Polymer 50 (2009) 1316–1323

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Simultaneously increasing cryogenic strength, ductility and impact resistance of epoxy resins modified by *n*-butyl glycidyl ether

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A R T I C L E I N F O

Article history:
Received 27 August 2008
Received in revised form
25 November 2008
Accepted 30 December 2008
Available online 10 January 2009

Keywords:
Epoxy resin
n-Butyl glycidyl ether
Mechanical properties

A B S T R A C T

Epoxy resins are increasingly used in cryogenic engineering areas due to rapid developments of spacecraft and superconducting cable technologies as well as large cryogenic engineering projects (e.g., International Thermonuclear Experimental Reactor). Cryogenic mechanical properties are important parameters for epoxy resins to be employed in such areas. In this paper, a traditional reactive aliphatic diluent, namely *n*-butyl glycidyl ether (BGE, JX-013) with a low viscosity, was used to modify diethyl toluene diamine (DETD)-cured diglycidyl ether of bisphenol-F (DGEBF) epoxy system for enhancing cryogenic mechanical properties at liquid nitrogen temperature (77 K). The results showed that the cryogenic strength, ductility and impact resistance (impact strength) have been simultaneously enhanced by the addition of BGE with appropriate contents. Moreover, the comparison of the mechanical properties between 77 K and room temperature (RT) indicated that at the same composition, the tensile strength and Young's modulus at 77 K were higher than those at RT but the failure strain and impact resistance showed the opposite results. Finally, differential scanning calorimetry (DSC) exhibited that the glass transition temperatures (T_g) of the epoxy resins decreased with increasing the BGE content.

1. Introduction

Epoxy resins have wide applications in aerospace, electrical, electronic and automobile industries as insulating materials [1,2], structural adhesives [3], and matrices for composites [4] because of their low cost, easy processability, good thermal, mechanical and electrical properties. With the rapid developments of spacecraft and superconducting cable technologies, and large cryogenic engineering projects such as International Thermonuclear Experimental Reactor (ITER), etc., epoxy resins have been increasingly employed in cryogenic engineering applications as impregnating materials, adhesives or matrices for advanced composites [5–7]. In cryogenic engineering, liquid nitrogen and liquid helium are generally employed as cooling media and liquid nitrogen is more often used due to its low cost. Pure epoxy resins normally have poor crack resistance at room temperature, for example see Refs. [8,9] and are more brittle at cryogenic temperatures [9,10], which makes them unsuitable for cryogenic engineering applications. Mechanical properties including strength, ductility and impact resistance, etc., at cryogenic temperatures are important parameters for engineering materials to be applied in cryogenic engineering. Therefore, it is necessary to improve the cryogenic strength, ductility and impact resistance of brittle epoxy resins so that they can be successfully used in cryogenic engineering areas.

Diglycidyl ether of bisphenol-F (DGEBF) is one promising epoxy resin for cryogenic use [9]. Liquid aromatic amine (DETD) has a low viscosity and a low toxicity without physiological problems associated with other aromatic diamine hardeners such as 4,4′-diaminodiphenylmethane (DDM), 4,4′-diaminodiphenyl sulphone (DDS), etc. In this study, DGEBF and DETD will be employed as epoxy precursor and hardener, respectively. Though DETD-cured DGEBF system shows a high mechanical strength, it is brittle particularly at cryogenic temperatures. Hence, it is important to modify this epoxy system to broaden its applications in cryogenic engineering. The most common approach to toughen a brittle epoxy resin is introduction of a toughening agent into the networks of the brittle epoxy resin. Previous studies were mainly focused on investigation of fracture resistance or toughness at room temperature (RT), but only a few studies have been conducted on cryogenic fracture resistance or toughness of epoxy resins [9–16]. Furthermore, the mechanical behaviors of materials at RT are generally very different from those at cryogenic temperatures so that their

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doi:10.1016/j.polymer.2008.12.048

mechanical properties obtained at RT cannot simply be transferred to the cryogenic case. It is thus of scientific significance to investigate the cryogenic mechanical behaviors of toughened epoxy resins.

A successful routine to improve the fracture resistance of brittle epoxy resins is via rubber toughening. For example, carboxyl terminated butadiene acrylonitrile rubber (CTBN) [17–20], amine terminated butadiene acrylonitrile rubber (ATBN) [21,22], epoxy terminated butadiene acrylonitrile (ETBN) [22–24] and hydroxyl terminated polybutadiene liquid rubber (HTPB) [25] have been used to enhance the fracture resistance or toughness of epoxy resins. Rubber-modified brittle epoxy resins show increased fracture resistance or toughness, but also exhibit the deterioration of other important properties compared to the unmodified epoxy resin. For example, an obvious disadvantage is that introduction of rubber toughening generally lowers strength and modulus of epoxy resins [17–23,25].

To improve the fracture resistance or toughness without sacrificing strength and modulus, engineering thermoplastics which are tough, ductile, chemically and thermally stable have been employed as an alternative method to improve the poor fracture resistance or toughness of epoxy resins. In early stage (1983), Raghava [26] and Bucknall and Partridge [27] studied thermoplastic-toughened epoxy resins. Unfortunately, their investigation of introducing commercial grades of poly(ether sulfone) into epoxy resins did not bring about an obvious increase in fracture toughness and in some cases, the fracture toughness was reduced. Later it was realized that it is important to increase the compatibility and interfacial adhesion between epoxy matrix phase and thermoplastic modifier in order to improve the fracture resistance or toughness. Consequently, poly(sulfone) [28], polysiloxane [29], polyetherimide [30,31], poly(ether sulfone) [12,32,33] and poly(ether ether ketone) [34,35] etc., have been successfully used to blend with epoxy resins as dispersed phases to effectively toughen epoxy resins. For thermoplastic-toughened epoxy systems, one major problem with the poor processability in using such engineering thermoplastic modifiers with a high viscosity, which is mainly caused by poor compatibility with uncured epoxy resins, still remains unresolved.

