEO Epoxy Resins and the DGEBA/DGEBAEO-6 Blends

Samples	Resin composition	Viscosity <sup>1</sup> (cp)
–	Neat DGEBA	11,000
–	Neat DGEBAEO-2	2500
–	Neat DGEBAEO-6	950
EB-1	7.5 wt % DGEBAEO-6 + 92.5 wt % DGEBA	9910
EB-2	15 wt % DGEBAEO-6 + 85 wt % DGEBA	7400
EB-3	30 wt % DGEBAEO-6 + 70 wt % DGEBA	4410
EB-4	50 wt % DGEBAEO-6 + 50 wt % DGEBA	2670

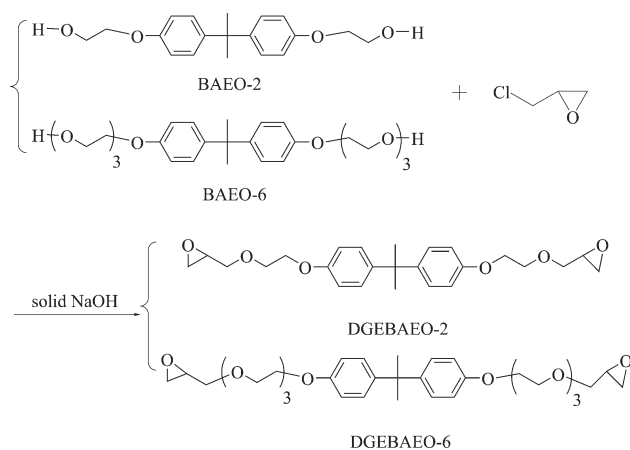
<sup>1</sup> Measured at 25°C.

sponded to one hydrogen atom of amino groups. The mixtures were heated to 100°C and stirred for 5 min to ensure complete dissolution of the cure agent, followed by degassing under reduced pressure until no bubbles arose. Then, the mixtures were poured into the Teflon molds and cured at 100°C for 3 h, followed by 3 h at 180°C.

The <sup>1</sup>H-NMR was carried out on a BRUKER AVANCE 400 MHz NMR spectrometer; the samples were dissolved in deuterated chloroform; and tetramethylsilane was used as internal reference. The bulk viscosities of epoxy resins were measured on a Brookfield model DV-II+cone and plate viscometer (Brookfield, Massachusetts, US). The Fourier transform infrared (FTIR) measurement was conducted on a BRUKER TENSOR-27 FTIR spectrometer at room temperature (25°C) in the range of 4000–400 cm<sup>-1</sup>. The gel fraction of the cured samples was determined by Soxhlet extraction using acetone as solvent for 24 h. The insoluble materials were drying at 120°C under vacuum for 24 h and weighted to determine the gel fraction.

Thermogravimetric analyses (TGA) were run on a Seiko TGA/DTA6300 thermal analyzer at a heating rate of 10°C min<sup>-1</sup> in nitrogen; the same instrument equipped with a DSC6220 differential scanning calorimeter module was used to obtain DSC curves. To characterize the curing process, the epoxy blends were heated at a rate of 10°C min<sup>-1</sup> in nitrogen. In measuring the glass transition temperatures of the cured epoxy resins, the samples were scanned twice at a heating rate of 15°C min<sup>-1</sup>; the first scan served to eliminate the thermal history. The dynamic mechanical tests were carried out on a TA Q800 in the double-cantilever mode under nitrogen atmosphere, at a frequency of 1.0 Hz and with a heating rate of 5°C min<sup>-1</sup>, and the sample dimensions were 60 × 15 × 2 mm<sup>3</sup>.

No-notch impact strength of the cured epoxy samples was determined at room temperature by a JC-



**Figure 1** Synthetic schemes of DGEBAEO-2 and DGEBAEO-6.

25 impact tester (Chengde, China) according to China National Standard GB1043-79; the sample size was  $80 \times 10 \times 4 \text{ mm}^3$ . The impact strength  $\sigma_i$  is calculated by the equation:  $\sigma_i = W/(b \cdot d)$ , where  $W$ ,  $b$  and  $d$  are the impact energy, width, and thickness of the sample, respectively. At least five specimens for each sample were tested, and the data were averaged. The measurements of the mechanical properties were performed with an Instron model 3365 universal tester (Instron, Canton, MA) at room temperature. The tensile properties were tested according to China National Standard GB/T1040-90: the strain rate was  $2 \text{ mm min}^{-1}$ , and the sample was double-shovel shaped with total length of 75 mm. The flexural properties were determined according to China National Standard GB/T9341-88 in a three-point bending mode by using samples of dimensions  $80 \times 10 \times 4 \text{ mm}^3$ , the span was 48 mm, and the strain rate was  $1 \text{ mm min}^{-1}$ . The morphology of the impact-fractured surfaces was observed by a scanning electron microscope (SEM: JSM-6700F) at an activation voltage of 5 kV. The fracture surfaces were coated with thin layers of gold of about 100 Å.

