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Preparation and mechanical properties of modified epoxy resins with flexible diamines

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Abstract

Diglycidyl ether of bisphenol A (DGEBA) is one of the most widely used epoxy resins for many industrial applications, including cryogenic engineering. In this paper, diethyl toluene diamine (DETD) cured DGEBA epoxy resin has been modified by two flexible diamines (D-230 and D-400). The cryogenic mechanical behaviors of the modified epoxy resins are studied in terms of the tensile properties and Charpy impact strength at cryogenic temperature (77 K) and compared to their corresponding properties at room temperature (RT). The results show that the addition of flexible diamines generally improves the elongation at break and impact strength at both RT and 77 K. The exception is the impact strength at 77 K filled with 21 wt% and 49 wt% D-400. Further, two interesting observations are made: (a) the cryogenic tensile strength increases with increasing the flexible diamine content; and (b) the RT tensile strength can only be improved by adding a proper content of flexible diamines. It is concluded that the addition of a selected amount namely 21–78 wt% of D-230 can simultaneously strengthen and toughen DGEBA epoxy resins at both RT and 77 K. However, only the addition of 21 wt% D-400 can simultaneously enhance the strength and ductility/impact strength of DGEBA epoxy resins at RT. The impact fracture surfaces are examined using scanning electron microscopy (SEM) to explain the impact strength results. Finally, differential scanning calorimetry (DSC) analysis shows that the glass transition temperature (T_g) decreases with increasing the flexible diamine content. The presence of a single T_g reveals that the flexible diamine-modified epoxy resins have a homogeneous phase structure.

Keywords: Epoxy resin; Flexible diamines; Cryogenic mechanical properties

1. Introduction

Epoxy resins are a most important class of thermosetting resins for many engineering applications because of their high strength and stiffness, good dielectric behavior, resistance to chemicals, corrosion and microbial organisms, low shrinkage during cure and good thermal characteristics [1–7]. With the rapid developments in spacecraft and superconducting cable technologies, and large cryogenic engineering projects such as the International Thermonuclear Experimental Reactor (ITER) etc., epoxy resins have been increasingly employed in cryogenic engineering technologies as impregnating materials, adhesives or matrices for fiber-reinforced composites [8–10]. In cryogenic engineering, liquid nitrogen or liquid helium is often employed as cooling media and hence the environment temperature is 77 K or 4.2 K, respectively. The cryogenic temperature in scientific research on cryogenic properties of materials refers more often to 77 K since liquid nitrogen (77 K) is much cheaper than liquid helium (4.2 K). Epoxy resins normally have poor crack resistance at room temperature [11,12] and are also highly brittle at cryogenic temperature [13], which makes them unsuitable for many cryogenic engineering applications. Thus, it is necessary to improve the toughness and ductility of epoxy resins so that they can be gainfully used in such cryogenic technologies.

Diglycidyl ether of bisphenol A (DGEBA) is one of the most widely used epoxy resins and it has found many cryogenic engineering applications [14]. Liquid aromatic amine (DETD) has low viscosity and low toxicity and is often used as a hardener

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for curing DGEBA. Therefore, DGEBA and DETD will be employed, respectively, as epoxy precursor and hardener in this study. Though DETD cured DGEBA system shows the high mechanical strength, it is brittle, particularly at cryogenic temperature. Hence, it is important to modify this epoxy system to broaden its acceptance for applications in cryogenic engineering.

The most common approach to toughen brittle epoxy resins is introduction of a toughening agent into the epoxy network. Toughening agents, such as epoxidized natural rubber [15], poly(sulfone) [16], polysiloxane [17], polyetherimide [18–20], poly(ether sulfone) [21–23], and poly(ether ether ketone) [24,25] etc., have been reported to improve the toughness of epoxy resins. Modification of the epoxy structure is also an effective method to improve crack toughness, including for example, chemical modification from a given rigid epoxy backbone to a more flexible backbone structure, increase of epoxy monomer molecular weight, decrease of crosslink density of a cured resin [26–28], etc. However, most past investigations were focused on the improvement of toughness at room temperature (RT), and very few studies at cryogenic temperature [29]. Moreover, among the above-mentioned toughening methods, rubber toughening might also lead to significant reduction in Young's modulus and tensile strength, which is undesirable for engineering applications at cryogenic temperature. Also, RT mechanical behaviors of materials are generally very different from those at cryogenic temperature so that their mechanical properties obtained at RT cannot simply be transferred to the cryogenic case.

Very low molecular weight polyether diamines such as D-230, D-400 and D-418 have been used as curing agents for DGEBA epoxy resins [30–33]. These include studies on cure kinetics by DSC [30], cure reactions by fluorescence and IR spectroscopic techniques [31], and by dynamic-mechanical behavior [32]. DGEBA resins cured with a mixture of two agents (mPDA and D-230) were also conducted [33]. Addition of a small amount of aliphatic amine increases the toughness but decreases the rigidity and the glass transition temperature. At a cryogenic temperature such as liquid hydrogen temperature (77 K), most chain segments of polymers are frozen and are brittle but the polyether chain segments are not completely frozen and rotational freedom is still permitted [34]. Hence, it is likely that polyether diamines can improve the cryogenic toughness of DGEBA epoxy resins. However, little work has been done to-date on the cryogenic mechanical properties of DETD cured DGEBA based epoxy resins modified by polyether diamines. This is the main purpose of the present paper.