In addition to rubber toughening and thermoplastic toughening, reactive aliphatic diluents can make the epoxy resin networks more flexible through chemical reaction [36] and thus have also been employed as modifiers to toughen epoxy resins [37,38]. The fracture toughness of modified epoxy resins increased to some extent as the weight percentage of methyl methacrylate reactive diluent increased [37]. Diglycidyl ether of 1,4-butanediol was also used for toughening epoxy/amine networks in order to improve fracture toughness [38]. Moreover, the viscosity of epoxy resins is too high for some applications (e.g., impregnating application etc.). It is hence of importance to lower the viscosity of epoxy resins by addition of various diluents [39]. Epoxy systems modified with the reactive diluent of 1,1-diphenylethane (DPE) revealed low viscosity, good chemical resistance and almost unchanged mechanical, thermal and electrical properties [39]. *n*-Butyl glycidyl ether (BGE, JX-013) with a low viscosity of 2–3 mPa s at 25 °C is a traditional reactive aliphatic diluent, which contains one soft segment and one epoxy segment (see Fig. 1). It is thus expected that introduction of BGE into epoxy resins can reduce viscosity for improving processability and meanwhile, can be used as a modifier to toughen epoxy resins.

In this paper, the *n*-butyl glycidyl ether modifier (BGE) was used to modify the DETD-cured DGEBF epoxy system. The cryogenic mechanical properties including strength, ductility and impact resistance of unmodified and BGE-modified epoxy resins were studied at liquid nitrogen temperature (77 K) and were compared with their corresponding properties at room temperature (RT). Moreover, the glass transition temperature as a function of BGE content was also examined by differential scanning calorimetry (DSC).

2. Experimental

2.1. Materials and preparation of samples

The epoxy resin used in this work was diglycidyl ether of bisphenol-F (DGEBF, YDF-175, Kukdo Chemical Ind. Co., Korea) with the epoxide weight equivalence in the range 156–178 g/mol. The curing agent was diethyl toluene diamine with an amine weight equivalence of 44.5 g/mol (DETD, ETHACURE-100, Albemarle Co., USA) being a mixture of 2,4- and 2,6-isomers. *n*-Butyl glycidyl ether (BGE, JX-013) with an epoxide value of 0.6 eq/g and a low viscosity of 2–3 mPa s at 25 °C (Changshu Jiafa Chemistry Co., China) was used as the modifying agent. The chemical structures of DGEBF, DETD and BGE are given in Fig. 1.

The content of the added BGE varied from 0 to 60 phr (parts per hundred parts of epoxy resin) in DGEBF/BGE blends. Uncured DGEBF/BGE blends were prepared by mechanical mixing; BGE was dissolved in the epoxy resin at 40 °C with constant stirring under vacuum condition. After complete dissolution, the equivalent amount of DETD, shown in Table 1, was added and dissolved completely. The blends were transparent in the uncured state, indicating good compatibility between DGEBF and BGE. The

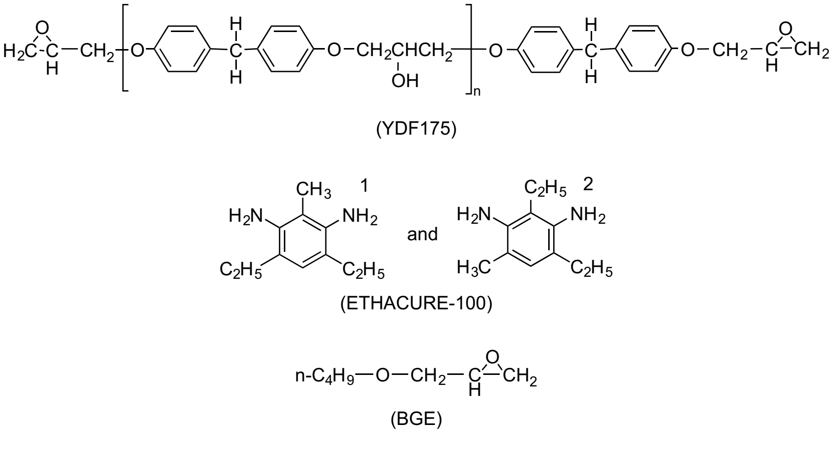

Fig. 1. Chemical structures of DGEBF, DETD and BGE.

Table 1
Formulations of epoxy resin systems.

