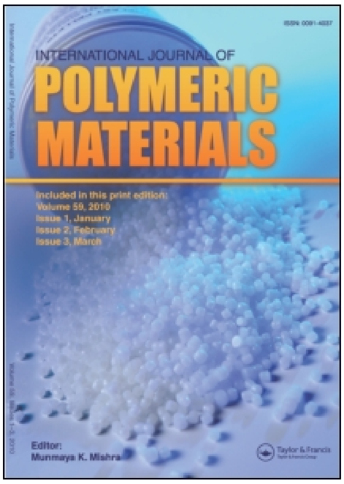

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Toughening of Diglycidyl Ether of Bisphenol-A Epoxy Resin Using Poly (Ether Ether Ketone) with Pendent Ditert-Butyl Groups

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Toughening of Diglycidyl Ether of Bisphenol-A Epoxy Resin Using Poly (Ether Ether Ketone) with Pendent Ditert-Butyl Groups

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Poly(ether ether ketone) (PEEKDT), hydroxyl terminated poly(ether ether ketone) (PEEKDTOH) and fluorine terminated poly (ether ether ketone) (PEEKDTF) with pendent ditert-butyl groups were synthesized by the nucleophilic substitution reaction of 4,4′-difluorobenzophenone with 2,5-ditert-butylhydroquinone in N-methyl-2-pyrrolidone medium using anhydrous potassium carbonate as catalyst. Diglycidyl ether of bisphenol-A epoxy resin was blended with PEEKDT, PEEKDTOH, and PEEKDTF, and cured with 4,4′-diaminodiphenylsulfone (DDS). The polymers formed heterogeneous blends before curing, and upon curing the polymers got dispersed in the epoxy matrix. The mechanical properties of the cured blends were slightly lower than that of the unmodified resin. The fracture toughness increased with the addition of ditert-butyl PEEK into epoxy resin and the extent of improvement was dependent on the type of modifier used. Hydroxyl terminated polymers gave up to 40% increase in fracture toughness. The dynamic mechanical spectrum of the blends showed only a single T_g *due to the proximity of the glass transition temperature of modified PEEK and DDS cured epoxy resin.*

Keywords: ditert-butyl PEEK, epoxy resin, fracture toughness, mechanical properties, morphology

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INTRODUCTION

Epoxy resins are some of the most commonly used thermosetting resins in composite industry. They are widely used as matrices for carbon fiber composites and in aerospace industry. Cured epoxy resins have good mechanical properties, thermal stability, and corrosion resistance. Also mold shrinkage is low and no volatile products are formed during curing [1]. A wide variety of chemical compounds can react with epoxy resin and hence a range of properties can be achieved by proper selection of the curing agent. A serious drawback of epoxy resins is their brittleness due to highly crosslinked structure. One method to improve the toughness of epoxy resins is the addition of rigid particulate fillers like silica, glass beads, and so on to epoxy resin. The degree of toughness was found to depend on the volume fraction, particle size, and shape of the filler [2–3]. Another method to improve toughness is the addition of rubber to epoxy resin. Two-phase systems with improved fracture toughness were formed on curing [4–7]. In rubber-modified systems toughening was achieved with reduction in modulus and high-temperature properties. Another way to improve the toughness is the addition of engineering thermoplastics to epoxy resins. Engineering thermoplastics can be used to toughen difunctional as well as multifunctional epoxy resins and toughness was achieved without loss of mechanical and thermal properties. Engineering plastics like polyether sulfone (PES), polyether imide (PEI), polyesters, and so on are used to toughen epoxy resins [8–20].