Here, two flexible polyoxypropylene diamines (D-230 and D-400) are selected to modify DETD cured DGEBA epoxy resins due to their compatibility and ease of mixing. Also, flexible polyoxypropylene diamines can be simply incorporated into the epoxy cured network structure via normal cure reaction between amine and epoxy. The mechanical behaviors at RT and 77 K of the cured epoxy resins are studied in terms of the tensile properties and impact strength by taking into account the effects of the flexible diamine content. The glass transition temperature (T_g) as a function of the flexible diamine content is examined by DSC analysis.

2. Experimental work

2.1. Materials and preparation of samples

The epoxy resin CYD128 used in this study was a low molecular weight liquid diglycidyl ether of bisphenol A (DGEBA) with an epoxide equivalent weight of 184–194 purchased from YueYang Baling Petrochemical Technology Ltd. Diethyl toluene diamine (DETD) (ETHACURE-100), which existed as a mixture of the two DETD isomers (74–80% 2,4-isomer and 18–24% 2,6-isomer, amine equivalent weight = 44.3), was purchased from Albemarle Corporation, USA. The flexible diamines, namely polyoxypropylene diamines including Jeffamine D-230 (molecular weight (MW) = 230, amine equivalent weight = 57.5) and D-400 (MW = 400, amine equivalent weight = 100), were obtained from Huntsman Chemical Co. The chain length of D-400 is larger than that of D-230. The chemical structures of epoxy, DETD and polyoxypropylene diamines are shown in Fig. 1.

The hardener DETD was first mixed with flexible diamines homogeneously and the relative flexible diamine content in the mixed system varied from 0 to 100% in weight. The mixtures of two diamines served as the hardener. Then the equal equivalent amount of epoxy resin was added. Namely, the stoichiometric ratio of epoxy/amine, $[E]/\{[H]_{\mathrm{DETD}}+([H]_{\mathrm{D\text{-}230}}\text{ or }[H]_{\mathrm{D\text{-}400}})\}=1$, was used for this study, where $[E]=\mathrm{weight}_{\mathrm{CYD128}}/\text{epoxide equivalent weight}$, $[H]_{\mathrm{DETD}}=\mathrm{weight}_{\mathrm{DETD}}/\mathrm{amine}_{\mathrm{DETD}}\text{ equivalent weight}$, $[H]_{\mathrm{D\text{-}230}}=\mathrm{weight}_{\mathrm{D\text{-}230}}/\mathrm{amine}_{\mathrm{D\text{-}230}}\text{ equivalent weight}$ and $[H]_{\mathrm{D\text{-}400}}=\mathrm{weight}_{\mathrm{D\text{-}400}}/\mathrm{amine}_{\mathrm{D\text{-}400}}\text{ equivalent weight}$. Formulas employed in this study are listed in Table 1. The resultant materials were completely mixed by a mechanical stirrer and degassed with a vacuum pump to eliminate air bubbles. The bubble-free mixtures were then poured into the preheated steel mold in an oven. The inner geometry of the steel mold is following the recommendation of ASTM D638-96 for making tensile specimens. The dimensions of tensile specimens are 4 mm × 6 mm in the working section. The inner dimensions of the steel mold for making impact specimens are 4 mm × 10 mm × 80 mm. The modified epoxy resins were cured at 60 °C for 8 h, then 100 °C for 12 h at normal pressure, while the unmodified epoxy resin was cured at 80 °C for 8 h, then 130 °C for 12 h at normal pressure. It should be pointed out here that it was also tried to cure the unmodified epoxy system at 100 °C but it was unsuccessful. In the later discussion, it will be clarified that the effect of curing temperature difference can be ignored on mechanical properties. The samples were dried in an oven before mechanical testing.

2.2. Measurement and characterization

The tensile samples were prepared according to the recommendation of ASTM D638-96. The tensile properties were measured on a RGT-20A REGER mechanical tester under