Sample code	BGE content (phr)	DGEBF (g)	DETD (g)	Second droplet phase size (μm)[a]
1	0	100	25.8	–
2	10	100	28.47	0.99
3	20	100	31.14	1.72
4	40	100	36.48	2.72
5	60	100	41.82	3.83

[a] Note: 50 measurements were carried out on SEM micrographs of cryo-fractured surfaces of the samples using SemAfore 4.0 Software to get the average second phase sizes.

resulting solution was evacuated to remove bubbles. After evacuation the mixtures were cast into an open mold. The blends were cured at 80 °C for 8 h, and then post-cured at 130 °C for 10 h. After curing, the blends were allowed to be cooled naturally to room temperature. The unmodified epoxy resin was also prepared following the same procedure except no addition of BGE. The stoichiometric ratio of epoxy/amine, $\{[E]_{\mathrm{DGEBF}}+[E]_{\mathrm{BGE}}\}/[H]_{\mathrm{DETD}}=1$, was used in this study, where $[E]_{\mathrm{DGEBF}}=\mathrm{weight}_{\mathrm{DGEBF}}/\mathrm{epoxide}_{\mathrm{DGEBF}}$ equivalent weight, $[E]_{\mathrm{BGE}}=\mathrm{weight}_{\mathrm{BGE}}/\mathrm{epoxide}_{\mathrm{BGE}}$ equivalent weight, and $[H]_{\mathrm{DETD}}=\mathrm{weight}_{\mathrm{DETD}}/\mathrm{amine}_{\mathrm{DETD}}$ equivalent weight. The formulations are summarized in Table 1.

2.2. Characterization

The tensile samples were prepared according to the recommendation of ASTM D 638-96. The tensile properties were measured on an RGT-20A Reger mechanical tester under a 10 kN load cell with a crosshead speed of 2 mm/min. The dimensions of the tensile specimens are 6 mm × 4 mm in the working section. The cryogenic temperature condition was achieved by dipping the samples fixed on the clamps in a liquid nitrogen-filled cryostat designed in our laboratory.

The Charpy impact strength of the samples was measured with a Reger Impact Tester according to the ASTM D-256 standard. The specimen dimensions are 80 mm × 10 mm × 4 mm. Specimens for impact testing were immersed in liquid nitrogen for over 5 min so that they could be cooled down to 77 K before being mounted onto Charpy impact tester. The pendulum of the impact tester was released immediately after the specimen was mounted onto the impact tester and one impact testing was completed in a couple of

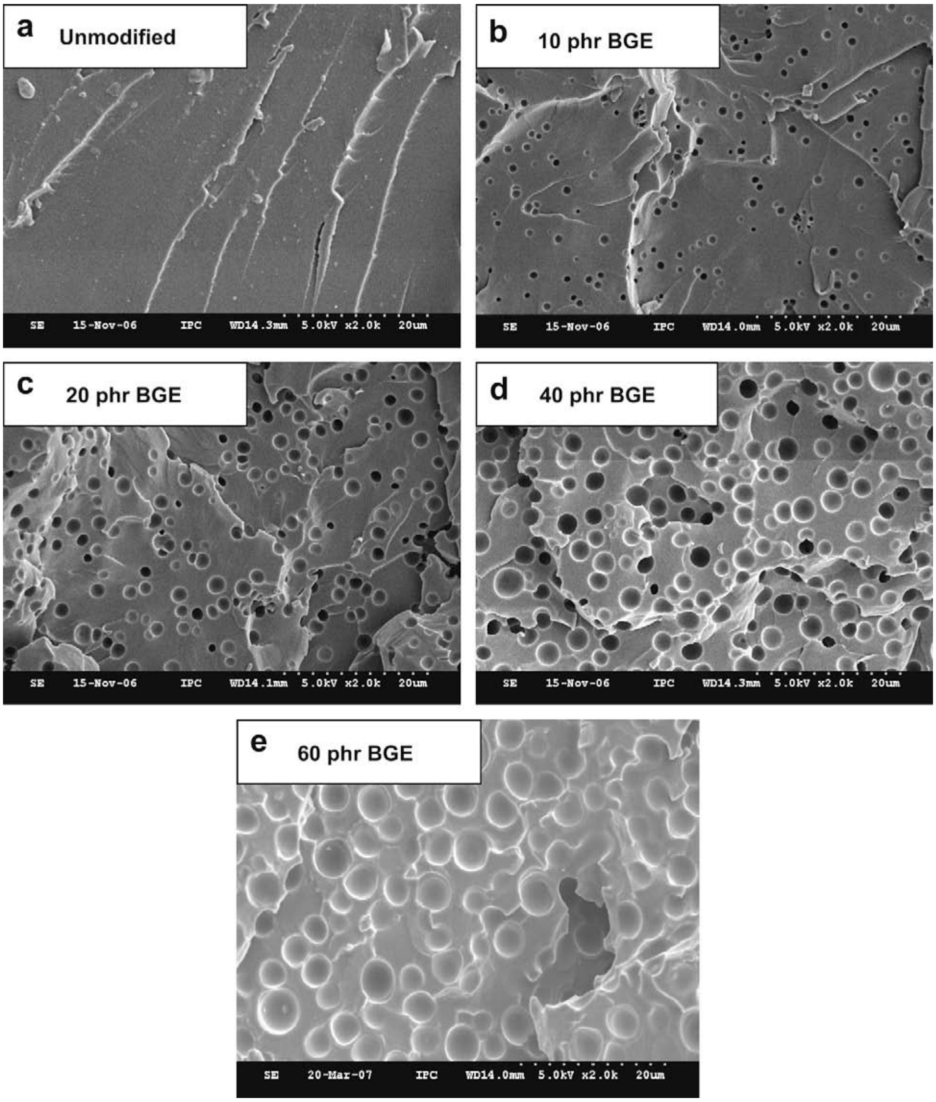

Fig. 2. SEM micrographs of cryo-fractured surfaces of unmodified and BGE-modified epoxy resins: (a) unmodified, (b) 10 phr BGE, (c) 20 phr BGE, (d) 40 phr BGE, and (e) 60 phr BGE.

seconds. At least five specimens were tested for each composition. The temperature inside the specimens was examined to have no obvious change after the specimens were taken out from liquid nitrogen for a few seconds using cryogenic thermocouples embedded inside the specimens. Therefore, the temperature for the impact testing was approximately regarded as 77 K [14].

