



Research Article

PREPARATION, MORPHOLOGY AND THERMO/MECHANICAL PROPERTIES OF EPOXY RESINS MODIFIED BY POLYURETHANE

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Article History:Received 21st December, 2023Received in revised form 13th January, 2024Accepted 19th February, 2024Published online 28th February, 2024**Key words:**

Polyurethane (PUT); epoxy resins; modification; fracture toughness.

ABSTRACT

A series of blends were prepared by adding a Polyurethane (PUT) in varying proportions to diglycidyl ether of bisphenol A epoxy resin (DGEBA) cured with p-diamino diphenyl sulfone (DDS). The microstructure and thermo-mechanical properties were investigated as a function of the concentration of PUT and curing conditions. The thermal properties, measured by differential scanning calorimetry and thermogravimetric analysis showed that PUT could enhance the glass transition temperature (T_g) of the DGEBA epoxy resin and retain its thermal stability. The microstructure changed from sea-island to phase-inverted structure with the various concentrations of PUT. The fracture toughness, expressed as notched impact strength, increased with the addition of PUT and made the maximum value with 15-phr PUT. Fracture mechanisms such as crack deflection and branches, ductile microcracks, ductile tearing of the thermoplastic was responsible for the increase in the fracture toughness of the blends.

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INTRODUCTION

Epoxy resins have been utilized in high-performance composite applications because of their many desirable properties, such as high tensile strength and modulus, excellent chemical and solvent resistance, high dimensional and thermal stability, good creep resistance and adhesive properties. However, the epoxy resins are generally brittle due to their high crosslink densities, which limits their further proliferation into other applications which require more impact resistant. This drawback has prompted many studies devoted to increasing their fracture toughness without compromising their desirable attributes. For 10 years, the use of rigid thermoplastics to toughen highly crosslinked epoxy networks has emerged as an alternative to avoid the classical compromises between toughness and thermal stability associated with the rubber toughening [1-3], such as polyurethane (PUT) [4-5], polysulfone (PSF) [6-8], poly (ether sulfone) (PES) [9,10], poly (ether imide) (PEI) [11-13], polycarbonate (PC) [14,15], poly (ether ether ketone) (PEEK) [16,17] and so on. It is evident that the modifier types, concentration, molar mass and curing procedures all affect the curing reaction and phase separation of thermoplastic/ epoxy resin blends, varying one parameter may vary both the thermodynamics and kinetics of the curing process, which will have an influence on final morphologies, and hence on mechanical properties.

Polyurethane is a widely used polymer with flexible segments for elastic property and stiff segments to provide physical crosslinks for mechanical strength. The chain flexibility was

enhanced by introducing biphenyl into the polymer backbone, thereby improving its toughness and processabilities, making PUT more suitable for toughening epoxy resins. The use of PUT and its analogues as toughening agents for epoxy resins has not been reported in the open literature. Therefore, a series of blends were prepared by adding PUT to an epoxy resin to investigate the effect of cure cycles on the thermal properties, fracture toughness and phase morphology of the blends. The toughening mechanisms were also investigated in detail.

MATERIALS AND METHODS

The epoxy resin used in this study was two diglycidyl ether of bisphenol A (DGEBA), a two-functional, low-viscosity, amber liquid sold as WSR618 (weight per epoxide = 185-208 g) supplied by Sigma-Aldrich, India. The curing agent was p-diaminodiphenylsulfone (DDS) (supplied by Sigma-Aldrich, India), a pale pink powder. The thermoplastic toughening agent was an amorphous Polyurethane (synthesized using reported method [18] $M_w = 46\,325\text{ g mol}^{-1}$, $M_n = 22\,650\text{ g mol}^{-1}$), whose glass transition temperature is 268°C. The chemical structure of DGEBA, PUT and DDS are shown in Figure 1.

Sample preparation

All the blends were prepared using the melt mixing technique. The PUT was first dissolved in DGEBA epoxy resin at 130°C with constant mechanical stirring, until the PUT was completely dissolved. Stoichiometric (corresponding to a 1: 1 epoxy to amine molar ratio) hardener (DDS) was then added

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at the same temperature and mixed continually until the DDS had also completely dissolved. The ternary blends were transparent and visually homogeneous before curing. The samples were prepared with 0, 5, 10, 15, 20 phr of PUT in the DGEBA/DDS mixture, where phr represents the weight parts of PUT per hundred parts of the DGEBA epoxy resin. Each sample was poured into an open chrome steel mould and put into a vacuum oven to degas, then to cure in an air circulating oven in two procedures. After curing the oven was switched off and the plaques were allowed to cool slowly to room temperature in order to prevent cracking. Two different curing conditions were used in the sample preparations as follows:

- A. 150°C for 3 h plus 170°C for 3 h
- B. 150°C for 3 h plus 170°C for 3 h plus 200°C for 3 h.