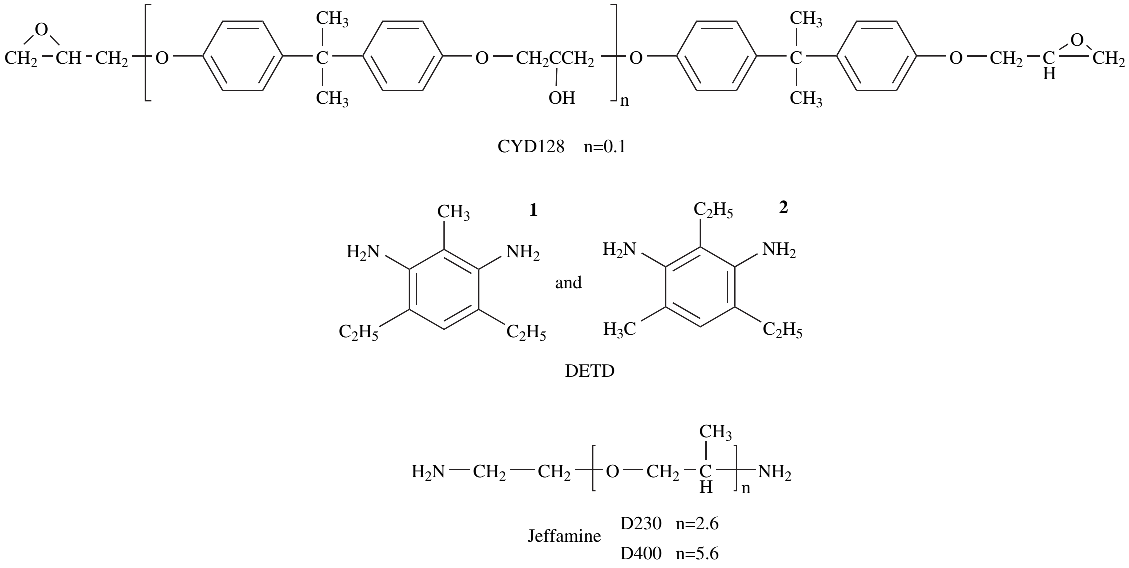

Fig. 1. Chemical structures of CYD128, ETHACURE-100, D-230 and D-400.

a 10 kN load cell with a crosshead speed of 5 mm/min at RT and a crosshead speed of 2 mm/min at 77 K. The cryogenic temperature condition was achieved by dipping the samples fixed on the clamps in a liquid nitrogen filled cryostat designed in our laboratory. Charpy impact strength of the samples was measured with a REGER Impact Tester according to ASTM D-256. Charpy impact testing was conducted at both room temperature and 77 K. Impact testing at 77 K was performed with the specimens dipped in a liquid nitrogen filled cryostat for over 10 min and was completed in seconds after taking the specimens out from the cryostat. At least five specimens were tested for each composition.

The fracture surfaces of the tensile samples were examined by scanning electron microscopy (SEM, Hitachi S-4300). Prior to examination, the fracture surfaces were cleaned with alcohol in order to eliminate impurities like dusts, if any [41]. This procedure does not produce any artifacts since alcohol does not etch the investigated materials (neat and toughened epoxy resins). The fracture surfaces were then coated with a thin evaporated layer of gold to improve conductivity.

The glass transition temperatures (T_g) of the samples were measured by differential scanning calorimeter (DSC) under nitrogen atmosphere, with a heating rate of 10 °C/min using a NETZSCH STA 409PC. The heating temperature ranges from 30 °C to 200 °C. A second scan was used to evaluate the final glass transition temperature of the cured materials. The peaks of T_g's on the curves of DSC after the first scan are too wide to hardly preciously define the position of T_g's. The peaks after the second scan became relatively narrow. It was thus convenient to define the position of T_g's after the second scan.

Table 1
Formulas of the unmodified and modified epoxy resins

Relative flexible diamine content (wt%)		CYD128 (g)	D-230 (g)	D-400 (g)	DETD (g)
D-230	0	442.6	0	0	100
	21	421.3	21	0	79
	49	392.8	49	0	51
	78	363.3	78	0	22
	100	341.0	100	0	0
D-400	0	442.6	0	0	100
	21	390.8	0	21	79
	49	321.8	0	49	51
	78	250.3	0	78	22
	100	196.0	0	100	0

3. Results and discussion

3.1. Tensile test

The stress–elongation curves of the unmodified and modified epoxy resins at both RT and 77 K are shown in Figs. 2 and 3. Clearly, the elongation at break of epoxy resins at both RT and 77 K increases with increasing the content of D-230 and D-400 flexible diamine. The epoxy resins exhibit ductile behaviors at room temperature for the cases of 78 wt% and 100 wt% D-230 and the case of 100 wt% D-400. However, the epoxy resins show brittle behaviors at cryogenic temperature for all compositions. In addition, two interesting phenomena have been observed: (a) the addition of a proper content of flexible diamines (21–78 wt% for D-230 and 21 wt% for D-400) leads to enhancement of the RT tensile strength; and (b) the tensile strength at 77 K increases with increasing the content of the flexible diamine. These two interesting observations will be explained later. The data for the tensile strength, Young's modulus and the elongation at break of the epoxy resins at RT and 77 K can be obtained from the tensile stress–elongation curves via Commercial REGER Testing Software. The results are summarized in Table 2.

In general, the addition of soft matters like rubber and polyurethane to epoxy resins results in reductions of the tensile strength at RT [35,36]. Nonetheless, it is interesting to observe

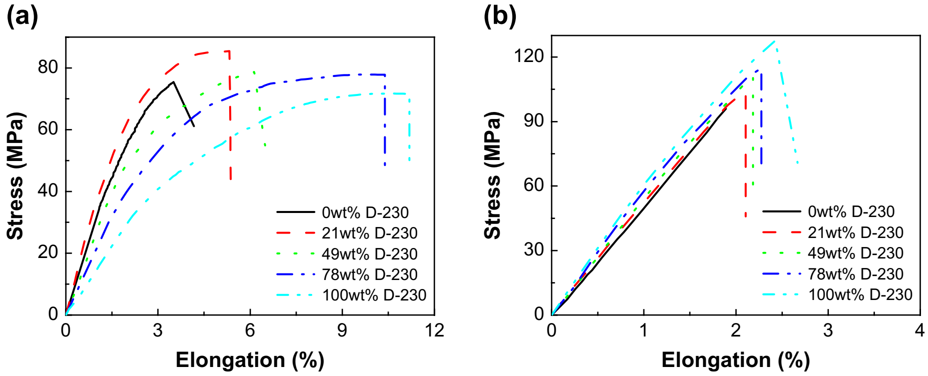

Fig. 2. Typical stress–elongation curves of unmodified and modified epoxy resins with different contents of D-230 at (a) RT and (b) 77 K.