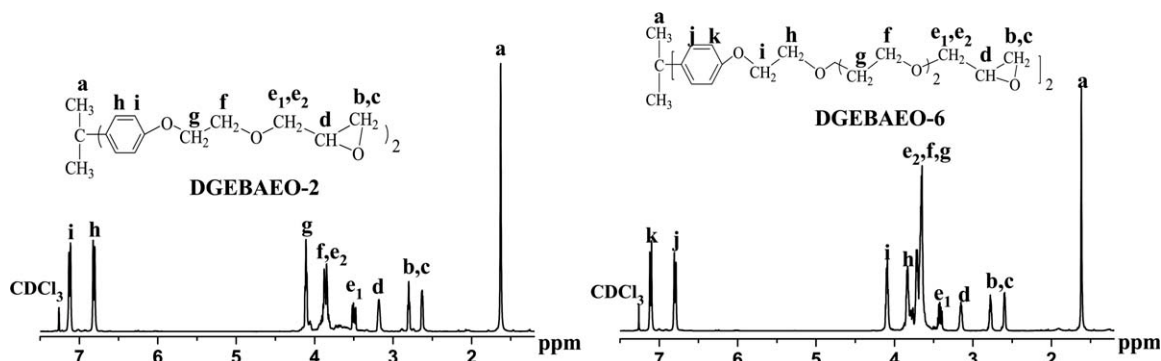
## RESULTS AND DISCUSSION

### Synthesis and characterization of the DGEBAEO epoxy resins

The synthetic schemes of DGEBAEO-2 and DGEBAEO-6 epoxy resins are shown in Figure 1. It is known that a one-step epoxidation of aliphatic alcohols by epichlorohydrin is more difficult than that of phenols, and, thus, in the former literatures,<sup>15,21</sup> a phase-transfer catalyst (such as tetrabutylammonium hydrogensulfate) was used in the synthesis of epoxy resins derived from polyols. However, for the preparation of DGEBAEO-6, the organic phase was difficult to separate from the reaction mixture due to emulsion formation in the presence of the phase-transfer catalyst, which inevitably caused a poor reaction yield and a high content of catalyst residue in the final resins. Therefore, the phase-transfer catalyst was not applied in the synthesis.

Here, we used solid NaOH as the catalyst instead of aqueous NaOH, as we found that the conversion of alcohol to glycidyl ether exceeded 90% when solid NaOH was used but did not reach 50% with 30% aqueous NaOH. The  $^1\text{H-NMR}$  spectra of DGEBAEO-2 and DGEBAEO-6 with peak assignments are given in Figure 2. The epoxy values of DGEBAEO-2 and DGEBAEO-6, calculated from the  $^1\text{H-NMR}$  spectra, were 0.41 and 0.32, respectively, which were close to the theoretical values (0.44 for DGEBAEO-2 and 0.33 for DGEBAEO-6).

The viscosities of the DGEBAEO epoxy resins and the DGEBA/DGEBAEO-6 blends are listed in Table I. Clearly, the introduction of oxyethylene units into the DGEBA epoxy resin decreased its viscosity effectively, and more oxyethylene units incorporated, greater the viscosity decreased. The decrease in viscosity, when oxyethylene groups were introduced into the DGEBA epoxy resin, might be mainly due to the decrease in hydrogen bonds, which was caused by secondary hydroxyl groups. As described above, maintaining the processability while improving the fracture toughness of epoxy resin is



**Figure 2**  $^1\text{H-NMR}$  spectra of DGEBAEO-2 and DGEBAEO-6.

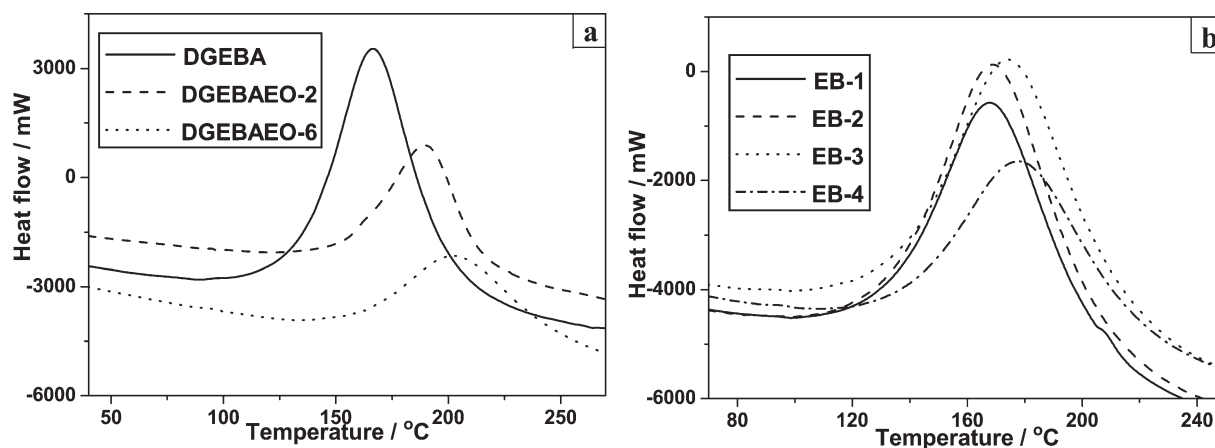


Figure 3 DSC curves for (a) three neat epoxy resins and (b) DGEBA/DGEBAEO-6 blends cured by DDM.