Characterization techniques

Infrared studies were conducted to investigate the completion of curing reaction. Fully cured samples were powdered and the spectra of these samples in nujol mull pellets were recorded using a Perkin Elmer 257, USA Fourier transform infrared (FTIR) spectrometer from 4000 to 400 cm^{-1} . The glass transition temperature (T_g) for the cured samples was carried out by differential scanning calorimetry (DSC) using a DSC 2920 differential scanning calorimeter apparatus at a heating rate of 10°C min^{-1} under nitrogen. Thermogravimetric analyses were performed with a Perkin - Elmer Pyres 1 analyzer to investigate the thermal stabilities of DGEBA/PUT blends from 30 to 700°C at a heating rate of 20°C min^{-1} in a nitrogen atmosphere. The notched impact strength test was performed using the charpy impact strength measurement set (XCJ-4) according to the ASTM D 5942-96. The specimen dimensions were 60 mm \times 6 mm \times 4 mm. Five samples were used to measure the average impact strength reported for each condition. The fracture surfaces of the failed specimens from toughness measurement were analyzed with a KYKY2800B scanning electron microscope (SEM). In order to investigate the phase morphologies of the blends, the fracture surfaces after impact strength tests were etched with chloroform for 48 h to remove the PUT phase and then dried in vacuum for 24 h to remove the solvent. All the specimens were sputter-coated with a layer of gold before they were examined by microscope.

RESULTS AND DISCUSSION

Fourier transforms infrared studies

The FTIR spectra of the DGEBA/15 phr-PUT blends are given in Figure 2. The epoxy peak at 915 cm^{-1} disappeared after curing, indicating that no unreacted epoxy groups were present and the cure reaction reached completion. Other samples had the same phenomenon. This was further confirmed from DSC by the absence of an exothermic peak for the cured blends (see Figure 3).

Thermal behaviors of the DGEBA/PUT blends

In order to investigate the effect of the PUT on the glass transition temperatures (T_g) and thermal stabilities of the blends, the pure and toughened epoxy networks were measured by DSC and thermo gravimetric analysis (TGA), respectively. Figure 3 shows the DSC traces of these blends curing in condition B, which had no residual exothermic peak and no endothermic peak due to the melting of the DDS curing agent, indicating the completion of the curing reaction. A similar trend was observed in curing condition A. There was

only one single glass transition in the various content PUT of the blends except for 20 phr PUT. This did not mean that a homogeneous phase occurred but the concentration of PUT was too low, or may be the density of the crosslink networks were so high that the thermal effect of the molecular chain mobile was too small to be detected by the DSC with low sensitivity.

The two phase structures of blends were verified by the following micrograph of SEM (see Figure 6 below). The values of the glass transition temperatures are summarized in Table 1. It can be seen that the T_g of the blends was significantly higher than that of the pure DGEBA epoxy resin with the addition of PUT and the increasing curing temperature. However, curing temperature had a larger effect on the T_g than the loading of PUT due to the reduced viscosity at higher temperature, which enabled the epoxy resin to overcome any steric hindrance, react further, and produce a higher crosslink density material. The TGA traces provide the thermal stability and thermal degradation behaviors of the cured epoxy samples. Figure 4 shows the TGA thermo grams of the cured DGEBA/PUT systems in a nitrogen atmosphere. It is generally accepted that the thermal stability factors which are the indication of the thermal stability, including the initial decomposed temperatures (IDT), the temperature of maximum rate of degradation (T_{max}), and the activation energy for decomposition (E_t), can be determined from the TGA thermo grams [19]. The E_t value is calculated from TGA curves by the integral method of Horowitz and Metzger [20], according to the following equation:

$$\ln \left[\ln(1 - \alpha)^{-1} \right] = E_t \theta / RT_{max}^2 \quad (1)$$

where α is the decomposed fraction, E_t is the activation energy for decomposition, T_{max} is the temperature at the maximum rate of weight loss, $\alpha = T - T_{max}$, and R is the gas constant. The results of the IDT, T_{max} , and E_t of the blends with varied PUT contents are listed in Table 2.