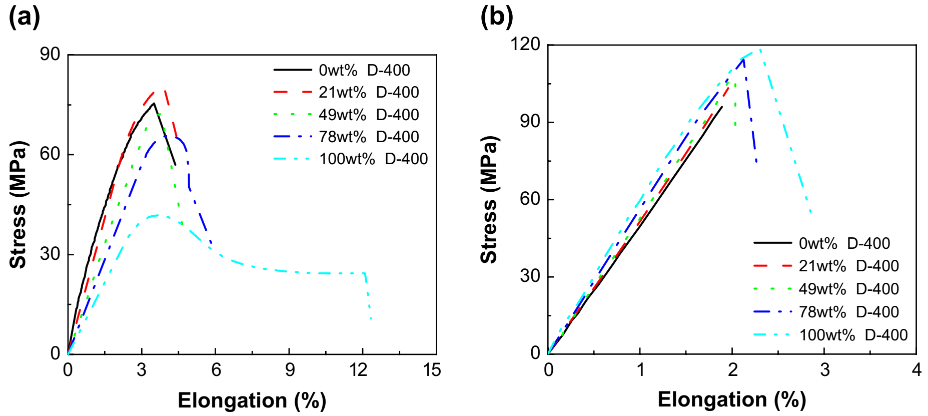

Fig. 3. Typical stress–elongation curves of unmodified and modified epoxy resins with different contents of D-400 at (a) RT and (b) 77 K.

that the RT tensile strength is improved by adding suitable amounts of flexible diamines (at 21 wt%, 49 wt% and 78 wt% of D-230 and at 21 wt% of D-400). Similar observations were reported elsewhere [37,38]. It is well known that the internal stress in epoxy resins cured at high temperature is produced by bulk shrinkage occurring during the cooling process from the curing temperature to RT [37–39]. The internal stress within the bulk material can greatly affect the performance of the finished product by creating micro-cracks and voids. Conversely, the introduction of soft segments into brittle epoxy resins can dramatically reduce the internal stress [37,38]. Thus, the increase in the strength by including suitable amounts of flexible diamines could be attributed to the reduction of internal stress in the samples by the introduction of soft segment into the brittle epoxy network.

It should be noted that the unmodified and modified epoxy systems were cured at 130 °C and 100 °C, respectively. The difference in the curing temperature is due to the different reactivity between aromatic and aliphatic amines. When the effect of thermal history is considered, it will be shown that the

Table 2
Tensile properties at RT and 77 K of the unmodified and modified epoxy resins with various relative D-230 and D-400 contents in the curing system[a]

Relative flexible diamine content (wt%)		Tensile strength (MPa)		Young's modulus (GPa)		Elongation at break (%)	
		RT	77 K	RT	77 K	RT	77 K
D-230	0	73.16 ± 3.16	103.55 ± 9.32	2.85 ± 0.03	5.00 ± 0.07	4.37 ± 0.69	1.84 ± 0.02
	21	85.44 ± 2.76	106.44 ± 9.10	3.22 ± 0.21	5.06 ± 0.12	5.37 ± 0.51	2.09 ± 0.01
	49	78.70 ± 1.90	107.6 ± 5.44	2.80 ± 0.17	5.11 ± 0.18	5.94 ± 0.55	2.18 ± 0.05
	78	77.91 ± 0.46	114.8 ± 5.42	2.0 ± 0.33	5.16 ± 0.03	10.13 ± 0.59	2.27 ± 0.11
	100	71.73 ± 0.71	127.6 ± 9.79	1.59 ± 0.07	6.23 ± 0.31	10.93 ± 0.59	2.66 ± 0.08
D-400	0	73.16 ± 3.16	103.55 ± 9.32	2.85 ± 0.03	5.00 ± 0.07	4.37 ± 0.69	1.84 ± 0.03
	21	80.97 ± 2.41	106.37 ± 3.87	2.73 ± 0.07	5.08 ± 0.09	4.51 ± 0.15	1.96 ± 0.02
	49	72.34 ± 6.05	108.02 ± 9.92	2.28 ± 0.25	5.23 ± 0.03	4.69 ± 0.17	2.03 ± 0.04
	78	65.76 ± 5.09	114.44 ± 7.21	1.82 ± 0.06	5.81 ± 0.06	5.96 ± 1.18	2.30 ± 0.04
	100	41.77 ± 5.2	115.16 ± 10.67	1.32 ± 0.10	6.00 ± 0.14	12.13 ± 1.9	2.84 ± 0.06

[a] Note: Data are expressed as average value + standard error.

result for the tensile response of the modified systems can still be interpreted in terms of the internal stress. If the modified epoxy resins were cured at 130 °C instead of 100 °C, the internal stress would be reduced more to some extent according to Ref. [39] reporting that internal stress in epoxy resins was almost absent in the curing period when curing temperature was much higher than glass transition temperature T_g and indeed, 130 °C is higher than T_g for the modified epoxy systems (shown in Table 4). Quantitative discussions on the effect of internal stress are given below on the tensile response.

