Preparation and Characterization of DGEBA/EPN Epoxy Blends with Improved Fracture Toughness

Morteza Khalina[a], Mohammad Hosain Beheshty[a*], and Ali Salimi[b]

[a] *Department of Composites, Iran Polymer and Petrochemical Institute, Tehran, Iran*
[b] *Department of Resin and Adhesives, Iran Polymer and Petrochemical Institute, Tehran, Iran*

Abstract   The physical and mechanical properties of blends composed of two kinds of epoxy resins of different numbers of functional groups and chemical structure were studied. One of the resins was a bifunctional epoxy resin based on diglycidyl ether of bisphenol A and the other resin was a multifunctional epoxy novolac resin. Attempt was made to establish a correlation between the structure and the final properties of cured epoxy samples. The blend samples containing high fraction of multifunctional epoxy resin showed higher solvent resistance and lower flexural modulus compared with the blends containing high fraction of bifunctional epoxy resin. The epoxy blends showed significantly higher ductility under bending test than the neat epoxy samples. The compressive modulus and strength increased with increasing of multifunctional epoxy in the samples, probably due to enhanced cross-link density and molecular weight. Morphological analysis revealed the presence of inhomogeneous sub-micrometer structures in all samples. The epoxy blends exhibited significantly higher fracture toughness (by 23% at most) compared with the neat samples. The improvement of the fracture toughness was attributed to the stick-slip mechanism for crack growth and activation of shear yielding and plastic deformation around the crack growth trajectories for samples with higher content of bifunctional epoxy resin as evidenced by fractography study.

Keywords   Epoxy; Blend; Functionality; Mechanical property; Toughness

INTRODUCTION

Epoxy resins are widely used as matrix for fiber reinforced composites due to high mechanical strength and modulus, good adhesion property, and dimensional stability. However, as a consequence of their highly cross-linked structure, these materials tend to suffer from brittleness, poor crack resistance, and low fracture toughness, which limits their applications in certain areas[1–4]. Therefore, much research has been carried out to enhance the toughness of the cured epoxy resins without any significant loss in other properties[5–9]. Several methods have been proposed for increasing the toughness of epoxy resins[10–14], and one of the most effective approaches is the introduction of a second component which is capable of phase separation such as reactive liquid rubber[14–18], thermoplastic[19–22], or core-shell particles[22–25]. Considerable attention has been paid to the use of functionalized curing agents for epoxy resins.

The toughness of the epoxy resins could be improved by designing molecular structure of curing agents or synthesizing flexible curing agents, which is an increasingly popular option now. Crosslinked structures are formed using the functional groups of the resin components during cure process. The relationship between the chemical structures of the resin components and the mechanical properties of the cured resins has been studied by several groups[25–30]. Most of these studies treat the epoxy crosslink structures as homogeneous networks[31–37]. In the case of a given epoxy and a curing agent, highly crosslinked networks have shown considerable heat resistance and relatively low deformation capability. In addition to the conventional strategies expressed above for increasing the fracture toughness of epoxy materials, other approaches have also been employed for improving the toughness of these thermoset materials, including the use of different curing agents and blending epoxies of different functionalities and/or a combination of these methods.

Chen and Jan investigated the effect of matrix ductility on toughness in a carboxyl-terminated butadiene acrylonitrile rubber (CTBN)-toughened diglycidyl ether bisphenol A (DGEBA)-piperidine system[29]. These researchers changed the average matrix ductility *via* blending a DGEBA epoxy with two other resins with different ductility. The two epoxy systems added to the main DGEBA epoxy included a rigid and poly-functional 4,4′-diaminodiphenol methane (DDM) and a flexible diglycidyl ether of propylene glycol. Their results revealed that the fracture energy of the neat epoxy increased slightly with the increase in the resin ductility. Chen and Jan claimed that increasing matrix ductility increases the size of the plastic deformation zone and thus, contributing to