The fracture surfaces of the specimens after impact testing were examined using scanning electron microscopy (SEM, Hitachi S-4300). Prior to examination, the fracture surfaces were coated with sputter-gold to improve conductivity.

The glass transition temperature (T_g) of the samples was measured using differential scanning calorimetry (DSC, NETZSCH STA 409 PC) under nitrogen atmosphere at a heating rate of 10 °C/min. 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, which is adopted in this study. The peak of T_g on the curves of DSC after the first scan is too wide to hardly preciously define T_g. The peak after the second scan became relatively narrow. It was thus convenient to define T_g after the second scan [12].

Sample dimensions used for measurement of the relaxation time T_2 were 10 mm in length and 3–4 mm in diameter. Samples were placed into a glass tube and were measured in native state. T_2 measurement was done using the IIC MR-CDS 3500 Crosslink Density Spectrometer and the measurement temperature for BGE-modified epoxy resins was 120.0 ± 0.1 °C. The time domain signal was used for data analysis. Each signal decay covered 1024 data points at an acquisition time of 10.24 ms. For determination of the relaxation time, 64 measurements at different tau-values (T_2) were carried out. Data analysis was performed with the IIC Analysis Software Package using a non-linear Marquardt–Levenberg Algorithm.

3. Results and discussions

3.1. Miscibility of BGE/DGEBF blends and morphology before and after curing

The bisphenol-F based epoxy resin was blended with BGE at 40 °C and the binary DGEBF/BGE blends were transparent. There was no visual evidence for heterogeneities in the blends before addition of the curing agent. This observation suggests that these blends are homogeneous because the selected BGE is miscible with DGEBF. The binary DGEBF/BGE blends became opaque after curing with DETD, indicating the possibility of formation of a phase-separated structure. This morphology of the cured blends was confirmed by means of SEM examination. Fig. 2a shows the homogeneous morphology of the unmodified epoxy system, while Fig. 2b–e shows the typical phase-separated morphology of the modified epoxy systems containing 10, 20, 40 and 60 phr BGE. And the second phase size increased with increasing BGE content. Francis et al. [40] reported that such separated phase morphology might be attributed to the change of the entropy of the systems. The entropy was increased upon mixing before curing [41], and the mixing entropy was high because of the high randomness of small molecules of BGE with a low molecular weight. High entropy facilitates miscibility since it reduces the free energy of mixing. Upon curing, the molecular weight of the epoxy resin was increased, resulting in the decrease of the entropy of the mixture and hence the immiscibility of the cured epoxy system [42]. As a consequence, the system becomes phase-separated as shown in Fig. 2b–e. In addition, the dispersed phases become larger when the BGE content was increased (Fig. 2). Such an increase in size of the dispersed phase displayed in Table 1 might be associated with the re-agglomeration or coalescence of the dispersed phases [43].

3.2. Mechanical properties

3.2.1. Tensile properties

The stress–strain curves of the unmodified and modified epoxy resins at both RT and 77 K are shown in Fig. 3. Clearly, the cryogenic tensile strength and failure strain can be simultaneously enhanced by the addition of BGE with appropriate contents. Moreover, the epoxy resins exhibit relatively ductile behaviors at room temperature compared to that at 77 K. The data for the tensile strength, Young's modulus and failure strain of the unmodified and modified epoxy resins at RT and 77 K were obtained from the tensile stress–strain curves using the commercial REGER testing Software. The results for the tensile properties are summarized in Table 2.

In general, the addition of soft phase like rubber and polyurethane, etc., to epoxy resins results in reduction of the tensile strength at RT [21,25]. This is also observed for the high BEG content cases as shown in Table 2. Nonetheless, Table 2 shows that the tensile strength of the blend containing 10 phr BGE at RT is slightly