The internal stress in the final epoxy samples can be divided into two parts based on the mechanisms causing the stress [39]. One is the shrinkage internal stress σ_1 produced by bulk shrinkage during curing period; another is the thermal stress σ_2 due to the difference of thermal expansion coefficient between the epoxy resin and the steel mold. The shrinkage internal stress σ_1 is given by [39]

$$\sigma_1 = K_1 E \Upsilon \qquad (1)$$

where K_1 is a constant, E the elastic modulus of the cured resin, and Υ the bulk shrinkage fraction of the cured resin during the curing period. The internal stress σ_2 can be obtained from [39]

$$\sigma_2 = K_2 \int_{T_1}^{T_2} E(\beta_1 - \beta_2)\mathrm{d}T \qquad (2)$$

where K_2 is a constant, β_1 and β_2 are the linear expansion coefficients of the epoxy and steel mold, respectively.

When the curing temperature is higher than T_g, the bulk shrinkage of the cured resins can be released by the relaxation of chain segments and the shrinkage internal stress can be neglected. When the cooling temperature is near T_g, the internal stress is mainly caused from Eq. (1) and is relatively low. When the curing temperature is lower than T_g, the motion of chain segments is restricted, which is converted to shrinkage internal stress. At a curing temperature much lower than T_g, the internal stress is the sum of Eqs. (1) and (2) and is high. In the present study, 130 °C (if used as the curing temperature) is higher than T_g (shown in Table 4) for the modified epoxy systems, and the corresponding internal stress would be lower than that in the modified epoxy systems cured at 100 °C (the actual curing temperature). Thus, it could be expected that the tensile response for the modified epoxy system if cured at 130 °C would be higher than the present values to a more or less degree.

On other hand, as the flexible diamine content increases, the cross-linking density decreases, so the tensile strength of the samples reduces with increasing the relative content of the flexible diamines. This observation is similar to those for rubber and polyurethane modified epoxy resins. Additionally, the D-230 modified epoxy shows higher strength than the D-400 modified epoxy. It can be explained using Fig. 4. Fig. 4(a), (b) and (c) represents the curing network structures of unmodified, D-230 and D-400 modified epoxy resins, respectively. Because the chain length of D-400 is larger than that of D-230, the space between cross-linking points is larger for D-400 than D-230 cured epoxy resins. Larger space leads to small network structure density. Thus, the network structure density of the cured system containing D-400 is lower than that of the cured system containing D-230 at the same content. The compact curing network structure leads to the high strength, thus the tensile strength of the D-230 cured epoxy systems is higher than that with D-400 as the modifier at the same content.

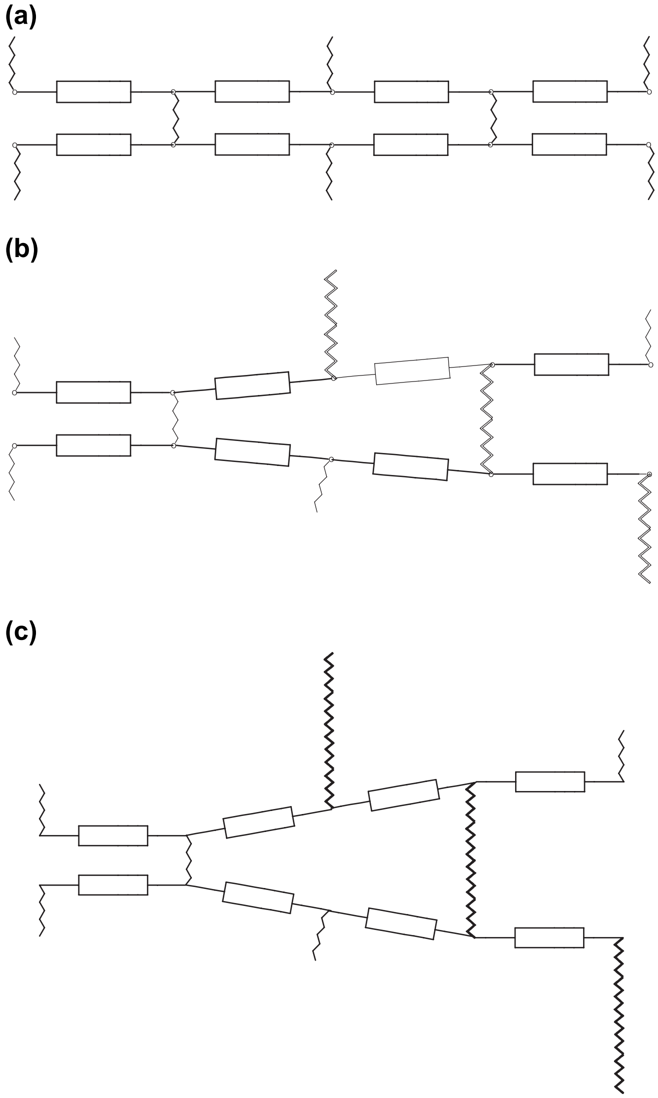

Fig. 4. Schematic representation of curing network structures of (a) unmodified, (b) D-230 modified and (c) D-400 modified epoxy resin system. ▭: DGEBA moiety; 〰: DETD moiety; ⩘⩘⩘⩘⩘: D-230 moiety; ⩘⩘⩘⩘⩘⩘⩘⩘⩘⩘: D-400 moiety.