further toughening[29]. One may criticize this study by the fact that the network formed by blending two kinds of epoxies may be heterogeneous and that, this may affect the crack growth resistance of the material. Kishi *et al.*[30] examined the local strains in unmodified and rubber-toughened epoxies under multiaxial stress states. Matrix ductility was varied by using epoxide resins of different molecular weights. Similar to what was reported by Pearson and Yee[24], these researchers also observed that increasing the matrix ductility increases the plastic strain to failure, especially in a rubber-modified blend. Franco *et al.*[31] examined the relationship between mechanical properties and the degree of cross-linking in epoxy blends containing different amounts of polyoxypropylene (POPTA) *via* altering the hardener-to-epoxy ratio. They observed that the lowest fracture energy was obtained at the stoichiometric ratio of amine to epoxy[31]. They reported more ductile behavior when the cross-link density decreased at nonstoichiometric ratios of amine to epoxy. Arias *et al.*[33] varied the matrix ductility by changing the cross-linking agent. They used piperidine and 3DCM in curing of a DGEBA based epoxy resin. They reported a more ductile matrix in the piperidine-cured system where a larger post-yielding strain softening occurred. Kishi *et al.*[35] prepared four kinds of resin mixtures using seven types of DGEBA oligomers having different molecular weight distributions. Microscopy studies revealed the existence of inhomogeneous nanoscale gel structures in the cured resins. The morphological difference in terms of the size and the connectivity of the inhomogeneous gel structures and the relative magnitude of the heterogeneity would cause the difference in environmental resistance and the mechanical properties[35]. Zhang[36] reported a one-pot synthesis of aromatic polyester hyperbranched epoxy resin and its effect on the mechanical and thermal performance of the modified bisphenol-A (E51) hybrid resin. The hyperbranched resin had an important effect on the performance of the hybrid resin, and the performance of the resulting blends had maximum with the increase of hyperbranched resin content. The impact strength and fracture toughness of the hybrid resin with 9 wt% hyperbranched resin were almost 3.088 and 1.749 times of E51 performance, respectively. Mc Aninch *et al.*[37] blended high molecular weight DGEBA-based epoxies with liquid DGEBA to create several resins with equal epoxy equivalent weights. Overall, the increased polydispersity had almost negligible effect, with the main difference occurring in the slope of the glassy coefficients of thermal expansion; more polydisperse epoxies showed a slower increase in the coefficient of thermal expansion. Kishi *et al.*[38] studied the stability of nanostructures of epoxy/acrylic triblock copolymer blends. PMMA-*b*-PnBA-*b*-PMMA triblock copolymers (acrylic BCPs) having several compositions on the ratio of the block chains and the molecular weight were blended with diglycidyl ether of bisphenol-A epoxy thermosets. Several nanostructures, such as spheres, cylinders, curved lamellae, were observed in the cured blends. The stability of the nanostructures of the epoxy/acrylic BCP blends was attributed to the self-assembly mechanism[38]. Acebo *et al.*[39] used multiarm star polymers, with a hyperbranched poly(ethyleneimine) (PEI) core and poly(caprolactone) (PCL) arms end-capped with acetyl groups as toughening agents for epoxy/anhydride thermosets. The addition of the star polymers led to an improvement up to 130% on impact strength and a reduction in the thermal stresses up to 55%[39].

The present work was aimed to study the structure and properties of blends of epoxy resins of different functionalities. Two epoxy resins were employed, *e.g.*, a bifunctional DGEBA epoxy resin and a multifunctional EPN epoxy novolac resin. The effects of blend composition and network functionality were systematically investigated on the microstructure, mechanical properties, fracture toughness and solvent resistance of the resulting thermoset materials, hoping to establish a structure-property correlation.

EXPERIMENTAL

Materials

Two types of epoxy resins with the trade names of LV1189 (Iran Mokarar Co., Iran) and Epikote828 (Momentive Co., USA) were used in this work. LV1189 is a multifunctional epoxy resin while the Epikote828 is a bifunctional epoxy resin. 1,4-Butanediol diglycidyl ether (BDDGE), as a bi-functional linear reactive diluent (Iran Mokarar Co., Iran) was used to control the viscosity of compositions. The chemical structures of epoxy resins and BDDGE used in this work are shown in Scheme 1. An aliphatic amine curing agent with the trade name of HA76 (Iran Mokarar Co., Iran) was used for curing process.
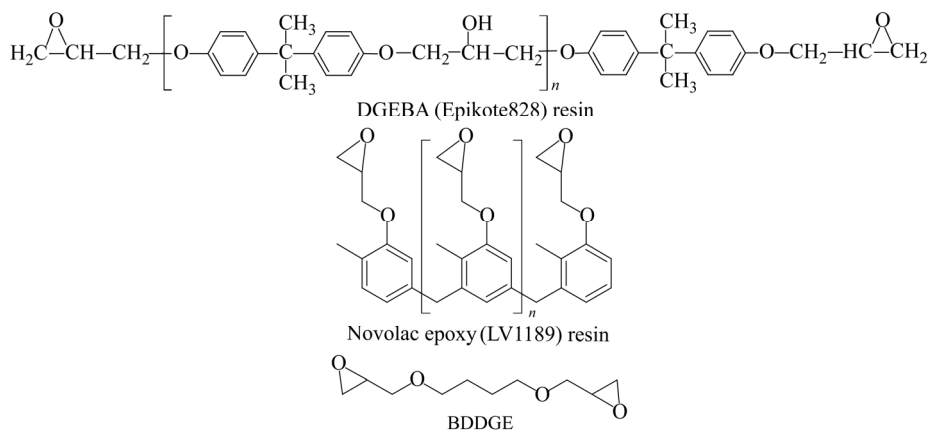
Scheme 1   Chemical structures of epoxy resins and BDDGE diluent

The general characteristics of the raw materials used in present work are shown in Table 1. LV1189 is a novolac-based epoxy resin, which is a semi-solid resin at ambient temperature. To measure its viscosity, the resin was firstly heated up to 80 °C and then its viscosity was measured at 80 °C.