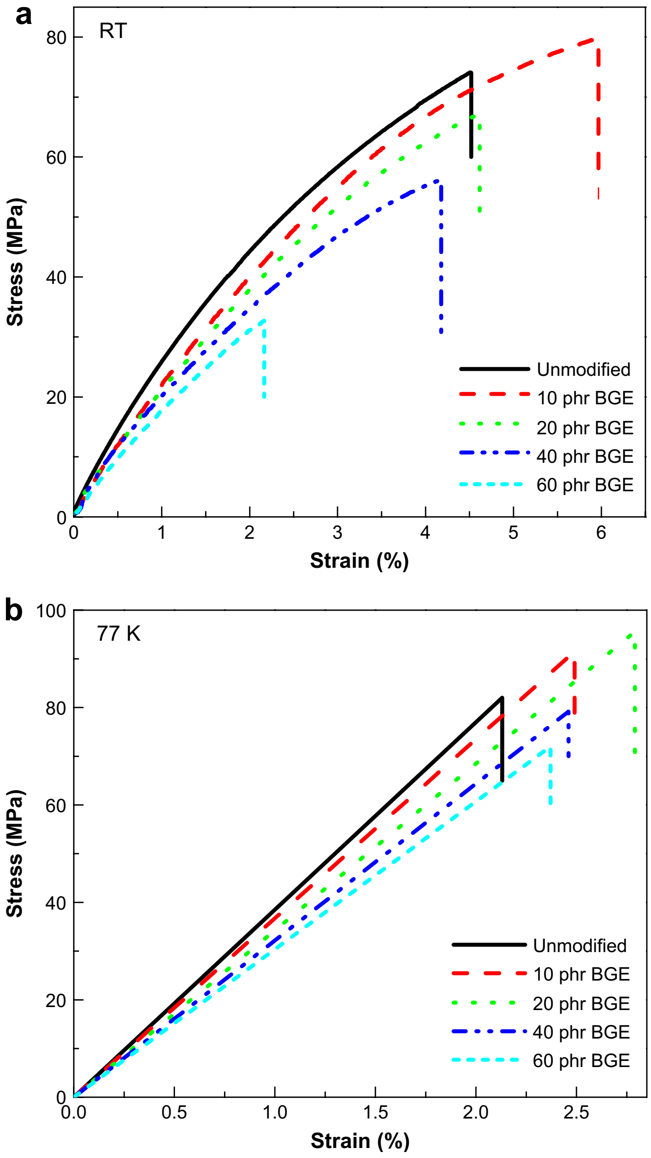

Fig. 3. Typical stress–strain curves of unmodified and BGE-modified epoxy resins with different amount of BGE at (a) RT and (b) 77 K.

Table 2
Tensile properties of unmodified and BGE-modified epoxy resins at RT and 77 K.

Modifier agent	Relative BGE content (phr)	Tensile strength (MPa)		Young's modulus (GPa)		Failure strain (%)	
		RT	77 K	RT	77 K	RT	77 K
BGE	0	72.84 ± 2.78	78.47 ± 13.09	2.67 ± 0.13	4.63 ± 0.05	4.52 ± 0.58	2.18 ± 0.02
	10	75.27 ± 0.01	86.90 ± 9.43	2.44 ± 0.46	4.61 ± 0.36	5.90 ± 1.42	2.32 ± 0.05
	20	60.17 ± 4.31	91.58 ± 9.65	2.34 ± 0.37	4.60 ± 0.28	4.62 ± 0.31	2.50 ± 0.04
	40	51.17 ± 3.12	85.19 ± 14.63	2.28 ± 0.32	4.52 ± 0.21	4.16 ± 0.17	2.45 ± 0.02
	60	28.62 ± 2.34	65.78 ± 11.88	2.23 ± 0.14	4.50 ± 0.18	2.12 ± 0.38	2.41 ± 0.12

enhanced by the addition of BGE, followed by a rapid decrease with further addition of BGE. The addition of a low content BGE produced the second phase particles uniformly distributed in the modified epoxy system (as shown in Fig. 2b). In rubber-toughened epoxy resins, the dispersed soft silicon rubber particles are assumed to effectively reduce the internal stress in epoxy resins caused during curing, which is attributed to the complete separation of rubber phase from epoxy matrix and acts as a stress relieving agent [44]. It can also be noted that the introduction of soft hyperbranched polyglycerol phase with small sizes (below about 130 nm on an average) at appropriately low contents into epoxy resins could lead to the enhancement in tensile strength though the effect of particle size on the tensile strength was not explicitly explored [45]. Experimentally, it is clear that soft second phases with fine sizes are beneficial to enhancement of the tensile strength of epoxy resins [12,45]. Similarly, the uniformly distributed soft second BGE phase with a small droplet size can release internal stress caused during curing to enhance the tensile strength. The dependence of the tensile strength of modified epoxy resins on the BGE content as shown in Table 2 is determined by the two competing effects of reduced internal stress and lowered strength by introduction of soft BGE phase. In other words, on the one hand the addition of soft second BGE phase would reduce internal residual stress, leading to the increased tensile strength; on the other hand, the strength of BGE phase is relatively low since the blend containing 60 phr BGE is quite lower than for the unmodified system as shown in Table 2, bringing about the decreased tensile strength. When the former effect dominates, the strength of the blend would be enhanced by the BGE addition. Otherwise, the strength would be decreased by the BGE addition. Consequently, with the addition of BGE, the tensile strength first increases and then decreases. The effect of internal stress on the tensile response will be further discussed after presentation of glass transition temperature.

Table 2 also shows the tendency of the cryogenic tensile strength of epoxy resins with varying the BGE content at 77 K. The cryogenic tensile strength has been obviously enhanced by addition of BGE at appropriate contents. The cryogenic strength showed an initial increasing tendency with increasing the BGE content and reached the maximum at the 20 phr BGE rather than at the 10 phr BGE. This is because at cryogenic temperature the epoxy resins become more brittle, the release of internal residual stress caused during curing will play a more important role in enhancing the tensile strength. As a result, the effect of reducing internal residual stress by the soft second phase would predominate in determining the strength of the blend at the 20 phr BGE, leading to the peak value of the strength. The effect of soft second phase size on the strength of the epoxy blend is an interesting issue [12,45] and its theoretical prediction should be of great interest to material scientists but is out of the scope of this paper. Afterwards the cryogenic tensile strength is decreased by further increasing the BGE content for the BGE/DGEBF blend. This observation is similar to that at RT due to appearance of large second BGE phase aggregates. Table 2 also shows that the tensile strength is higher at 77 K than at RT with the same composition. This can be explained as follows. When the temperature decreases from RT to 77 K, the chemical bond and molecules of the epoxy resin will shrink and the binding forces between molecules will become strong [12] and thus a larger load is needed to break the sample at 77 K. On the other hand, relatively strong interface bonding between the BGE phase and epoxy phase at 77 K due to thermal shrinkage can better facilitate the stress transfer and make contribution to the increase in the tensile strength. Moreover, the soft BGE phase becomes stronger at 77 K than at RT since the strength of 60 wt% BGE-modified epoxy system is higher at 77 K than at RT as shown in Table 2. As a result, the tensile strength of the epoxy blend with the same BGE content is higher at 77 K than at RT.