desirable; hence, lowering the viscosity of the blends was an advantage of DGEBAEO epoxy resins as toughening modifiers.

#### Curing of the DGEBAEO epoxy resins and DGEBA/DGEBAEO-6 blends

The curing process was monitored by DSC scans. Figure 3(a,b) shows the curing behaviors of DGEBA, DGEBAEO-2, and DGEBAEO-6 epoxy resins, and the DGEBA/DGEBAEO-6 blends, respectively; the DSC results are summarized in Table II. There arose evident changes to the curing behavior as oxyethylene units were introduced. First, the curing reactivity, reflected by the high-temperature-moving of curing peak temperature ( $T_p$ ), decreased as the oxyethylene units increasing. It was reasonable because the electron-withdrawing effect of benzene groups on the epoxy groups was attenuated, as the oxyethylene units were inserted as a spacer between them; when the length of oxyethylene groups increased (from 1 to 3), the effect was attenuated greater. Second, due to the decrease in epoxy value, the curing exothermic enthalpy also decreased with

increasing the oxyethylene units. The same trends were observed for DGEBA/DGEBAEO-6 blends as shown in Figure 3(b).

It is well known that the properties of epoxy system are strongly dependent on the extent of cure, which in turn is dependent on the curing conditions used. The maximum properties are obtained for epoxy resin with a fully crosslinked network; undercuring leads to reduction in thermal and mechanical properties. Therefore, it is necessary to make sure that the curing reaction reached completion. In this study, FTIR studies and gel fraction measurements were conducted to check the degree of curing reaction. The IR spectra of the epoxy resins before and after curing are given in Figure 4. The gel fraction of the cured sample was calculated through eq. (1):

$$\alpha = (W_1/W_0) \times 100\% \quad (1)$$

where  $\alpha$  is the gel fraction,  $W_0$  and  $W_1$  are the weights of samples before extraction and after vacuum drying. The results are listed in Table III.

The absence of the characteristic epoxy peak at  $915\text{ cm}^{-1}$  in the IR spectra and the approximate

TABLE II  
DSC and DMA Results for the DGEBA/DGEBAEO-6 Blends and DGEBAEO-2 Cured by DDM

Samples	DSC			DMA		
	$T_p^1$ (°C)	$\Delta H$ (mJ mg <sup>-1</sup> )	$T_g$ (°C)	$E''^2$ (GPa)	$E''^3$ (MPa)	$T_g^4$ (°C)
DGEBA	166.4	406	159.2	2.02	1.10	157.6
DGEBAEO-2	189.5	250	84.3	1.94	0.20	89.6
DGEBAEO-6	201.7	211	31.2	—	—	—
EB-1	167.8	363	150.5	2.21	0.67	151.4
EB-2	168.7	349	140.9	2.01	0.64	141.0
EB-3	174.1	347	117.4	2.30	0.36	121.1
EB-4	177.8	268	92.9	2.24	0.21	100.5

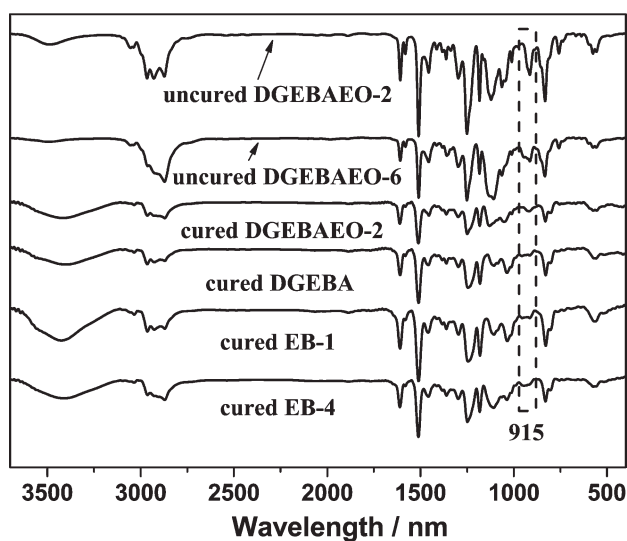
<sup>1</sup> Curing peak temperature.

<sup>2</sup> Storage modulus at 50°C.