Table 1   Main characteristics of raw materials used in this work

Material	Trade name	Epoxy equivalent weight (EEW) (g/mol)	Viscosity (mPa·s)
Multifunctional resin	LV1189	185	2400 (80 °C)
Bifunctional resin	Epikote828	182	12000 (25 °C)
Diluent	BDDGE	132	14.1 (25 °C)
Curing agent	HA76	52*	12.5 (25 °C)

*Amine H equivalent weight; AHEW

Measurement of Epoxy Equivalent Weight (EEW)
The epoxy equivalent weight was measured according to ASTM D1652 standard. The resin was first dissolved in an appropriate solvent such as di-chloromethane and then the resulting solution was reacted in direct or inverse titration using hydrogenbromide. The epoxy equivalent weight of the mixture (EEW_{mix}) was calculated from the Eq. (1).

$$EEW_{mix} = \frac{W_{mix}}{\dfrac{W_a}{EEW_a} + \dfrac{W_b}{EEW_b} + \cdots} \qquad (1)$$

where W_i and EEW_i are the weight and epoxy equivalent weight of component i in the mixture, respectively.

Sample Preparation
At room temperature, Epikote828 is a liquid resin while the LV1189 is a semi-solid resin. The blends of Epikote828 and LV1189 epoxy resins of different compositions were prepared. The raw resin was weighed for each sample and the predetermined amount of diluent was added. The resin-diluent mixture was mixed for 20 min by a mechanical mixer running at 400 r/min to obtain a homogenous resin and to cool down to ambient temperature. In the next stage the curing agent was added to the homogenous resin-diluent mixture and was mixed for further 15 min by a mechanical mixer running at 400 r/min.

The amount of curing agent (CA) required per 100 g of resin mixture under the stoichiometric conditions was calculated by Eq. (2).

$$CA\,(phr) = \frac{AHEW \times 100}{EEW_{mix}} \qquad (2)$$

where AHEW and EEW_{mix} are amine H equivalent weight and epoxy equivalent weight of mixture, respectively. At the end of mixing process and to remove the trapped bubbles, the mixture was placed in a vacuum oven at 25 °C and allowed to rest for 5 min, following another 5 min in vacuum. The E*x*L*y* notation was employed to refer to the different epoxy blends. The E and L denote the Epikote828 (bifunctional) and LV1189 (multifunctional) epoxies while the *x* and *y* refer to the weight fraction of individual epoxies in the blends. For example, E8L2 refers to the blend containing 80 wt% Epikote828 and 20 wt% LV1189. The composition and notation of different samples prepared are shown in Table 2.

All the samples were cured in moldings at ambient temperature for 24 h. They were then post-cured for 4 h at 80 °C to complete the curing process.

Chemical Resistance Test
The chemical resistance of the samples against acetone and methyl ethyl ketone (MEK) was evaluated. To determine the chemical resistance, a rectangular specimen of resin with the dimension of 75 mm × 25 mm × 3.2 mm was prepared and its weight was measured after complete curing and drying. The specimen was then immersed in acetone and MEK solutions and the change in weight of the sample after 24 h was recorded.

Mechanical Properties Test
The mechanical properties of the samples were measured under the bending and compression tests according to ASTM D790and ASTM D695 standards, respectively. To measure the bending properties specimens with the dimension of 80 mm × 13 mm × 3.2 mm were prepared and subjected to three-point bending test using SANTAM STM-150 universal testing machine (UTM). In the case of compression test, the specimens with the dimension of 13 mm × 13 mm × 20 mm were prepared and subjected to compression test. All the mechanical tests were carried out at room temperature at crosshead speed of 5 mm/min, and the reported mechanical properties are the average of at least four repetitions.

Fracture Toughness Test
The three-point single-edge notch bend (SENB) specimens were used to measure the fracture toughness of the samples according to ASTM D5045 standard test method. Rectangular specimens of approximately 57 mm × 12.7 mm × 6.4 mm were prepared; a notch of about 2 mm in depth was inserted using a fresh saw, and then a line of 1.0 mm in depth was drawn in the notch root with a fresh razor blade. The samples were then tested using the SANTAM STM-150 UTM device set at a bending speed of 10 mm/min at room temperature.