Poly (ether ether ketone) (PEEK) is a tough, semicrystalline high-performance thermoplastic polymer with good thermomechanical properties. Because of its semicrystalline nature, it is difficult to blend PEEK with epoxy resins. Hence only few references are available on blends of epoxy resins with PEEK polymers. Because the processing is difficult, amorphous PEEK like phenolphthalein poly (ether ether ketone) (PEK-C) or functionally terminated PEEK with bulky pendent groups were used for modifying epoxy resin [21–26]. Bennet et al. [17] investigated the fracture toughness and mechanical properties of DGEBA epoxy resin toughened with amine terminated tert-butylhydroquinone, methylhydroquinone, and bisphenol-A-based PEEK oligomers. In another study, Song et al. [21] found that amorphous PEEK (PEK-C) formed homogeneous blends with tetrafunctional epoxy resin. The fracture toughness decreased slightly with increase in PEK-C content. The effects of curing agent and curing conditions on the morphology were also investigated. According to Zhang et al. [22] lowering of cure temperature favoured homogeneous morphology in amine cured DGEBA/PEK-C blends. But Guo et al. [23] obtained heterogeneous blends at higher cure temperature. Also, Guo et al. [24] found that the morphology of epoxy/PEK-C blends depend on the nature of curing agent used. The phthalic anhydride cured system gave homogeneous morphology whereas maleic and hexahydrophthalic anhydride cured systems gave heterogeneous morphology. Recently, efforts were made by Brostow et al. [27–28] to develop low friction epoxy by the addition of fluorinated polyether ketone. They obtained 30% reduction in friction by the addition of 10% fluorinated polyether ketone and the properties were found to depend strongly on the morphology of the blends.

From the earlier discussion it is clear that the processability of blends could be improved by using PEEK with terminal functional groups and bulky pendent groups. The final properties are dependent on the morphology developed, which in turn is dependent on the type of curing agent and curing conditions employed. In the present authors' laboratory, a series of PEEK polymers were synthesized with pendent alkyl groups, which were used for toughening epoxy resin cured with 4,4′-diaminodiphenylsulfone. It was found that epoxy/modified PEEK blends followed autocatalytic curing mechanism [29] and PEEK with pendent methyl and tert-butyl group modified epoxy resin were tougher than the unmodified epoxy resin [30]. As a continuation of our effort to generate new class of blend systems, the authors synthesized PEEK with pendent ditert-butyl groups and blended it with epoxy resin. The phase behavior, mechanical properties, and fracture toughness are discussed in this article.

EXPERIMENTAL

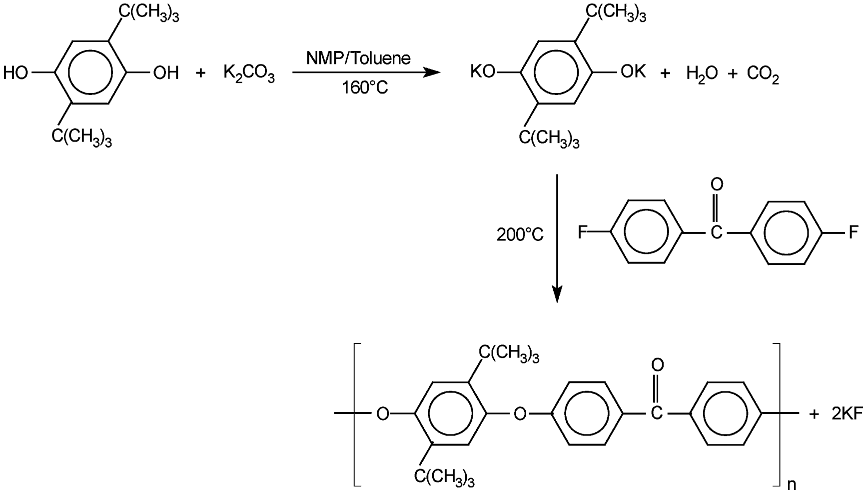
Materials Used

High purity 2,5-ditert-butylhydroquinone (DTBHQ) (Merck), 4,4′-difluorobenzophenone (DFBP) (Spectrochem), potassium carbonate (Qualigens), N-methyl-2-pyrrolidone (NMP) (SRL), and toluene (Qualigens) were used for the synthesis. DTBHQ and DFBP were vacuum dried at 90 and 60°C, respectively. Potassium carbonate was dried at 400°C in a muffle furnace before using. NMP was distilled under reduced pressure over P_2O_5 and stored over molecular sieves. Toluene was distilled over sodium and stored over sodium wire.

Diglycidyl ether of bisphenol–A (DGEBA) (LY 556, Ciba Geigy) with epoxide equivalent weight 188.68 and 4,4′-diaminodiphenylsulfone (DDS) (Merck) were used as received.