Furthermore, Table 2 shows that an increase in the BGE content led to a progressive decrease in elastic modulus of the modified epoxy resin. This is because BGE is a soft phase which has a lower modulus than the epoxy matrix phase. Thus, according to the modified rule of mixtures for particulate composites [46] which is also applicable to the case of polymer blends with second phase, the Young's modulus of the blend will then monotonically decrease with increasing BGE content. On the other hand, the internal stress has influences only on the fracture properties like (fracture) tensile strength or fracture toughness but not on the modulus that is a low strain property. That is why the modulus changes in a different way from tensile strength with increasing BGE content as shown in Table 2. Nonetheless, the magnitude of this reduction is significantly smaller than that of the epoxy resins modified by rubbers [47].

In addition, Young's modulus at 77 K is higher than that at RT with the same composition. This is because the molecules of the epoxy resin become stiffer due to the restrained mobility of the molecules when the temperature decreases from RT to 77 K. Similarly, the soft second BGE phase also becomes stiffer at 77 K than at RT. As a result, in terms of the modified rule of mixtures for particulate composites [46] which is also applicable to the case of polymer blends with second phase, it can be easily inferred that the Young's modulus of the blend becomes higher than that at RT.

Finally, Table 2 displays that the cryogenic failure strain of the BGE-modified epoxy resins at 77 K has been enhanced by addition of BGE at appropriate contents. Contrary to the tensile strength and Young's modulus, the failure strain at 77 K was smaller than that at

Table 3
Impact strength of the unmodified and BGE-modified epoxy resins at RT and 77 K and glass transition temperature (T_g) of the unmodified and BGE-modified epoxy resins.

Relative BGE content (phr)	Impact strength (kJ/m^2)		T_g (°C)
	RT	77 K	
0	11.76 ± 0.48	10.62 ± 0.94	131.1
10	17.63 ± 1.74	12.66 ± 0.14	121.3
20	17.21 ± 2.17	13.32 ± 1.30	112.3
40	20.88 ± 2.33	14.85 ± 4.21	90.5
60	14.83 ± 0.62	12.76 ± 0.86	73.0