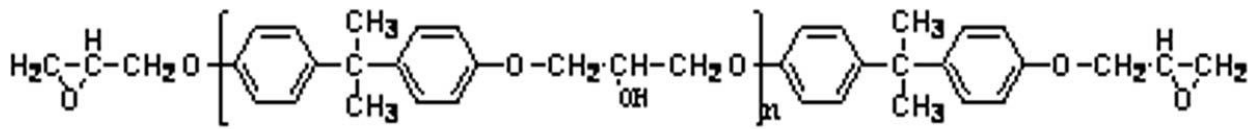
As results, the values of E_t was close to that of the unmodified epoxy resin, whereas the value of IDT and T_{max} were constant, indicating no deterioration in the thermal stability of the blends.

Fracture toughness and SEM observation

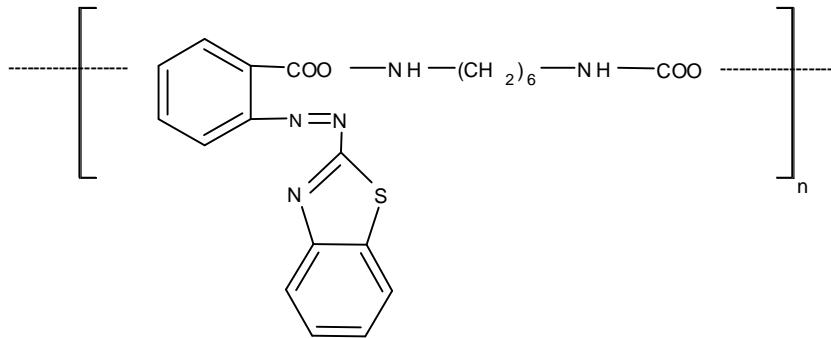
The fracture toughness is the resistance of a material to crack initiation and propagation. In the present case, the fracture toughness of the blends, expressed as notched impact strength, is plotted in Figure 5 as the function of the PUT concentration at different cure conditions. It can be seen that the impact strength of the epoxy resin increased with the addition of PUT, and the maximum values appeared at 15 phr PUT in curing condition B. In this case, a 65% increase in fracture toughness was obtained. However, the toughness of the samples were generally higher in curing condition B than that of curing condition A. This indicated that post-cure at a higher temperature reduced the number of unreacted sites and imparted greater mobility to all the species equally, allowing further phase separation to occur to increase the toughness [21].

The increase in fracture toughness occurred for many reasons, including the amount of the modifier in the blend, the interfacial adhesion between the phases, the curing conditions and so on [22-24]. One important requirement for obtaining

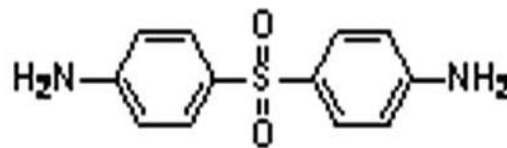
enhanced fracture toughness in a thermoset/thermoplastic blend is a two-phase morphology [25-28]. All of the blends in



DGEBA



PUT



DDS

Fig. 1 Chemical Structure of DGEBA, PUT and DDS

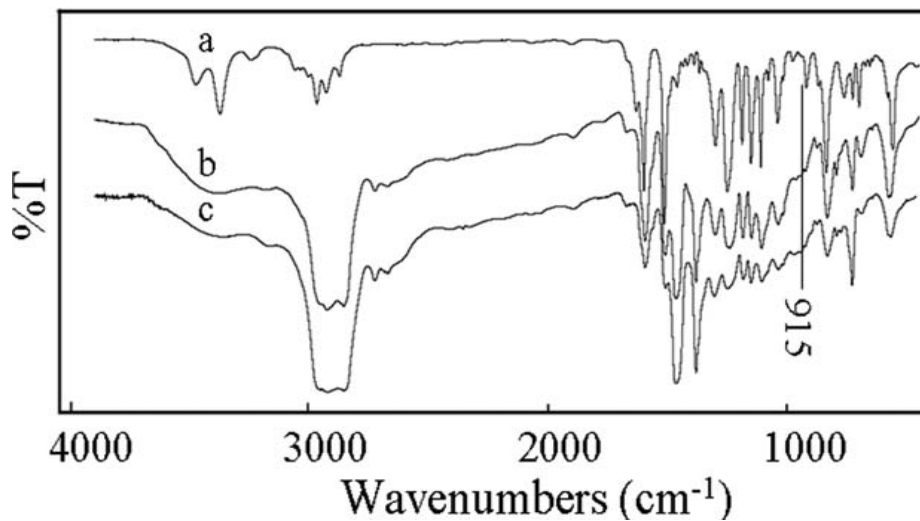


Fig. 2 FTIR spectrum of DGEBA / PUT (15-phr): (a) before curing; (b) after curing in condition A; (c) after curing in condition B.