Synthesis of PEEK with Pendent Ditert-Butyl Groups

A hydroxyl terminated PEEK (PEEKDTOH), fluorine terminated PEEK (PEEKDTF), and a randomly terminated polymer (PEEKDT) with pendent ditert-butyl groups were synthesized by the nucleophilic substitution reaction of DFBP with DTBHQ, using excess of dihydroxy monomer, difluoro monomer, and 1:1 ratio of monomers, respectively. The reaction route for the synthesis of PEEKDT is given in Scheme 1. A typical procedure for the synthesis of PEEKDT is as follows. The polyether synthesis was conducted in a clean and dry four-necked flask equipped with a mechanical stirrer, thermowell, nitrogen inlet, and Dean-Stark trap outfitted with a condenser. The flask was purged with dry nitrogen before starting the reaction and charged with 32 g (0.18 mols) of DTBHQ, 44 g (0.22 mols) of potassium carbonate, and 295 ml NMP. The compounds were carefully washed into the flask using NMP. 150 ml toluene was added to the solution as an azeotroping agent. The reaction mixture was heated at 160°C for 4 h with constant stirring. Water formed during the reaction was removed as an azeotrope with toluene through the Dean-Stark trap. After 4 h, the reaction temperature was brought down to 100°C and 30 g (0.18 mols) of DFBP and 100 ml NMP were added to the flask. The reaction mixture was heated at 200°C for 3 h and cooled to room temperature. The polymer formed was precipitated by adding distilled water at room temperature. Complete precipitation was ensured by heating the



SCHEME 1 Reaction scheme for the synthesis of PEEKDT.

solution at 60°C with constant stirring. The precipitated polymer was filtered, purified by refluxing with water repeatedly, followed by soxhlet extraction using acetone as solvent and the product was dried under vacuum at 120°C for 24 h.

Blend Preparation

The polyethers were blended with epoxy resin using chloroform as solvent. Chloroform was removed by heating at 45°C with constant stirring and the residual solvent was removed by keeping the solution in vacuum for 24 h. On removal of solvent, the polyether reappeared as a fine dispersion in epoxy resin. PEEKDTOH blends were heated with 0.5 phr triphenylphosphine (TPP) to catalyze the reaction between epoxy and hydroxyl groups. No TPP was added along with PEEKDTF and PEEKDT blends. Stoichiometric amount of DDS was added to the blend, dissolved completely at 180°C and the mixture was evacuated in a vacuum oven at 180°C. After evacuation the mixture was transferred into an open mold kept at 180°C. The blend was cured in an air convection oven at 180°C for 3 h and post cured at 200°C for 2 h. After post curing the blends were allowed to cool slowly to room temperature. Blends with 0, 5, 10, and 15 phr polyether were prepared.

CHARACTERIZATION

The inherent viscosity of the polyethers was determined for 0.4% polymer solution in concentrated sulphuric acid at room temperature using Ubbelhode suspended level viscometer. The molecular weight and molecular weight distribution of the oligomers was determined using gel permeation chromatography (GPC) in chloroform. A Waters Alliance separation module in conjunction with Waters 410 differential refractive index detector was used. Flow rate was 1 ml/min and the machine was calibrated using polystyrene standards. Number average molecular weight ($\overline{M_n}$), weight average molecular weight ($\overline{M_w}$) and polydispersity index (PDI) were obtained from the chromatograms. The ^{13}C NMR spectrum of the polymer was recorded using Bruker Avance-300 spectrometer. $CDCl_3$ was used as solvent and tetramethyl silane as an internal standard. The FTIR spectrum of the polymer in KBr pellets was recorded using a Perkin Elmer Spectrum GXA FTIR spectrometer. The glass transition temperature of the polymers was determined using TA instruments model 2920 differential scanning calorimeter. A Siemens D5005 X-ray diffractometer with Cu-Kα radiation at 40 kV and 20 mA was used for the X-ray diffraction studies. The diffractograms were recorded at room temperature over 2θ range of 10–60°.

Mechanical Properties

Specimens for mechanical testing were machined to the required dimensions from cast laminates by cutting with a diamond wheel cutter. Tensile measurements were done according to ASTM D638. The measurements were done using a universal testing machine (model TNE 5000) at a crosshead speed of 10 mm/min. Flexural measurements were done according to ASTM D790 using rectangular specimens of $100 \times 10 \times 3$ mm at a crosshead speed of 10 mm/min. Flexural strength was calculated using the following equation:

$$\text{Flexural strength} = \frac{3\text{PL}}{2\text{bd}^2} \qquad (1)$$

where P is the load at break, L is the span length, and b and d are the breadth and thickness of the specimen, respectively. Flexural modulus was determined from the slope of the initial portion of flexural stress-strain curve.