<sup>3</sup> Loss modulus at  $T_g + 50^\circ\text{C}$ .

<sup>4</sup> Peak temperature of the  $\alpha$  transition.





**Figure 4** FTIR spectra of the epoxy resins before and after curing by DDM.

100% gel fraction for the cured samples both revealed that complete curing was achieved with the cure conditions used in this work.

It was also noted that, in the IR spectra, the intensity of the peak at about  $3400\text{ cm}^{-1}$  (assigned to hydroxyl groups) increased after cured with DDM. The change was attributed to the generation of secondary hydroxyl groups by the ring-opening reaction of epoxy groups. Because, the amount of hydroxyl groups of the cured epoxy resins is directly proportional to the epoxy value of the uncured resins, the intensity of hydroxyl group peaks is in the order of  $\text{DGEBA} \geq \text{EB-1} > \text{DGEBAEO-2} \geq \text{EB-4}$ , which is in accordance with that of their epoxy values.

### Mechanical properties

The impact strength of the cured compositions is shown in Figure 5, and the tensile and flexural properties are listed in Table IV. As can be seen, the impact strength of the DGEBA/DGEBAEO-6 blends increased linearly with the DGEBAEO-6 content, which meant that the toughness of DGEBA was significantly improved by the addition of DGEBAEO-6. It should be noticed that EB-4 exhibited impact strength very close to that of DGEBAEO-2. Consider-

ing that the two samples had almost the same content of oxyethylene units, it can be further concluded that the impact strength was indeed direct proportional to the oxyethylene content of the cured resins, which played as a flexible part in the system and improved the chain segment mobility.

The tensile and flexural properties of a cured epoxy system depend on the rigidity of polymer chains and the crosslink density, and in general, flexible additives will lead to a decrease of the mechanical properties of epoxy resins.<sup>22,23</sup> However, it was surprising to find that, compared to neat DGEBA, almost all the DGEBA/DGEBAEO-6 blends showed no decrease in either strength or modulus in the tensile and flexural tests. It was proposed that although an increase of DGEBAEO-6 content resulted in decrease of rigidity and crosslink density of the epoxy network, there were still enough crosslink sites and rigid aromatic rings, which worked as anchors, to limit the deformation of the flexible part and maintain the strength and modulus. The only exception was EB-4, it showed a slightly decrease of flexural strength and modulus compared to neat DGEBA, which was probably caused by plasticization because of too much introduction of flexible oxyethylene units.

### Thermal properties of the cured DGEBAEO epoxy resins

Figure 6(a) shows the glass transition of the cured DGEBAEO, DGEBA epoxy resins which is measured by DSC. It was found that when oxyethylene units were introduced, the glass transition temperature decreased linearly.  $T_g$  reflects the mobility of the chain segments, which is related to the crosslink density and chain rigidity for the thermosetting resins. The introduction of oxyethylene groups decreased both the epoxy value and the relative content of aromatic ring. The decrease in epoxy value resulted in decrease in crosslink density; decrease in relative content of aromatic ring resulted in decrease in chain rigidity. This indicated that the decrease in  $T_g$  was due to the decrease in both the crosslink density and the relative content of aromatic ring. As can be seen in Table II, for the DGEBA/DGEBAEO-6 blends, their  $T_g$  decreased linearly along with the

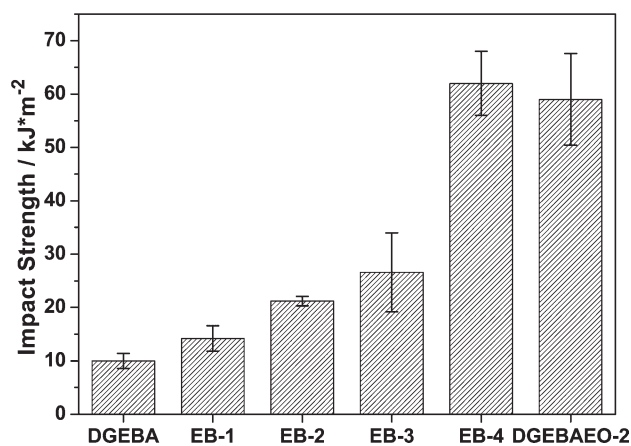
**TABLE III**  
Thermal Stability and Gel Fraction Data of the Neat Epoxy Resins Cured by DDM

Cured resins	$W_0$ (g)	$W_1$ (g)	$\alpha$ (%)	$T_{5\%}^1$ ( $^{\circ}\text{C}$ )	Char <sup>2</sup> (%)	$T_d^3$ ( $^{\circ}\text{C}$ )
DGEBA	1.113	1.119	100.65	371.9	17.7	375.8
DGEBAEO-2	1.037	1.040	100.29	374.5	13.7	379.2
DGEBAEO-6	1.197	1.186	99.08	378.6	8.4	390.7

<sup>1</sup> Temperature of 5% weight loss.