The plane strain critical stress intensity factor (K_{IC}), as a

Table 2   Composition and notation of different samples

Sample code	Epikote828 (phr)	LV1189 (phr)	BDDGE (phr)	EEW_{mix} (g/mol)	HA76 (phr)
E0L1	0	100	30	169.3	31.7
E2L8	20	80	30	168.9	31.8
E4L6	40	60	30	168.5	31.9
E6L4	60	40	30	168.1	31.9
E8L2	80	20	30	167.8	32.0
E1L0	100	0	30	167.4	32.1

measure of fracture toughness, was calculated using the Eq. (3).

$$K_{IC} = \frac{P_Q}{BW^{\frac{1}{2}}} f(x) \qquad (3)$$

$$f(x) = 6\sqrt{x} \frac{[1.99 - x(1-x)(2.15 - 3.93x + 2.7x^2)]}{(1+2x)(1-x)^{\frac{3}{2}}} \qquad (4)$$

where P_Q is the critical load for expansion of the sharp pre-crack, B is the sample thickness, W is the sample width and $f(x)$ is a dimensionless constant (shape factor) that depends on the geometry and mode of loading. Moreover, $x = \dfrac{a}{w}$ where a is the pre-crack length and w is the width of specimen.

The fractured surfaces of the samples were examined *via* SEM technique. The mode of failure and mechanisms of deformations were studied and proposed by the observation of fractured surface morphology of different samples.

Morphological Studies

The phase morphology of the samples was investigated by scanning electron microscopy (SEM) technique. For SEM analysis A VEGA model SEM operating at 15 kV made by Tescan Company was used to examine the fractured surface. The samples were cryo-fractured in liquid nitrogen and coated with a thin layer of gold prior to microscopic imaging.

RESULTS AND DISCUSSION

Chemical Resistance

Figure 1 shows the percentage of mass gain of different samples after being immersed in acetone and MEK solvents. In the case of neat epoxy resins (E0L1 and E1L0), the results reveal that the amount of mass gain for E1L0 resin in both solvents is higher than that for E0L1 resin. This is undoubtedly due to the microstructure of the E0L1 and E1L0 epoxy resins. E0L1 is a multifunctional epoxy while the E1L0 is a bifunctional epoxy resin. Therefore, it is expected that the network crosslink density in E0L1 epoxy should be much higher than that in E1L0 epoxy system. With an increase in crosslink density, the microstructure of epoxy resin becomes tighter which results in lower free volume and reduced
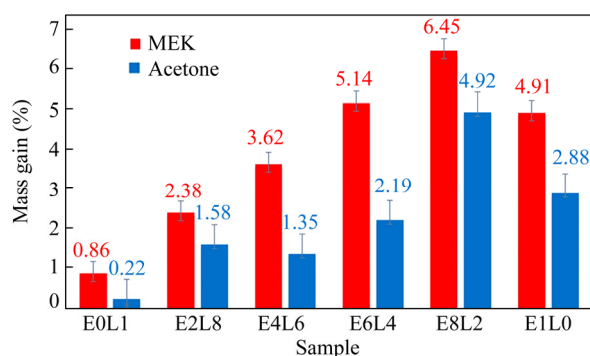
**Fig. 1** The amount of mass gain (wt%) after 24 h immersion in acetone and MEK

molecular chain movements[40–42]. As a result, the absorption and subsequent diffusion of solvent molecules into the epoxy microstructure become more restricted as the network crosslink density is increased. This is why the amount of mass gain for E0L1 epoxy in acetone (0.22%) and MEK (0.86%) solvents is much lower than that (4.91% for MEK and 2.88% for acetone) of E1L0 epoxy system.

It is clearly visible from Fig. 1 that with an increase in fraction of E1L0 epoxy in the blend up to 80% (*i.e.* E8L2 sample) the amount of mass gain for the resultant epoxy blend also increased. Further increase in the content of E1L0 epoxy to 100% led to a fall in the mass change in the presence of different solvents. The progressive increase in mass gain with E1L0 content in the epoxy blend up to 80% arises from the lower crosslink density of E1L0 epoxy than the E0L1 epoxy in the blend system, which gradually loosens the network structure of resulting epoxy system favorable for solvent absorption and diffusion into the bulk of epoxy blend. It is interesting to observe that when the epoxy system is composed of only E1L0 epoxy resin, a relatively significant fall in the amount of solvent absorbed happened. This is an unexpected result at first glance, as no fraction of multifunctional epoxy is present in this system. In fact, the solvent absorption data reveal that for E6L4 and E8L2 epoxy blends the extent of mass increase is higher than the neat Epikote epoxy sample (E1L0). In other words, blending at these compositions further facilitated the level of solvent absorption. It is believed that enhanced solvent absorption for E6L4 and E8L2 blend samples can result from the microstructure of these samples.