Fracture Toughness

Fracture toughness of the blends was determined according to ASTM STP410. Rectangular specimens of $100 \times 35 \times 3$ mm were used for fracture toughness measurements. A notch of 5 mm was made at the center of one edge. A natural crack was made by pressing a fresh razor blade into the notch. The analysis was done in tension mode. The fracture toughness was calculated using Eq. 2.

$$\text{Stress intensity factor, } \text{K}_{\text{Ic}} = \frac{\text{QPa}^{1/2}}{\text{bd}} \qquad (2)$$

where P is the load at the initiation of crack, a is the crack length, b is the breadth of the specimen, d is the thickness of the specimen, and Q is a geometry constant. Q is calculated using Eq. 3:

$$Q = 1.99 - 0.41\left(\frac{a}{b}\right) + 18.7\left(\frac{a}{b}\right)^2 - 38.48\left(\frac{a}{b}\right)^3 + 53.85\left(\frac{a}{b}\right)^4 \qquad (3)$$

Scanning Electron Microscopy

The fracture surfaces of cryogenically fractured specimens were analyzed using Philips XL 20 scanning electron microscope. The cryogenically fractured surfaces were etched with chloroform for 24 h to remove the thermoplastic phase. The specimens were dried in vacuum overnight to remove the solvent. All the specimens were sputter coated with gold before taking the micrographs. The number average ($\overline{D_n}$) and weight average ($\overline{D_w}$) domain diameters and polydispersity index (PDI) were calculated using the following equations:

$$Number\ average\ diameter,\ \overline{D_n} = \frac{\sum n_i d_i}{\sum n_i} \tag{4}$$

$$Weight\ average\ diameter,\ \overline{D_w} = \frac{\sum n_i d_i^2}{\sum n_i d_i} \tag{5}$$

$$Polydispersity\ index,\ PDI = \frac{\overline{D_w}}{\overline{D_n}} \tag{6}$$

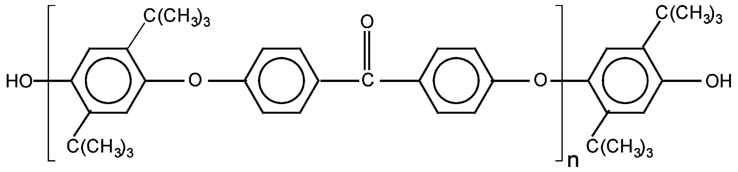
where n_i is the number of domains having diameter d_i.

Dynamic Mechanical Thermal Analysis

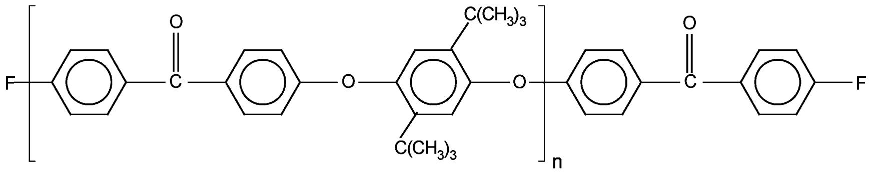
The viscoelastic properties of the neat resin as well as the blends were measured using a TA Instruments DMA 2980 dynamic mechanical thermal analyzer. Rectangular specimens of 60 × 10 × 3 mm were used for the analysis. The analysis was done in dual cantilever mode at a frequency of 10 Hz. The samples were heated from room temperature to 275°C at a heating rate of 3°C/min.

RESULTS AND DISCUSSION

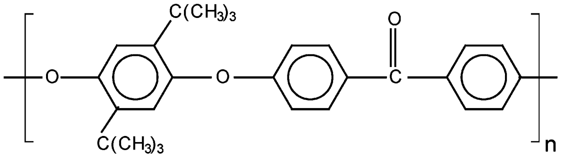
Hydroxyl terminated poly(ether ether ketone) (PEEKDTOH), fluorine terminated poly(ether ether ketone) (PEEKDTF) and random poly (ether ether ketone) (PEEKDT) with pendent ditert-butyl groups were synthesized by the nucleophilic substitution reaction of DFBP with DTBHQ in NMP medium using anhydrous potassium carbonate as catalyst at 200°C. PEEKDTOH and PEEKDTF were synthesized as per the modified Carother's equation. The chemical structures of the polymers are given in Figure 1. PEEKDTOH was taken as a representative among the various polymers for FTIR and NMR studies. The FTIR spectrum of PEEKDTOH gave absorption in the range 1450–1600 cm^{-1} corresponding to C=C stretching vibrations of aromatic ring. The peaks at around 1225 cm^{-1} and 1600 cm^{-1} are due to the stretching vibrations of ϕ–O and ϕ–CO respectively. The aromatic