It is interesting to observe that the tensile strength at 77 K increases with increasing amount of the two flexible diamines in a similar way. This pattern is different to that at RT and can be explained as follows. The tensile strength of epoxy resins decreases with increasing chain length of flexible diamines since the chain length affects the epoxy network structure density. The chain length of flexible diamines becomes shorter because of shrinkage when cooling down to 77 K, and hence the negative effect of the chain length at 77 K on the tensile strength is much less than at RT. Conversely, the decrease in the chain length of flexible diamines when cooling down to 77 K would likely lead to enhancement in the strength of the modified epoxy resins since the tensile strength of epoxy resins increases with decreasing chain length of flexible diamines. On the other hand, epoxy resins become more brittle at 77 K and thus the reduction in internal stress will be more important to enhance the tensile strength at cryogenic temperature than at RT. The flexible diamines with ether linkages are able to change bond angles and hence can effectively reduce the internal stress [40]. Thus, it is seen that the tensile strength at 77 K increases with increasing the flexible diamine content for both D-230 and D-400.

The elongation at break of the epoxy resins is shown in Table 2. The elongation at break at RT and 77 K increases with increasing the flexible diamine content owing to the flexible network structures within the rigid epoxy network structure. Moreover, it is observed that the elongation at break is lower for the modified system containing D-400 than that containing the same content of D-230. It can be explained using Fig. 4 that the difference in the chain length between D-230 and DETD is smaller than that between D-400 and DETD. It is thus suggested that smaller difference of the chain length between the two curing agents would facilitate the macromolecular mobility to some extent. In other words, DETD and D-230 have the better synergistic effect on improving the elongation at break of epoxy resins than D-400 and DETD do. In addition, it is shown that the elongation at break at 77 K is much lower than that at RT. This is because the macromolecular mobility is suppressed at 77 K, resulting in reduction of the ductility.

Table 2 also lists the Young's modulus of the epoxy resins at both RT and 77 K. The Young's modulus at RT tends to decrease with increasing the flexible diamine content for both D-230 and D-400 caused by the decrease in the curing network structure density except at 21 wt% D-230 content. However, Young's modulus at 77 K increases slightly with increasing the flexible diamine content for the same two reasons as given for the tensile strength at 77 K, viz, the smaller effect of chain length on curing network structure density and hence on Young's modulus at 77 K than at RT; and a more prominent role of reduction of internal stress in enhancing Young's modulus at cryogenic temperature than at RT. Also, Young's modulus and the tensile strength at 77 K are larger than those at RT with same composition. These results are very similar to those for other polymer materials [41,42]. It can be imagined that molecules are more closely compacted at cryogenic temperature and the binding forces between molecules at 77 K are high making positive contribution to the tensile strength and Young's modulus.

3.2. Impact test

Charpy tests were employed to obtain a qualitative indication of the impact strength of the epoxy resins under impact conditions. The impact strength of epoxy resins at RT and 77 K are summarized in Table 3. In general, the impact strength increases with increasing the flexible diamine content for both D-230 and D-400 except at 21 wt% and 49 wt% of D-400 at 77 K. At RT, the increased impact strength can be attributed to the reduction of internal stress due to the stress relaxation by flexible molecular chains of flexible diamines [43], when the samples were subjected to impact. At 77 K, flexible diamines containing ether linkages could still be flexible via changing the main chain bond angles since they could undergo deformation at cryogenic temperature even when their segmental motions are frozen out [40]. The improvement of the impact strength is closely related to the content of the flexible diamine. For the case of D-400 with relatively long chain length, a large difference in chain shrinkages between D-400 and DETD would occur when cooling down to 77 K, resulting in yet another internal stress in the D-400 modified epoxy resins though the original internal stress can be reduced due to the introduction of flexible segments. Therefore, the final impact strength of D-400 modified epoxy resins is determined by the above two competing effects. When 21 wt% or 49 wt% D-400 was added, the effect of the chain shrinkage difference would be superior, thus the impact strength was reduced when compared with the unmodified epoxy resin. At a higher flexible D-400 content, the effect of the reduction in the original internal stress due to introduction of a higher content of flexible segments would be predominant, thus the impact strength was enhanced compared to unmodified epoxy resin. For the case of D-230 with relatively short chain length, the reduction in the original internal stress is supposed to play the dominant role in determining the impact strength, hence the increase of the impact strength with increasing D-230 content is observed.

In addition, Table 3 also shows that the impact strength at 77 K is larger than that at RT with same compositions. This is because at 77 K, the molecules have less thermal energy thus less mobility, and it is difficult to deform when molecules suffer impact loading. Therefore, molecules absorb less energy at 77 K than at RT when subjected to impact.