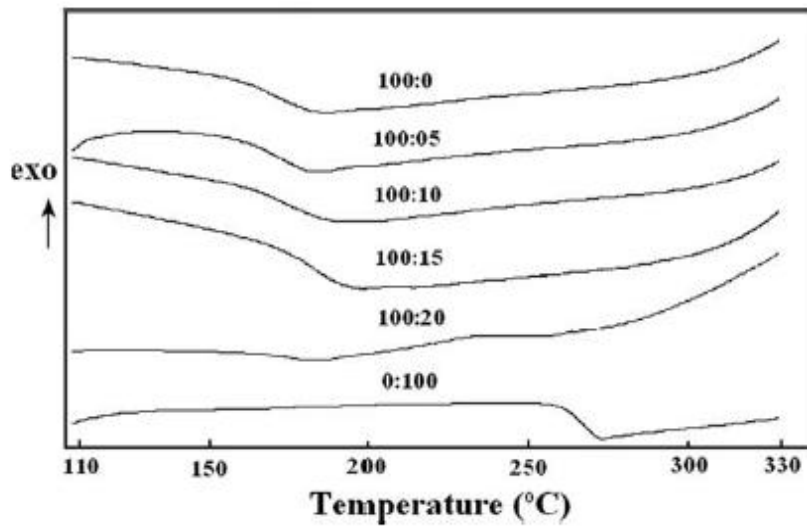


Fig. 3 DSC traces of DGEBA/PUT blends cured in condition B.

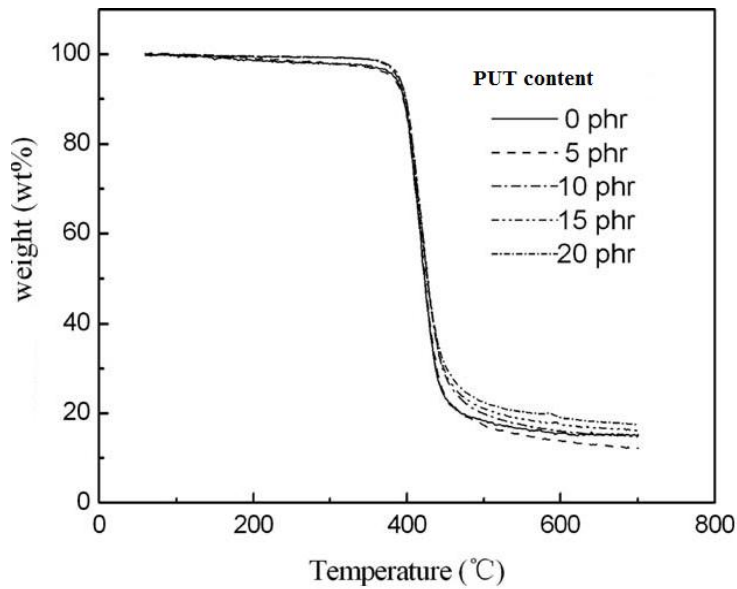


Fig. 4 TGA thermograms of DGEBA/PUT blends

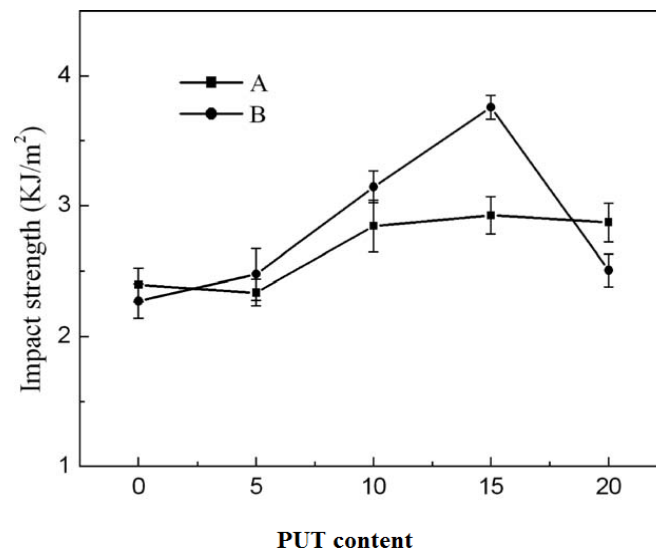


Fig. 5 Impact strength of DGEBA/PUT blends of varying curing conditions.