PEEKDTOH



PPEEKDTF



PEEKDT

FIGURE 1 Chemical structures of PEEKDTOH, PEEKDTF, and PEEKDT.

C–H stretching is observed at 3038 cm^{-1}. Absorption at 2960 cm^{-1} is due to the C–H stretching vibrations of the methyl groups. The occurrence of a broad band between 3000 and 3500 cm^{-1} confirms the presence of hydroxyl groups. The ^{13}C NMR spectrum of PEEKDTOH along with the peak assignments is shown in Figure 2. The ^{13}C NMR spectrum showed 13 peaks corresponding to 13 distinguishable carbons in the polymer. The chemical shift assignments of various carbon atoms are based on the additivity constants for substituted benzene. The peak due to carbonyl carbon is seen in the range 194.3 ppm. The ditert-butyl carbon peak is observed at 34.5 and 30.2 ppm. The other peaks in the spectrum are due to aromatic ring carbons of the polymer. The inherent viscosity, number

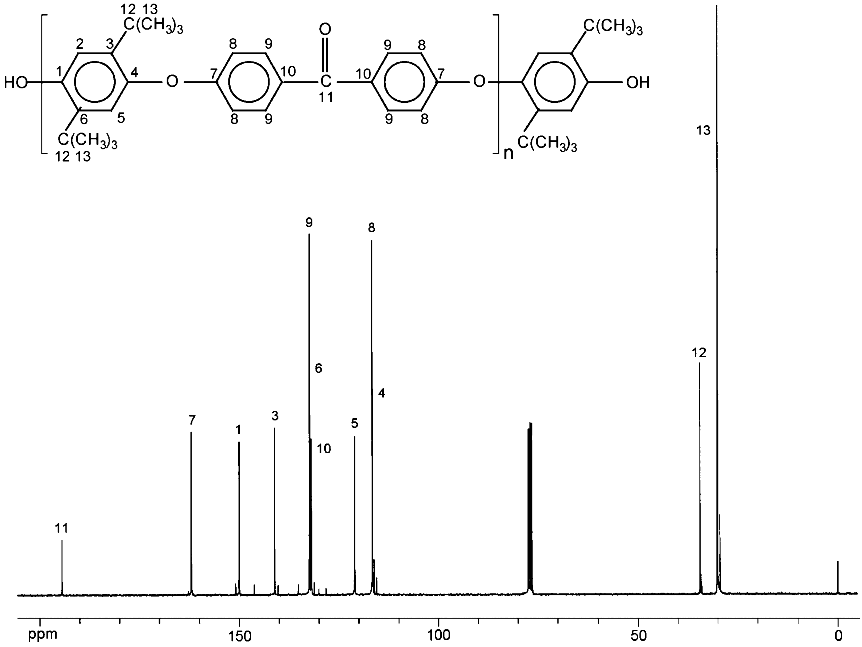


FIGURE 2 ^{13}C NMR spectrum of PEEKDTOH.

average molecular weight and T_g of the polymers are summarized in Table 1. The inherent viscosity increases with the molecular weight of ditert-butyl PEEK. The X-ray diffraction pattern of the polymers is given in Figure 3. All the polymers shows semicrystalline behavior, which is contrary to PEEK with pendent tert-butyl groups. PEEKDTF clearly gives sharp peaks in the figure revealing that it is more crystalline compared to PEEKDTOH and PEEKDT. The semicrystalline behavior of the PEEK with ditert-butyl groups is due to the symmetrical structure of the polymer.