The presence of some microstructural heterogeneities in the forms of micro- and/or submicron phase separations (domains) may be responsible for increased solvent absorption as compared with the neat homogeneous E1L0 epoxy though the crosslink density of the latter epoxy is lower than that of E6L4 and E8L2 blends. In the case of solvent type, the solvent absorption data from Fig. 1 exhibited much higher capability of MEK solvent for absorption by the epoxy network than the acetone solvent. This is probably due to the higher polarity of MEK solvent compared with acetone solvent which makes the former solvent more compatible with the epoxy samples than the latter one[43–46]. Moreover, the solubility parameter of MEK solvent is probably closer to that of the epoxy samples compared with the acetone solvent. The smaller difference between the solubility parameters of solvent and the epoxy polymer is also an important factor that determines the amount of interaction between the solvent and polymer[47–51].

Mechanical Properties

Figure 2 shows the stress-strain curves obtained from three-point bending test for different epoxy samples. For E0L1 sample a linear stress-strain response is visible which indicates a completely brittle behavior for E0L1 epoxy sample. The multifunctional structure of neat E0L1 epoxy sample severely restricts the molecular movements and leads to a brittle response. In contrast, the bifunctional E1L0 neat epoxy with lower crosslink density exhibits higher ductility than the E0L1 epoxy system.
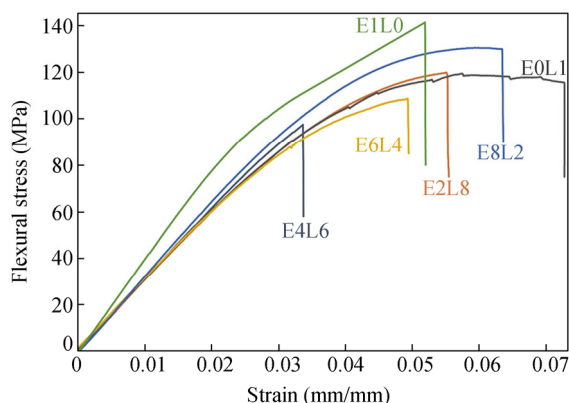
Fig. 2 The typical stress-strain curves of different epoxy samples obtained under bending test

For epoxy blend samples, the gradual incorporation of E1L0 epoxy into E0L1 epoxy up to blend containing 40% E1L0 epoxy gradually improved the ductility of the resulting material. Further increase in E1L0 fraction in the blend reduced the material's ductility to the level of E1L0 sample. The blend composition dependence of flexural strength also follows the same trend as that observed for the strain at break. It is interesting to observe that the E4L6, E6L4 and E8L2 blend samples show bending ductility higher than that of the neat E1L0 sample. A synergistic effect of the blending process on the material's ductility can be observed in these samples. This improved ductility comes from the microstructure of these blend samples. The flexural data obtained from the stress-strain curves are depicted in Table 3.

**Table 3** Mechanical properties of different samples obtained from bending tests

Sample code	Flexural strength (MPa)	Flexural modulus (GPa)	Deflection at break (%)
E0L1	100.0 ± 3.7	3.0 ± 0.1	3.7 ± 0.3
E2L8	123.7 ± 6.6	3.1 ± 0.2	6.6 ± 0.2
E4L6	121.7 ± 6.4	3.1 ± 0.1	6.4 ± 0.4
E6L4	108.3 ± 6.1	3.0 ± 0.1	6.1 ± 0.3
E8L2	129.0 ± 6.2	3.3 ± 0.2	6.2 ± 0.2
E1L0	140.7 ± 4.1	3.5 ± 0.2	4.1 ± 0.3

As can be seen in Table 3, the E1L0 neat epoxy showed higher flexural modulus than the E0L1 epoxy sample. The blending of 20%, 40% and 60% E1L0 epoxy with E0L1 epoxy did not change the flexural modulus of the resultant epoxy system. Further increase in fraction of E1L0 epoxy in the blend to 80% increased the flexural modulus of the ultimate epoxy, and the highest value of flexural modulus was observed for the neat E1L0 epoxy sample. The trend observed for flexural strength of epoxy samples as a function of blend composition is exactly the same as that observed for the flexural modulus. This is because these two parameters are directly related to the material's resistance to deformation. The higher flexural modulus and strength for E1L0 sample and epoxy blends achieved in Epikote epoxy compared with E0L1 sample and blends achieved in LV1189 indicate that the flexural modulus and strength are dominated by nonbonded intermolecular forces over chemical connection in glassy state[52, 53]. It appeared that the higher noncovalent intermolecular attractive forces drive the increased cohesive energy and result in the increased resistance to deformation and ultimate failure[52, 53].