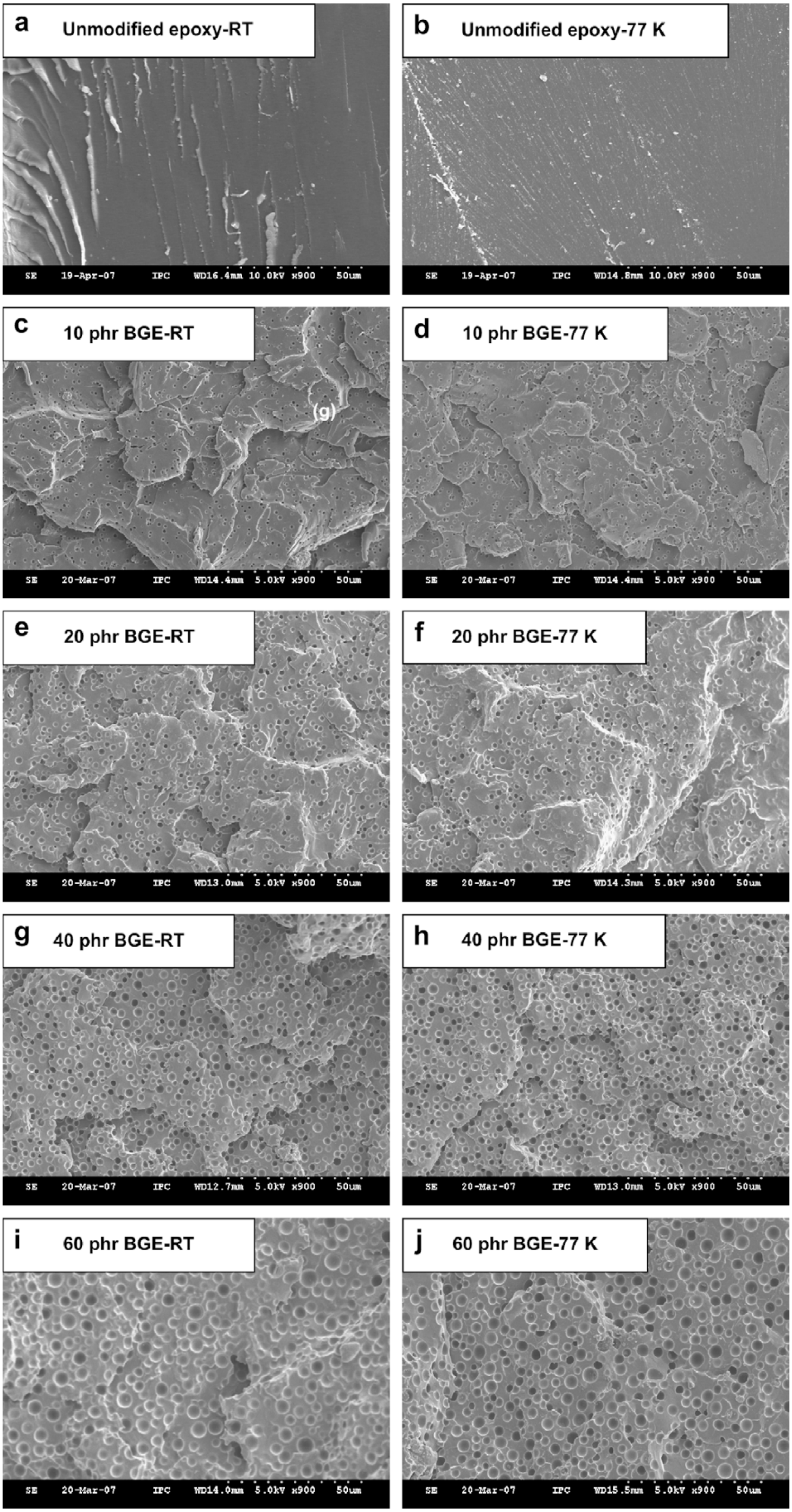

Fig. 4. Fractographs of unmodified and BGE-modified epoxy resins after impact testing: (a) unmodified resin at RT, (b) unmodified resin at 77 K, (c) 10 phr BGE at RT, (d) 10 phr BGE at 77 K, (e) 20 phr BGE at RT, (f) 20 phr BGE at 77 K, (g) 40 phr BGE at RT, (h) 40 phr BGE at 77 K, (i) 60 phr BGE at RT, and (j) 60 phr BGE at 77 K.

RT with the same composition. This is because the molecular shrinkage would occur and molecular mobility was suppressed at 77 K, leading to a reduction of the ductility [12,13,15].

3.2.2. Impact properties

Table 3 exhibits the dependence of the impact strength of the modified epoxy resins at RT and 77 K on the BGE content. As expected, the impact strength at RT was appreciably enhanced by the introduction of BGE in the epoxy resin. An addition of 40 phr BGE resulted in the 77.6% increase in the impact strength at RT compared to that for the unmodified epoxy but followed by a decrease when the BGE content was further increased. Table 3 also showed that the cryogenic impact strength at 77 K increased with an increase in BGE content and reached the maximum value with an increase of 39.8% for the system with 40 phr BGE followed by a rapid decrease with 60 phr BGE, which is similar to that at RT. The increase in the impact strength of the modified system by introduction of BGE up to 40 phr was due to the fact that the observed immiscible BGE-rich domains in Fig. 2 would enhance the impact strength (energy) through the crack trapping, bridging or blunting mechanisms of the dispersed soft second phases [12,48]. Moreover, even at 60 phr BGE, the impact strength at both RT and 77 K of the modified epoxy is higher than that of the unmodified epoxy. This is because at 60 phr BGE, on the one hand, the second phase-rich domains formed large agglomerates as shown in Fig. 2e, which would act as defects and then initiated failure to reduce impact strength; on the other hand, the soft second BGE phases are intrinsically tough, addition of BGE would bring about an increase in the fracture energy. These two competing effects finally lead to the higher impact strength of the modified epoxy at 60 phr BGE than the unmodified epoxy.

Moreover, Table 3 displayed that the impact strength at RT is larger than that at 77 K with the same composition for both the unmodified and modified epoxy systems. This is because the molecular mobility would be lowered when the temperature was down to 77 K from RT. When the impact loading was applied to the specimens, it would be difficult for the materials to yield efficient deformation at 77 K, hence lower impact energies would be required to break the specimens at 77 K than at RT.

3.3. Fractography

Representative SEM micrographs of fractured surfaces of the unmodified and BGE-modified epoxy resins after impact testing are shown in Fig. 4. At RT and 77 K, the fracture surfaces (Fig. 4a and b) of the unmodified epoxy resin show that cracks spread freely and irregularly, namely typical characteristics of brittle fracture, which accounts for its poor impact resistance (see Table 3).

In Fig. 4c–j, the fracture surfaces of the BGE-modified epoxy system show that all micrographs clearly exhibit a phase-separated morphology similar to rubber-modified epoxy resins. This morphological feature could presumably be considered to be responsible for the observed increase in the impact strength, and the modified system can be regarded as a particulate polymer composite based on epoxy matrix filled with second phase particles [49]. The toughening mechanisms of epoxy resins with rubber particles have been summarized in detail [50]. According to Bucknall [50], the rubber particles were considered to bridge the crack as it propagates through the material. Thus, the rubber particles were able to prevent the crack growing to a catastrophic size. Here, second phase particles are considered in this regard to act like rubber particles to block the propagation of the crack if occurred. Thus, the second phase particles as crack preventers are responsible for the enhanced impact resistance.