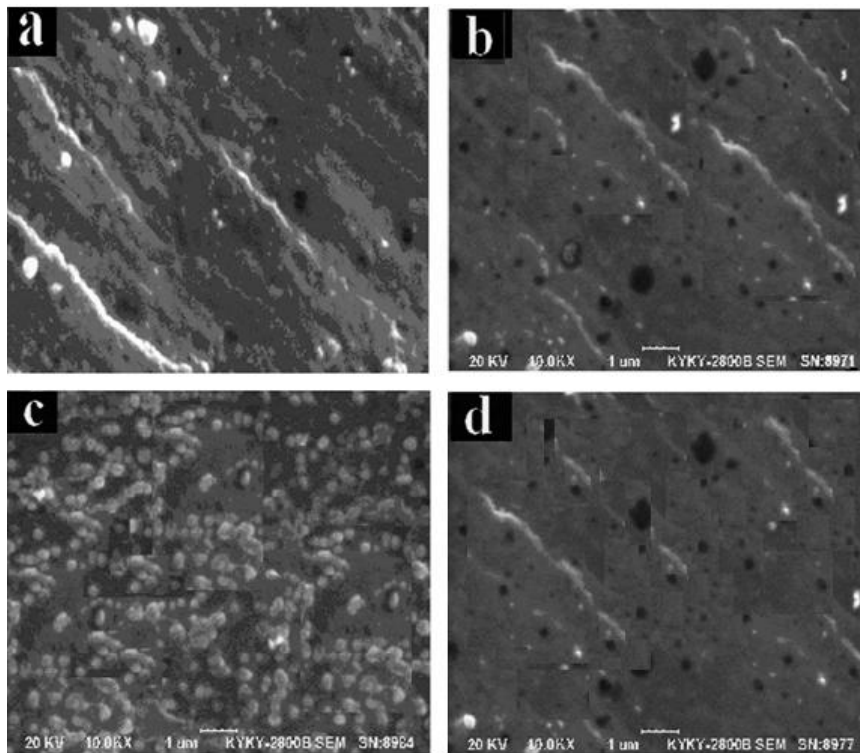


Fig. 6 SEM micrographs of DGEBA/PUT blends cured under condition B: (a) 5-phr PPBES; (b) 10-phr PPBES; (c) 15-phr PPBES ;(d): 20-phr PPBES.