In the case of deflection at break (Table 3), the data show that E0L1 sample had the lowest deflection. For E2L8 sample, the deflection increased sharply as compared with E0L1 sample. The gradual increase in E0L1 content in the epoxy samples from 20% up to 80% (*i.e.* E8L2 sample) tends to decrease the deflection at break of the resulting epoxy blend and finally a sudden fall in deflection can be observed for E1L0 sample. However, the deflection value of E1L0 sample is still greater than that of E0L1. The higher deflection at break for E1L0 sample compared with E0L1 sample is probably due to lower crosslink density in the former sample than the latter one. The lower crosslink density is corresponding to higher molecular weight between the crosslink points in the sample which is favorable to flexibility and deformability of the sample. The data demonstrate that the blend samples have higher deflection values than the neat epoxy samples. The highest deflection value was obtained for E2L8 sample.

The stress-strain curves of different epoxy samples obtained under the compression tests are depicted in Fig. 3. A ductile mode of failure can be observed for all samples in contrast with the bending tests presented earlier (Fig. 2). This is due to the difference in stress state and specimen geometry between the bending and compression tests[24]. The peak stress on the curves is related to the yield stress of the epoxy samples.
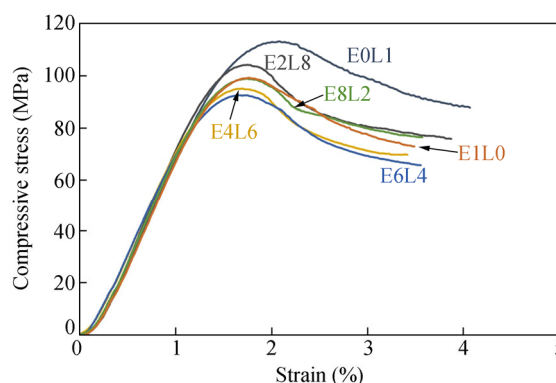
Fig. 3 Typical compressive stress-strain curves for epoxy samples

The compression modulus and strength of different epoxy samples are shown in Fig. 4. In the case of compression modulus, the data in Fig. 4 show that the E2L8 and E0L1 samples have the highest resistances against compression loadings. As can be seen in Fig. 4, the neat E0L1 epoxy has the highest compressive strength among the samples under investigation. The compressive strength of E1L0 sample is considerably smaller than that of the E0L1 sample. For the blend of epoxy samples, it can be observed that the addition of 20%, 40% and 60% E1L0 epoxy into E0L1 gradually reduced the yield strength of the epoxy sample to values even lower than that of neat E1L0 sample. The compressive strength of E8L2 is equal to that of neat E1L0 sample. It is interesting to note that the yield strength of E4L6 and E6L4 are lower than

that of neat E1L0 epoxy. This is because the aforementioned blends contained significant amounts of multifunctional E0L1 epoxy in their microstructure. This finding also results from the micro-structural morphology of the epoxy blends which renders lower yield strength values compared with the neat E1L0 epoxy resin[35]. These results indicate that the compressive properties are mainly dependent upon the crosslinking density in the samples, and the epoxy blends rich in multifunctional resin have higher compressive modulus, yield strength and compressive strength values than those rich in bifunctional resin. These findings indicate that the compressive mechanical properties are controlled by the chemical interconnectivity in the epoxy blends rather than intermolecular forces, opposed to flexural properties discussed earlier. The lower molecular flexibility as a result of higher crosslink density in epoxy blends rich in multifunctional resin shows more pronounced impact on the compressive modulus and strength rather than flexural modulus and strength in this work.
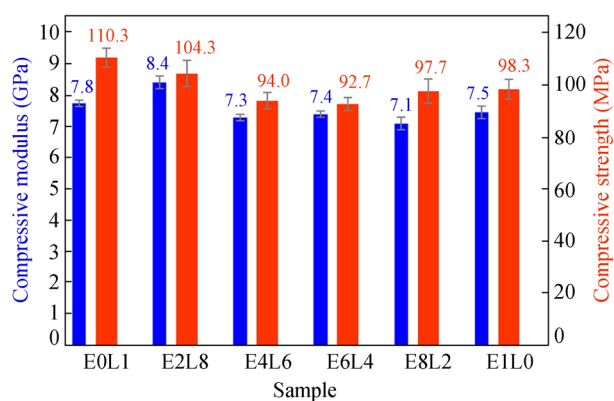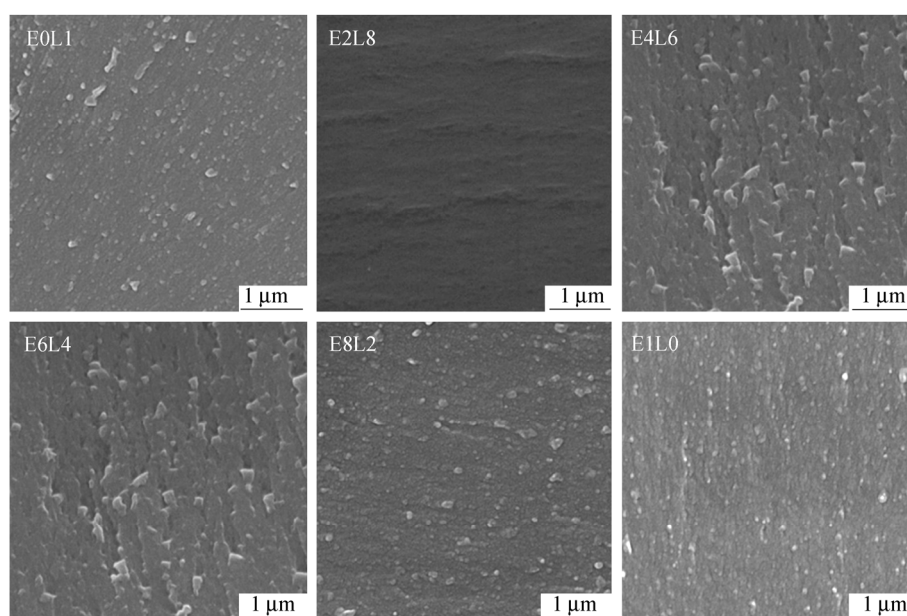