A simple Lange model is presented [46] to relate the fracture energy G_c to the line tension T:

$$G_c = G_m + \frac{T}{D_s} \tag{1}$$

$$D_s = 2d_p(1 - V_p)/3V_p \tag{2}$$

where G_m is matrix toughness; D_s defined by Eq. (2) is interparticle spacing depending on particle diameter d_p and particle volume fraction V_p. Eqs. (1) and (2) predict that the composite fracture energy increases with decreasing the second phase particle size d_p. On the other hand, G_c would improve with increasing V_p for a given d_p [49]. In this study, d_p increases with increasing V_p. Consequently, the two competing effects of increasing both the second phase content and particle size determine G_c. Therefore, the fracture energy (here impact energy, namely impact strength) would initially increase with increasing the second phase content and reach a maximum and then fall with further addition of second phase content.

Furthermore, when cracking occurred, the progress of the crack could be prevented by the second soft phase particles. The enhancement in the impact strength may also be due to the depression of main crack growth with the formation of multiple crack growth, consequently leading to rough fracture surfaces similar to that of the rubber-toughened epoxies [51]. Indeed, relatively rough fracture surfaces as exhibited in Fig. 4 at both RT and 77 K were observed for the modified epoxy resins compared to that of the unmodified epoxy resin. Therefore, the increase in the impact strength (impact resistance) has been naturally observed in Table 3 by the addition of BGE.

3.4. Glass transition temperature

Glass transition temperature T_g of the unmodified and BGE-modified epoxy resins was measured by means of DSC. The variation in T_g for the epoxy systems with respect to the BGE content is also given in Table 3. T_g of the neat epoxy resin is 131.1 °C and was decreased by the addition of BGE. The glass transition temperature depends primarily on the chain flexibility and cross-linking density, etc., [52,53]. Since no stiff phenyl group in BGE molecule structures as in the DGEBF molecule structure, the introduction of BGE into DGEBF/DETD matrix system would decrease the T_g of epoxy matrix. On the other hand, the cross-link density spectrometer can provide the value of the relaxation time T_2, which correlates to the highly mobile part of the polymer networks, and the relative amount of rigid and mobile fractions of the polymer network. For cross-linked thermoset polymers, the quantity T_2 has been shown to be inversely proportional to cross-link density [54]. Namely, the higher the T_2 value, the lower the cross-link density. So, it can be inferred from Table 4 that the cross-linking density was reduced by introduction of BGE in DETD-cured DGEBF system. The decrease of the cross-linking density of DETD-cured DGEBF system would have also a negative effect on the T_g of the cured systems. Therefore, the glass transition temperature of BGE-modified DETD-cured DGEBF system is lower than that of DETD cured DGEBF system.

Table 4
The relaxation time T_2 of the unmodified and BGE-modified epoxy resins.

Relative BGE content (phr)	T_2 (ms)
0	0.94 ± 0.21
10	12.54 ± 2.20
20	24.97 ± 3.69
40	33.41 ± 4.56
60	55.35 ± 3.62

Since the internal stress is related to T_g, it becomes now possible to have a quantitative discussion on the effect of internal stress on the tensile response. The internal stress in the final epoxy samples can be divided into two parts based on the mechanisms causing the internal stress [55]. One is the shrinkage internal stress σ_1 caused by bulk shrinkage during curing period; another is the thermal stress σ_2 produced by the difference of thermal expansion coefficient between the epoxy resin and the steel mold. The shrinkage internal stress σ_1 is given by [55]:

$$\sigma = K_1 E \Upsilon \tag{3}$$

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:

$$\sigma_2 = K_2 \int_{T_1}^{T_2} E(\beta_2 - \beta_2) \mathrm{d}T \tag{4}$$

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

When the curing temperature is lower than T_g, the internal stress is the sum of Eq. (3) and Eq. (4) and is high [55]. The curing temperature 80 °C used in this study is generally lower than T_g except the 60 phr BGE case as shown in Table 3, thus it can be inferred that there will exist a high internal stress in the cured epoxy resins. Therefore, the previous explanation is reasonable about reduction of internal stress by introduction of soft BGE phase as a stress-releasing agent leading to the enhancement in the tensile strength of modified epoxy resins for the cases of 10–40 phr BGE contents. For the 60 phr BGE content, the curing temperature 80 °C is higher than T_g, the internal stress would be low [53]. However, the BGE-rich domains are jointed together to form large agglomerates (as shown in Fig. 2e) that are relatively weak and cannot carry efficient loading, thus formation of large weak aggregates would results in low tensile strength at high BGE contents.

4. Conclusions

A traditional reactive aliphatic diluent, *n*-butyl glycidyl ether (BGE, JX-013) with a very low viscosity of 2–3 mPa s, has been successfully used to modify the DETD-cured DGEBF system. It was interesting to observe that the cryogenic strength, ductility and impact resistance have simultaneously been enhanced by introduction of BGE at appropriate contents. The SEM micrographs of impact fracture surfaces showed that BGE-modified epoxy resins indicated a phase-separated fine structure, and the morphology of impact fracture surfaces is correlated well with the changes of the impact resistance. The DSC analysis showed that the T_g decreased with increasing the BGE content. Consequently, the present study could provide some valuable information about developing toughened DGEBF epoxy system for cryogenic engineering applications.

Acknowledgements

We gratefully acknowledge the financial support from the Chinese Academy of Sciences (Grant Nos. CXJJ-204, 2005-1-3 and 2005-2-1) and the National Natural Science Foundation of China (Grant Nos. 10672161 and 50573090). The kind help in measurement of the relaxation time T_2 from Prof. Li-Qun Zhang and his colleagues of Beijing University of Chemical Technology is highly appreciated.

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