Table 3
Impact strength at RT and 77 K of the unmodified and modified epoxy resins with various relative D-230 and D-400 contents in the curing system[a]

Relative flexible diamine content (wt%)		Impact strength (kJ/m^2)	
		RT	77 K
D-230	0	19.20 ± 3.19	18.91 ± 2.58
	21	38.76 ± 8.64	20.55 ± 2.07
	49	45.42 ± 10.64	21.62 ± 4.17
	78	51.25 ± 4.17	23.32 ± 0.85
	100	53.56 ± 3.78	26.77 ± 2.41
D-400	0	19.20 ± 3.19	18.91 ± 2.58
	21	22.58 ± 4.96	15.66 ± 3.3
	49	23.65 ± 7.2	16.56 ± 6.99
	78	24.94 ± 4.85	23.72 ± 1.76
	100	48.04 ± 4.28	28.69 ± 7.64

[a] Note: Data are expressed as average value + standard error.

3.3. Fractography

Representative SEM micrographs of fractured surfaces of unmodified and D-230 modified epoxy resins after Charpy impact testing are shown in Fig. 5. At RT the fracture surface of unmodified epoxy shows typical characteristics of brittle fracture (see Fig. 5(a)). The fracture surfaces of the D-230 modified DGEBA epoxy resins are relatively rough. Tortuous

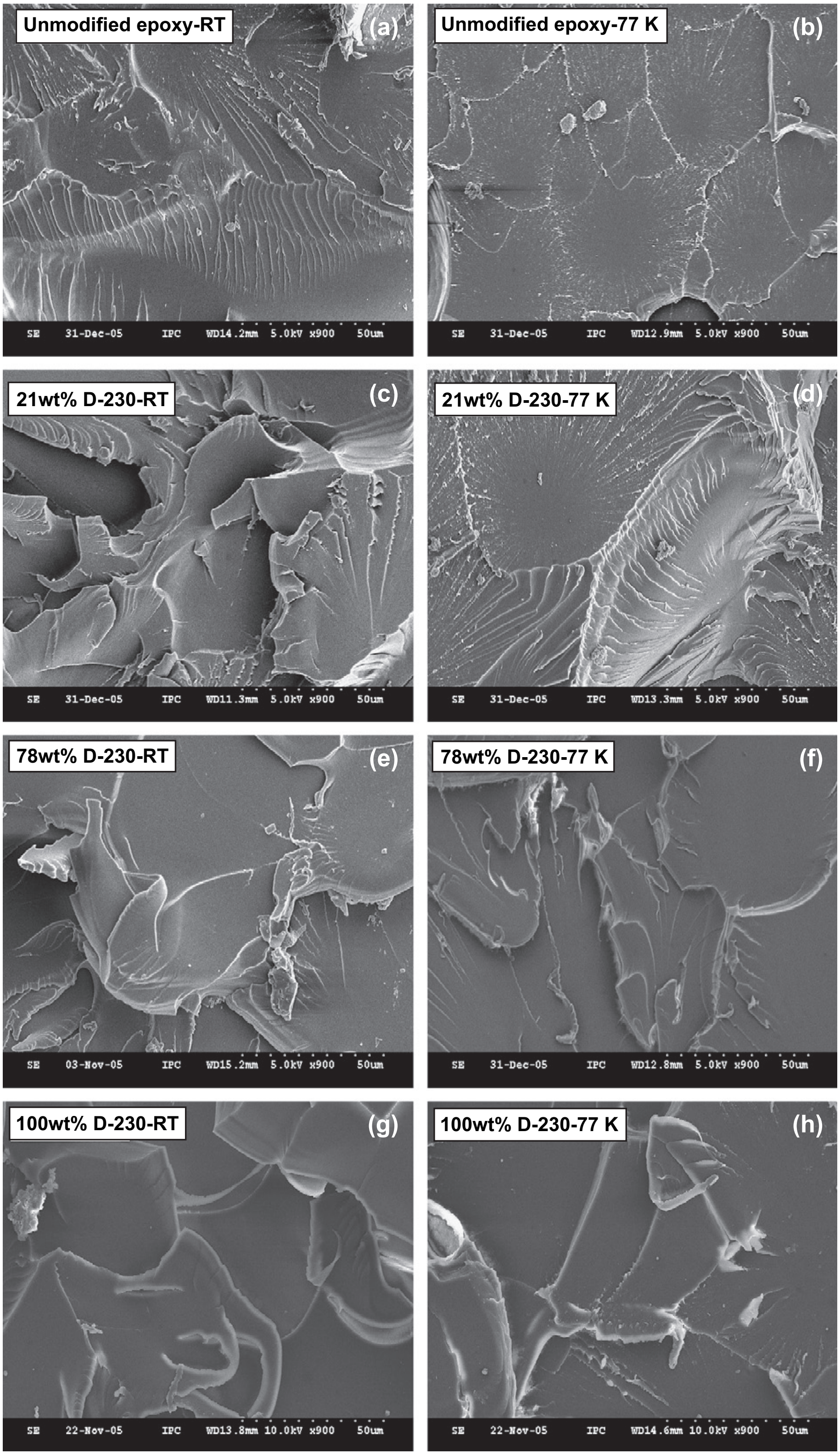

Fig. 5. Fractographs of unmodified and modified epoxy resins. (a) Unmodified epoxy at RT; (b) unmodified epoxy at 77 K; (c) 21 wt% D-230 content at RT; (d) 21 wt% D-230 content at 77 K; (e) 78 wt% D-230 content at RT; (f) 78 wt% D-230 content at 77 K; (g) 100 wt% D-230 content at RT; and (h) 100 wt% D-230 content at 77 K.

cracks, ridges and river marks can be seen on the fracture surfaces (see Fig. 5(c), (e) and (g)). The rough fracture surface indicates deflection of crack path, i.e. the crack deviation from its original plane, increasing the area of the crack. Hence, the required energy for the propagation of the cracks on the fracture surfaces increases.