Fig. 4 Compressive modulus and strength of different epoxy samples

Morphological Studies

The SEM micrographs taken from cryo-fractured surfaces of different epoxy samples are shown in Fig. 5. As can be seen, the morphological texture of neat epoxy samples is similar to that of different epoxy blends. In fact, no significant difference can be found in the SEM micrographs of neat samples and epoxy blends. The SEM micrographs reveal the presence of numerous sub-micron spherical structures (particles) in the structure of different epoxy samples prepared in this work. No coarse phase separation can be observed in the microstructure of different epoxy blends.

Fracture Toughness

The results of fracture toughness (K_{IC}) data for different epoxy samples are depicted in Fig. 6. In the case of neat epoxy samples, the data show that the E1L0 neat epoxy has slightly higher fracture toughness value than the E0L1 neat epoxy. This finding can be attributed to the lower crosslink density of neat E1L0 epoxy than the neat E0L1 epoxy sample[24, 28, 30]. Lower crosslink density of E1L0 sample as compared with E0L1 sample causes more ductile macroscopic response of E1L0 sample than the E0L1 one under the mechanical and fracture mechanics test. The higher degree of ductility of E1L0 epoxy is favorable for higher shear yielding and plastic deformation under the fracture test, which in turn leads to larger fracture toughness value[24, 28, 30]. The fracture toughness data reveal that all the epoxy blends have higher fracture toughness values compared with the neat epoxy samples. The fracture toughness values of E6L4, E4L6 and E2L8 blends are approximately the same and slightly higher than that of the E8L2 epoxy blend. The much higher fracture toughness of blends with respect to the neat epoxy samples may be due to the heterogeneous microstructure of epoxy blends[35].

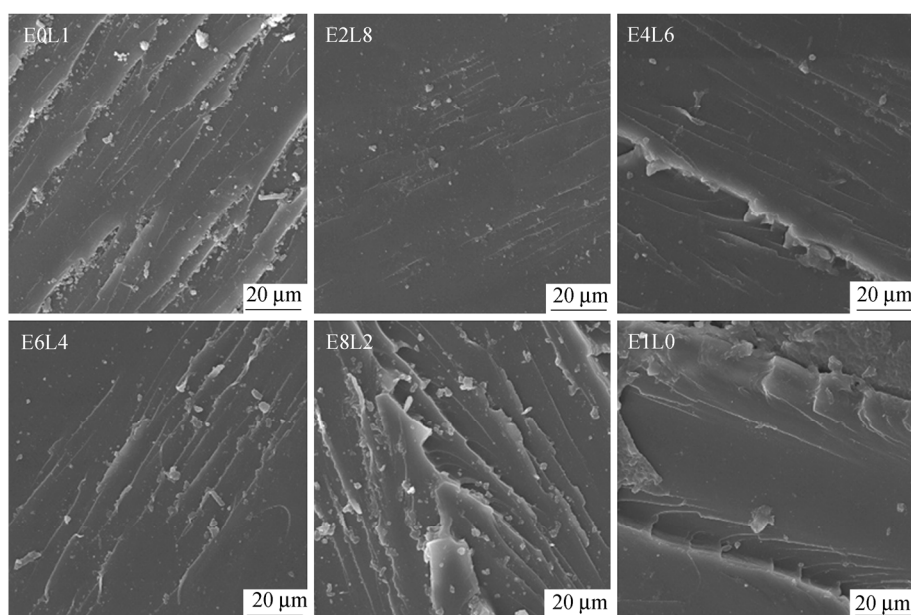**Fig. 5** FESEM micrographs taken from cryo-fractured surfaces of different epoxy samples
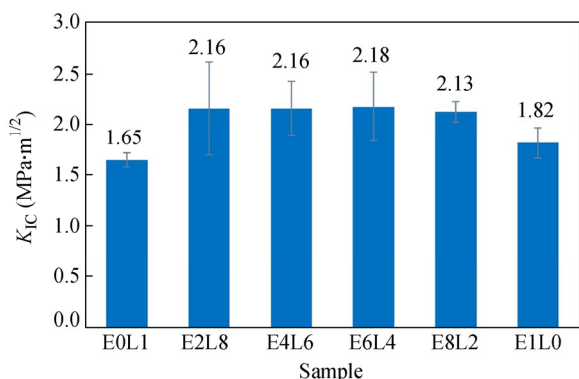
Fig. 6   Fracture toughness (K_{IC}) values of different epoxy samples