<sup>2</sup> Residue char at  $600^{\circ}\text{C}$ .

<sup>3</sup> Decomposition temperature.



**Figure 5** Impact strength of the DDM-cured DGEBA/DGEBAEO-6 blends.

ratio of DGEBAEO-6 blends. Ideal toughening should not deteriorate the good thermal property of epoxy polymer. An evident decrease in  $T_g$  is the main drawback of toughening with DGEBAEO-6 epoxy resin.

Figure 7 shows the TGA scans of DDM-cured DGEBAEO and DGEBA epoxy resins, and the results are summarized in Table III. The residual char decreased in the order of DGEBA > DGEBAEO-2 > DGEBAEO-6, mainly because the relative reduction in aromatic rings with the introduction of oxyethylene units. However, it was interesting to find that  $T_d$  and  $T_{5\%}$  increased, rather than decreased, with the content of oxyethylene units. This phenomenon seems unreasonable, because these temperatures should decrease with decreasing crosslink density and aromatic rings content. It is proposed that the higher  $T_d$  and  $T_{5\%}$  of DGEBAEO epoxy resins might be attributed to that the residual stress, which accelerated the thermal degradation of the cured epoxy resins, decreased with increasing oxyethylene units. Lower residual stress of DGEBAEO epoxy resins was caused by lower modulus and  $T_g$  of the resins.<sup>24,25</sup>

#### Miscibility and phase analysis of the DGEBA/DGEBAEO-6 blends

All the DGEBA/DGEBAEO-6 blends were transparent either before or after curing, which indicated

that DGEBAEO-6 was macroscopic compatible with DGEBA epoxy resin. Figure 6(b) shows the glass transition of the cured DGEBA/DGEBAEO-6 blends, the cured blends gave a single composition-dependent glass transition temperature between the  $T_g$  of the components, confirming the compatibility of all compositions.

The glass transition temperatures of the DGEBA/DGEBAEO-6 blends were theoretically studied by the Gordon–Taylor equation,<sup>26</sup> as given below:

$$T_g = (\omega_1 T_{g1} + k\omega_2 T_{g2}) / (\omega_1 + \omega_2) \quad (2)$$

where  $T_{g1}$  and  $T_{g2}$  are the glass transition temperatures of DGEBA and DGEBAEO-6, respectively,  $\omega_1$  and  $\omega_2$  are the corresponding weight fractions, and  $k$  is the interaction parameter, which is semiquantitatively related to the strength of the interaction between the two compositions.<sup>27,28</sup> If eq. (2) is rewritten as follows:

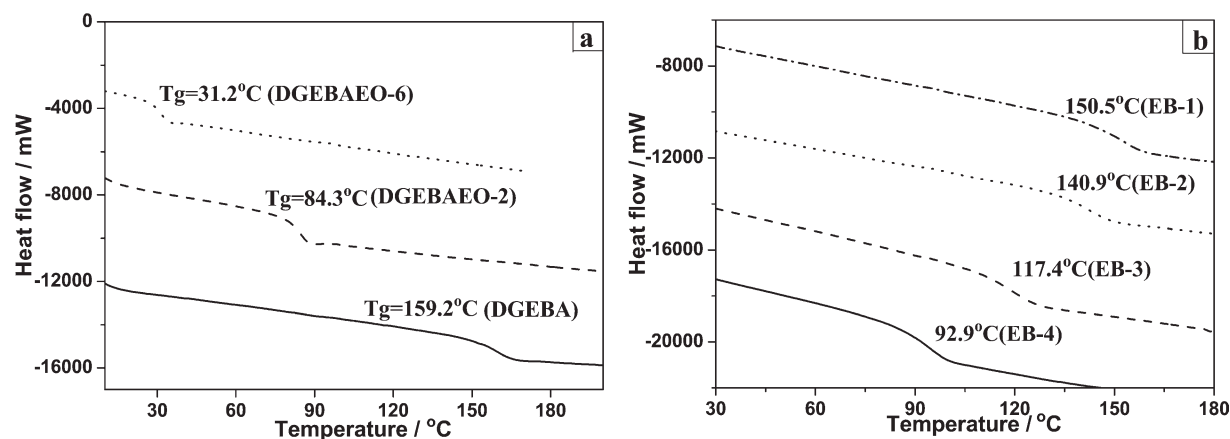
$$T_g = T_{g1} + k\omega_2(T_{g2} - T_{g1})/\omega_1 \quad (3)$$

and if  $T_g$  was plotted as a function of  $k\omega_2(T_{g2} - T_{g1})/\omega_1$ , a straight line was obtained for the DGEBA/DGEBAEO-6 blends and its slope  $k$  equaled 1.0 (Fig. 8). The high value of  $k$  indicated a strong interaction between DGEBAEO-6 and DGEBA epoxy resins. This strong interaction was undoubtedly due to the same BPA backbone structure and epoxy groups.