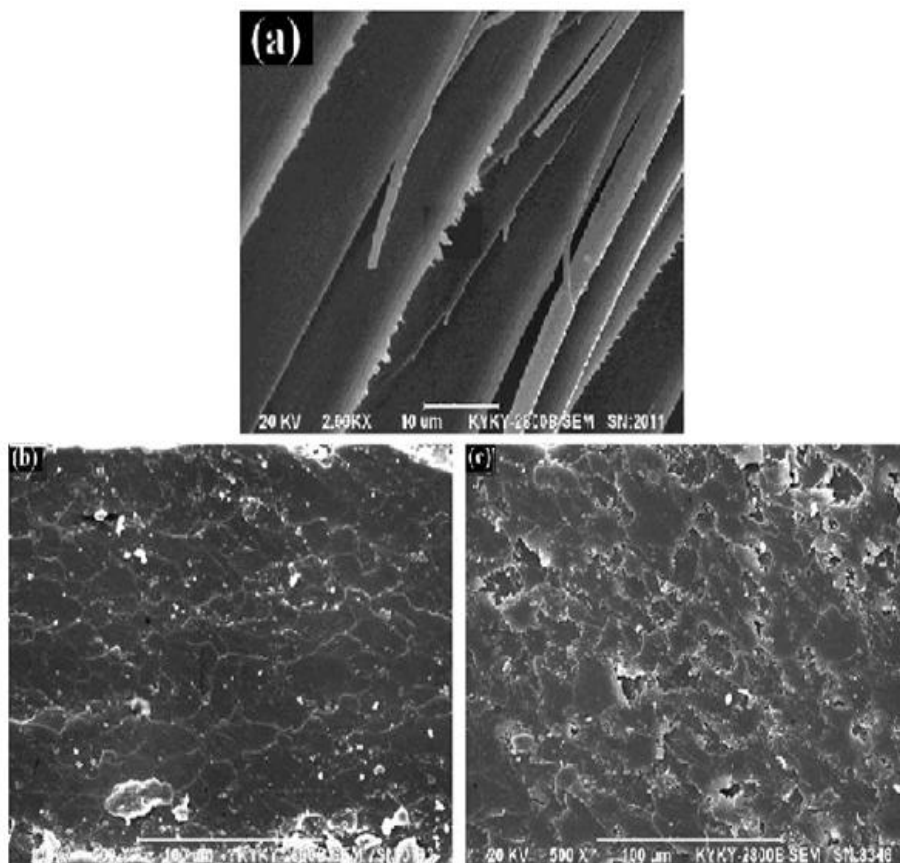


Fig. 7 Scanning electron micrographs of failed surfaces of DGEBA/PPBES blends cured by condition B: (a) neat epoxy resin; (b) 5-phr PPBES; (c) 15-phr PPBES.

Table 1 DSC data for the DGEBA/PUT blends.

| phr- PUT | Glass transition temperature (°C) | | | |
|------------|-----------------------------------|------------|-------------|------------|
| | A | | B | |
| | Epoxy phase | PUT phase | Epoxy phase | PUT phase |
| 0 | 154 | | 188 | |
| 5 | 158 | | 191 | |
| 10 | 160 | | 189 | |
| 15 | 175 | | 199 | |
| 20 | 178 | 248 | 208 | 257 |
| 100 | | 259 | | 259 |

Table 2 Thermal stability factors of DGEBA/PUT blends.

| phr- PUT | IDT (°C) | T _{max} (°C) | E _c (KJ mol ⁻¹) |
|-----------|------------|-----------------------|--|
| 0 | 402 | 425 | 188 |
| 5 | 399 | 422 | 186 |
| 10 | 398 | 420 | 166 |
| 15 | 398 | 419 | 165 |
| 20 | 400 | 420 | 158 |

this study were heterogeneous, and this satisfied an important condition for increased fracture toughness.

The morphologies of the PUT/DGEBA blends cured in condition B were analyzed by SEM. To get clear picture, the fractured surfaces were etched with chloroform. The scanning electron micrographs of the 5-, 10-, 15- and 20-phr blends are shown in Figure 6. Sea-island morphologies were observed in the blends except for the 15-phr PUT blend. The observed spherical cavities were due to the removal of the PUT inclusions during solvent etching, which indicating that there was no chemical interfacial bonding between epoxy and PUT and hence it retained its ductility that deformed plastically under loading. The 15-phr PUT showed a complete phase inverted structure. The interconnected epoxy resin globular particles distributed into the continuous PUT phase. This is why the fracture toughness was the maximum in this content. It can therefore be concluded that in the present case rigid non-functionalized thermoplastic particles have a small effect on the impact strength except for phase inversion.

To further investigate the toughening mechanisms, scanning electron micrographs were taken of the fractured surfaces of the failed specimens in different magnifications and these are shown in Figure 7. It can be seen that no plastic formation emerged on the fracture plane of the neat epoxy resin (see Figure 7(a)), and the fracture plane was smooth and featureless. This was a kind of typical brittle rupture. The fracture surfaces of the cured epoxy blends with PUT were different from that of the unmodified epoxy resin. The fracture surfaces were rough and river marks formed on the surfaces (see Figure 7(b) and (c)). These were evidence for the plastic deformation of the matrix, crack deflection and ductile nature of the crack. PUT, which diffused into epoxy resin, improved the plasticity of epoxy resin around the PUT dispersed phase. These diffused PUT particles can induce stress relaxation by way of local shear deformation. Furthermore, deformation energy was absorbed by the ductile drawing process of the PUT dispersed phase. In addition, the crack was split into some branches, which deviated from their original plane and initiated more ductile microcracks, resulting in increased

surface area of the crack, thereby increasing the toughness. All the aforementioned factors were favorable for the enhancement of the fracture toughness of the blends.

CONCLUSIONS

An investigation of the effects of curing conditions and the content of PUT on the thermo-mechanical properties of DGEBA/PUT blends was performed. It was found that the T_g of the blends was significantly higher than the pure epoxy in the two curing conditions, and the post-cure showed higher T_g. The TGA also proved the thermal stability of the blends was comparable with that of pure DGEBA epoxy resin. The SEM micrographs confirmed that all of the blends exhibited heterogeneity. The 15-phr PUT blend showed a complete phase-inverted structure and the maximum value of fracture toughness was obtained in this case. Several toughening mechanisms such as crack deflection and branches, ductile tearing of thermoplastic and the occurrence of ductile microcracks played a part in improving the toughness of the DGEBA/PUT blends.

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