Fractographic Analysis

The study of the morphology of the fractured surface provides useful information about the mode of failure and mechanism of crack growth as well as the micromechanical deformations involved in the fracture process[24, 27]. The FESEM micrographs of the fractured surfaces of fracture test for different epoxy samples are shown in Fig. 7. For E0L1 sample, the fracture surface is covered with the coarse patterns most probably due to the formation and propagation of various microcracks during the fracture process[24]. Many particulate structures are also visible within the coarse fracture paths on the fractured surface of E0L1 sample. No considerable plastic deformation can be observed on the fractured surface and at crack growth trajectories on the fracture surface for E0L1 sample. The crack growth patterns are also visible on the fractured surface of E1L0 sample. However, the number of crack growth trajectories formed on the fractured surface of E1L0 sample is smaller as compared with E0L1 sample. These patterns on the fractured surfaces are also called riverline patterns and the related shear steps are attributed to the coalescence of satellite cracks[50, 51]. High magnification micrograph from the crack growth paths for E1L0 sample

reveals the development and activation of shear yielding mechanism during the fracture process. The shear yielded deformation produces blunting of the crack tip, bringing about the reduction of stress concentration near the crack tip which consequently improves the fracture toughness. This is in accordance with the higher fracture toughness of E1L0 sample than the E0L1 one[45–50]. The greater shear yielding (and therefore fracture toughness) of E1L0 sample compared with E0L1 sample is probably due to lower crosslink density in the former sample than the latter one. The lower crosslink density is favorable to higher ductility and deformability of the sample.

As shown in Fig. 7, the incorporation of 20% E1L0 epoxy into E0L1 epoxy (*i.e.* E2L8 epoxy blend) significantly changed the pattern of fractured surface of the resulting material. Besides, the pattern of fractured surface of E2L8 blend is different from that of E0L1 sample. No evidence of coarse crack growth trajectories can be observed for E2L8 sample. This indicates the higher resistance of the E2L8 sample against crack initiation and subsequent propagation compared with the neat epoxy samples[24]. The patterns apparent on the fracture surface are probably due to the stick-slip phenomenon involved in the crack initiation and propagation during the fracture process of the sample[24, 27]. The stick-slip phenomenon is a consequence of stable crack growth, which in turn, is governed by localized yielding and plastic deformation ahead of crack tip. As stated earlier, plastic deformation at the crack tip causes the crack-tip blunting which reduces the stress intensity and triaxiality of the stress state at the root of crack tip. Therefore, plastic deformation around the crack tip delays the crack propagation through the material, which is manifested by an increase in the fracture resistance of the material. This is why the fracture energy of the epoxy blends is improved. Similar fractured surface textures can be observed for E4L6 and E6L4 epoxy blends.

Fig. 7   SEM micrographs taken from the fractured surfaces of fracture test for different epoxy samples

CONCLUSIONS

Blends composed of two kinds of epoxy resins of different numbers of functional groups and chemical structures were prepared and their physical and mechanical properties were investigated. The samples containing a high fraction of multifunctional epoxy novolac resin generally showed higher solvent resistance and lower flexural modulus compared with the samples containing a high fraction of bifunctional epoxy resin. The epoxy blends showed significantly higher ductility (measured as deflection at break) under the bending test than the neat epoxy samples. Under the compression test, the compressive modulus increased with a 20% of increase of multifunctional epoxy to the bifunctional resin. The fracture toughness of neat bifunctional resin was slightly higher than that of the neat multifunctional resin which might be due to its aliphatic chemical structure and all the epoxy blend exhibited significantly higher fracture toughness compared with the neat samples.

The morphological analysis of the samples revealed the presence of inhomogeneous sub-micrometer structures in the bulk of all samples with no clear and coarse phase separation for blend samples. Fractography study of fractured surfaces of samples revealed the stick-slip mechanism for crack growth in samples and activation of matrix shear yielding and plastic deformation around the crack growth trajectories for samples with higher content of bifunctional epoxy resin.

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