Dynamic mechanical analysis, which is usually more sensitive than DSC to the polymer blend morphology,<sup>29</sup> is used to further study the miscibility of the DGEBA/DGEBAEO-6 blends. As is shown in Figure 9, in the scan temperature range (from room temperature to 200°C), all the samples exhibited a single  $\tan \delta$  peak, which suggested a compatible state of the blends. However, some slight change can be observed through the comparison of the  $\tan \delta$  curves. It had been reported that the full width at half maximum of  $\alpha$  relaxation peak was sensitive to the homogeneity of the networks.<sup>30</sup> In this case, as the content of DGEBAEO-6 increased, the  $\tan \delta$  peak became broader and covered a wider temperature range, which indicated a more nonuniform distribution of chain lengths between crosslinks, due to the

**TABLE IV**  
Mechanical Properties of the DDM-Cured DGEBA/DGEBAEO-6 Blends and DGEBAEO-2

Samples	Tensile strength (MPa)	Tensile modulus (GPa)	Flexural strength (MPa)	Flexural modulus (GPa)
DGEBA	65.3 ± 5.4	1.77 ± 0.02	118.2 ± 5.9	2.77 ± 0.08
EB-1	82.0 ± 0.4	1.92 ± 0.03	122.6 ± 6.9	2.80 ± 0.06
EB-2	80.9 ± 3.6	1.98 ± 0.07	133.8 ± 2.6	3.02 ± 0.03
EB-3	78.7 ± 1.3	2.06 ± 0.06	132.5 ± 3.8	3.13 ± 0.05
EB-4	67.6 ± 0.8	1.99 ± 0.03	113.2 ± 2.1	2.71 ± 0.08
DGEBAEO-2	62.7 ± 4.6	1.85 ± 0.12	110.5 ± 1.7	2.86 ± 0.05



**Figure 6** Glass transition temperatures of the DDM-cured (a) three neat epoxy resins and (b) DGEBA/DGEBAEO-6 blends measured by DSC.

difference of epoxy values and curing rates between the two epoxy resins.

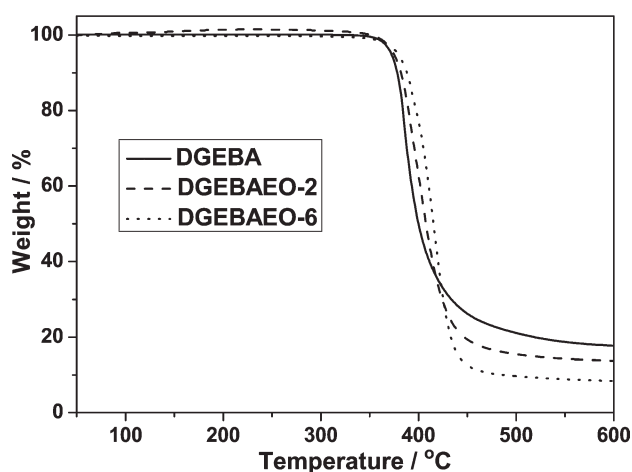
Rubber elasticity theory is a commonly used method to make qualitative comparisons of the crosslinking level of various polymers.<sup>31</sup> According to the simple rubber elasticity theory,<sup>32</sup> the loss modulus ( $E''$ ) at the temperature of  $T_g + 50^\circ\text{C}$  is inversely proportional to the molecular weight between crosslinks and directly proportional to the crosslink density. Because, the introduction of oxyethylene units extended the distance of the two epoxy groups in the resin molecule, there was an observed trend that  $E''$  (shown in Table III) decreased with increasing the amount of DGEBAEO-6, which meant the crosslink density of the cured blends decreased gradually with the DGEBAEO-6 contents.

The cured samples showed no obvious difference in storage modulus ( $E'$ ) as shown in Figure 10. In general, when flexible components are used to modify the epoxy resins and the crosslink density is

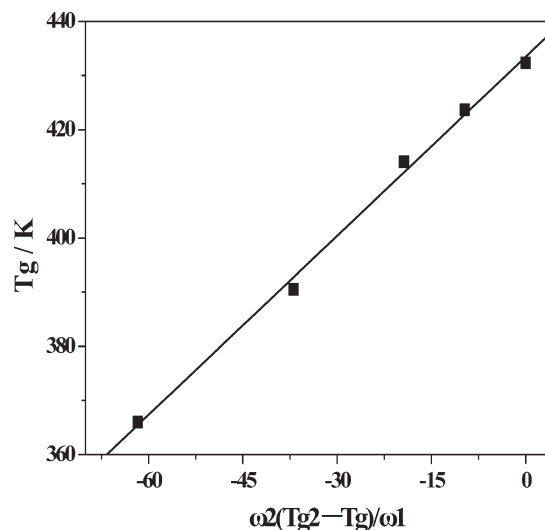
decreased, the storage modulus is usually sacrificed. In this case, however, the rigid units (BPA) of DGEBAEO played a significant role in maintaining high  $E'$  of the cured resins.