At 77 K, the fracture surface of the unmodified epoxy resin is very smooth, showing typical brittle fracture mode (see Fig. 5(b)). Nonetheless, ridges appear on the fracture surfaces of the D-230 modified epoxy resins (Fig. 5(d), (f) and (h)), indicating that a higher energy is required for the propagation of the cracks on the fracture surfaces of the modified epoxy resins though the modified epoxy resins still exhibit brittle fracture mode. In addition, Fig. 5 shows that the fracture surfaces of the epoxy resins at 77 K are clearly smoother than the corresponding fracture surfaces at RT. It is an indication of a more brittle failure mode at 77 K than at RT [41,42]. Hence, the impact strength at 77 K is lower than that at RT (see Table 3). Further, the morphology of the microscopic fracture surfaces show that all compositions investigated are homogeneous with no sign of phase separation, suggesting that homogeneous crosslinked network structures might be formed in all modified systems [44]. Similar fractography for D-400 has also been observed. For simplicity, it will not be repeated here.

3.4. Determination of glass transition temperature

The unmodified and modified epoxy resins were examined by DSC to determine their T_g after curing. The results are summarized in Table 4. Clearly, the T_g's of the epoxy resin cured only by DETD, D-230 and D-400 are 156.5 °C, 81.9 °C and 36.9 °C, respectively. This is because the molecular chains of D-230 and D-400 are more flexible than that of DETD and the chain length increases in the order of DETD $<$ D-230 $<$ D-400. The cross-linking density of the corresponding cured epoxy resin increases in the reverse order [45]. Because lower cross-linking density leads to lower T_g [46], hence the T_g descends in the order of DETD $>$ D-230 $>$ D-400. From Table 4, the addition of D-230 or D-400 results in a clear decrease in T_g's compared to the unmodified epoxy resin, and the magnitude of reduction increases with increasing the content of D-230 or D-400. The reduction in T_g is a disadvantage for some applications where a high T_g is required. However, the modified epoxy resins here are aimed to be used in cryogenic engineering applications in which a high T_g is not very important. Thus, the modified epoxy systems have potential applications in cryogenic engineering applications since they have the overall improved mechanical performance at low temperature (77 K).

Moreover, it can be seen from Tables 2 and 4 that lowering of T_g due to the addition of flexible diamines corresponds with lowering of the tensile strength and Young's modulus at RT except the case of no diamine contents, similar results have also been observed in the literatures [16,47]. On the other hand, however, lowering of T_g corresponds with increase of the tensile strength and Young's modulus at 77 K. This is an advantage with the addition of flexible diamines. In addition, only a single T_g exists in all cured epoxy systems. It indicates that the flexible diamine-modified epoxy resins possess homogeneous phase structures after curing on the scale of DSC resolution. This is to say that the flexible diamines participate in the curing reaction with epoxy resin. Otherwise, two or more glass transition temperatures would appear if there existed phase separation. These results are also consistent with SEM observations of the fracture surfaces as discussed above.

Table 4
Glass transition temperature (T_g) of the various cured epoxy resins

Relative flexible amine content (wt%)		T_g (°C)
D-230	0	156.6
	21	110.9
	49	99.9
	78	85.3
	100	81.9
D-400	0	156.6
	21	93.0
	49	58.6
	78	41.2
	100	36.9

4. Conclusions

In this paper, two flexible diamines (D-230 and D-400) with different chain lengths were used to modify DGEBA epoxy resin. The tensile properties, impact strength, microscopic fracture surfaces and glass transition temperature of unmodified and flexible diamine-modified epoxy resins were investigated. It was shown that both the elongation at break and impact strength at room temperature (RT) and cryogenic temperature (77 K) increased with increasing the content of these two flexible diamines except those samples with 21 wt% and 49 wt% D-400 contents. It was interesting to have observed that the tensile strength could be improved by adding a selected content (21–78 wt% D-230 and 21 wt% D-400) of the two flexible diamines at RT; moreover, the tensile strength at 77 K increased with increasing amount of flexible diamines. The Young's modulus at RT decreased with increasing the content of the flexible diamines except at 21 wt% of D-230. But at 77 K, the reverse trend was true and the Young's modulus was higher than that at RT at a given content of the diamines. The SEM micrographs of impact fracture surfaces correlated well with the changes of the impact strength. DSC analysis showed that the T_g decreased with increasing the content of both flexible diamines and a homogeneous cross-linking network structure was formed for all modified epoxy systems. Consequently, it can be concluded that addition of a selected amount of flexible diamines would simultaneously strengthen and toughen DGEBA epoxy resins at both RT and 77 K. The present study provided valuable information for improvement of the mechanical performance of epoxy resins modified with flexible diamines especially at 77 K and hence could help for choosing proper epoxy compositions for cryogenic engineering applications.

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