### Fracture Morphology

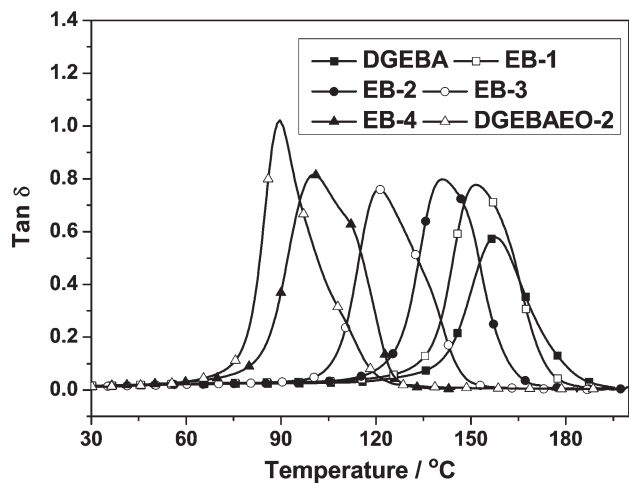
The toughening behaviors of the DGEBA/DGEBAEO-6 blends can be explained in terms of morphology observed by SEM. The SEM micrographs of the fracture surfaces of the cured blends with different contents of DGEBAEO-6 after impact tests are shown in Figure 11, with the neat epoxy resin for comparison. The fracture surface of the neat epoxy network [Fig. 11(a)] clearly revealed the typical characteristic of a brittle failure: a flat, smooth surface without any sign of deformation, and this accounted for its poor impact strength.



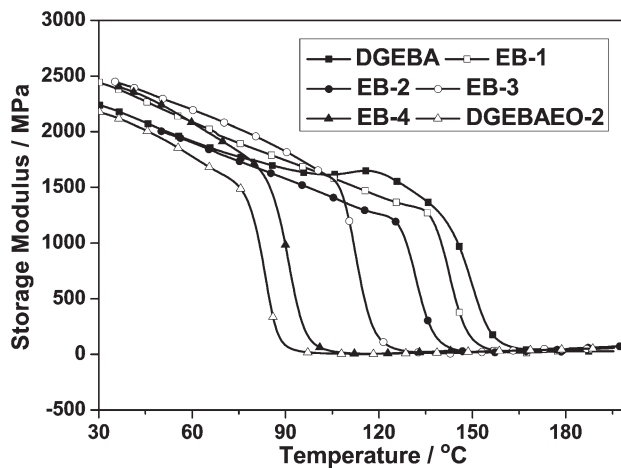
**Figure 7** TGA thermograms of three neat epoxy resins cured by DDM.



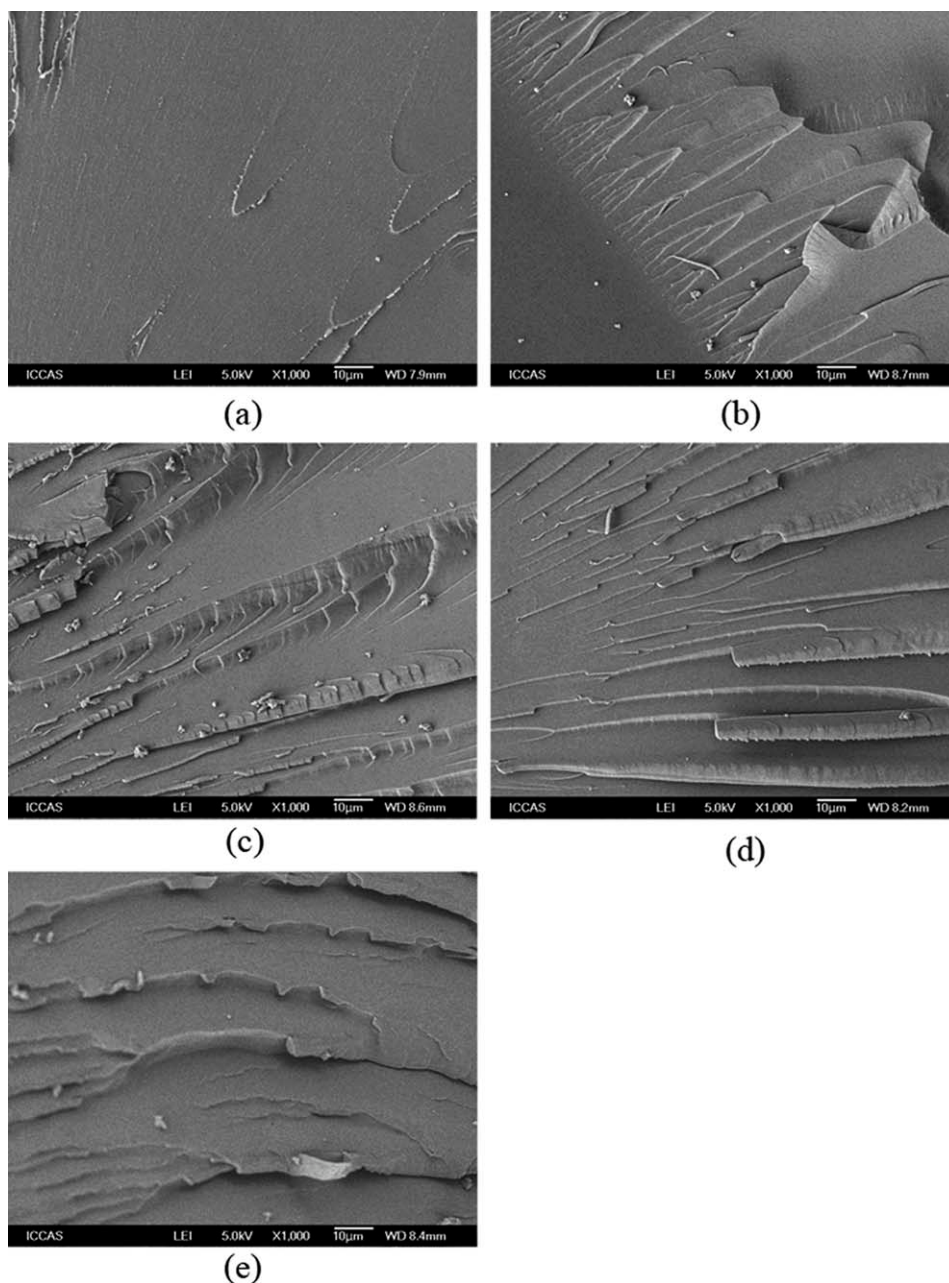
**Figure 8** Plot of the Gordon-Taylor equation for the DDM-cured DGEBA/DGEBAEO-6 blends.



**Figure 9** Loss factor ( $\tan \delta$ ) versus temperature for the DDM-cured DGEBA/DGEBAE0-6 blends and DGEBAEO-2 resin.



**Figure 10** Storage modulus ( $E'$ ) versus temperature for the DDM-cured DGEBA/DGEBAE0-6 blends and DGEBAEO-2 resin.



**Figure 11** SEM micrographs of the fracture surfaces of the DDM-cured DGEBA/DGEBAE0-6 blends under impact: (a) 1000 $\times$ , DGEBA; (b) 1000 $\times$ , EB-1; (c) 1000 $\times$ , EB-2; (d) 1000 $\times$ , EB-3; and (e) 1000 $\times$ , EB-4.



In the morphology of the fracture surfaces of the DGEBA/DGEBAEO-6 blends, neither particles nor cavities were observed, which meant there was no phase separation occurred in the blends. This observation was also consistent with the DSC and DMA analyses. Because of the small addition of DGEBAEO-6, EB-1 exhibited a relatively rougher crack surface compared to the neat DGEBA. The fracture surface of EB-2 became further rougher with some ridges, which acted as obstacles to cause the deflection of the crack; hence, the required energy for the propagation of the cracks on the fracture surfaces increased.<sup>33</sup> However, there was not obvious plastic deformation on the surface, indicating the brittle fracture characteristic of EB-2. For EB-3 and EB-4, ductile yielding (elongated or distorted layers) arose along the crack and large plastic deformation occurred, which meant the fracture behavior turned to ductile from brittle. The plastic deformation increased with increasing DGEBAEO-6 content. Because of plastic deformation dissipated much energy at failure, the impact strength was greatly improved.

### CONCLUSIONS

Two BPA-type epoxy resins with two and six oxyethylene units (DGEBAEO-2 and DGEBAEO-6) were synthesized and characterized, and DGEBAEO-6 was used as a toughening additive to improve the toughness of the conventional DGEBA epoxy resin. DGEBA/DGEBAEO-6 blends with different DGEBAEO-6 contents were cured with DDM, and their thermal and mechanical properties were examined. The DGEBA/DGEBAEO-6 blends exhibited a homogenous phase which was proved by the results of DSC and DMA measurements, and the glass transition temperature of the blends was inversely proportional to the content of DGEBAEO-6. The impact strength of the cured blends was directly proportional to the content of DGEBAEO-6, and reached five times higher than the neat DGEBA when 50 wt % DGEBAEO-6 was added; the same impact strength was achieved by curing DGEBAEO-2 with DDM. Meanwhile, the viscosities of the blends decreased with the addition of DGEBAEO-6, indicating an improved processability of the resins; the tensile, and flexural strengths and the thermal stabilities were not affected while toughening. SEM results confirmed that toughness improvement was achieved via the plastic deformation inducing by the incorporated flexible oxyethylene units. The DGEBAEO-toughened epoxy resins are expected to find many industrial applications, especially in situations where a very high  $T_g$  is not necessarily required.

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