TABLE 1 $\overline{M_n}$, Inherent Viscosity and T_g of PEEK Polymers with Pendent Ditert-Butyl Groups

Oligomer	$\overline{M_n}$ (g/mol)	Inherent viscosity (dl/g)	T_g (°C)
PEEKDT	17200	0.79	204
PEEKDTOH	8000	0.36	190
PEEKDTF	7500	0.27	184

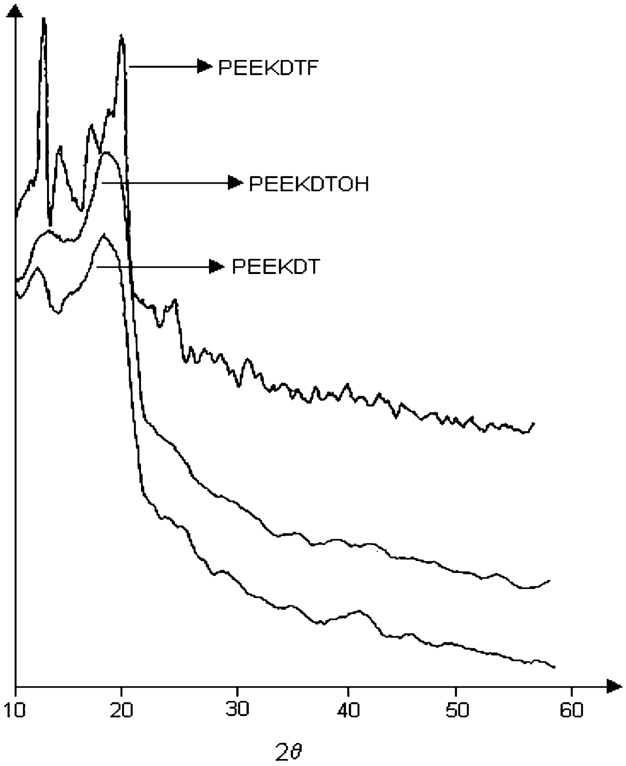
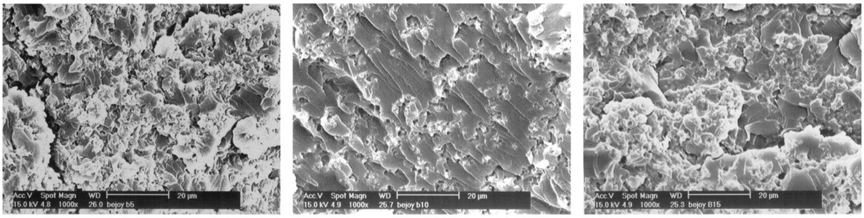


FIGURE 3 X-ray diffraction pattern of PEEK with pendent ditert-butyl groups.

Phase Morphology of the Blends

Epoxy resin/thermoplastic blend systems are divided into three main categories. They are homogeneous blends before and after curing, homogeneous blends that undergo reaction induced phase separation upon curing and blends that are heterogeneous before and after curing. DGEBA epoxy resin modified with PEEK with pendent ditert-butyl groups belonged to the third category. The modified PEEK polymers were immiscible with epoxy resin even at 200°C. Hence blends were prepared by dispersing the polymer in epoxy resin uniformly by using chloroform as solvent followed by evaporation of the solvent. The scanning electron micrographs of the extracted fracture surfaces of DGEBA/PEEKDTOH and 15 phr blends of PEEKDTF and PEEKDT with epoxy resin are shown in Figures 4



5phr 10phr 15phr

FIGURE 4 Scanning electron micrographs of DGEBA/PEEKDTOH blends.

and 5, respectively. All the systems showed similar morphology. Reaction-induced phase separation has not occurred due to heterogeneity in the blend before curing. As a result the domain distribution was not uniform even though the system looks to have uniform dispersion. The distribution of the domains was not as uniform as in hydroxyl-terminated PEEK with pendent tert-butyl groups (PEEKTOH) toughened epoxy resin [30]. Furthermore, the domains were not spherical as in reaction-induced phase-separated systems. The number average and weight average domain diameters and polydispersity index for the blends are given in Table 2. The domain size of DGEBA/PEEKDTOH blends increased with increase in PEEKDTOH in the blends. The domain diameters of 15 phr PEEKDTF and PEEKDT blends were higher than that of 15 phr PEEKDTOH modified epoxy resin. In general, the domain diameter of PEEKDT-modified epoxy resin was higher than hydroxyl and fluorine terminated ditert-butyl PEEK-modified epoxy resin due to the high molecular weight of the former.

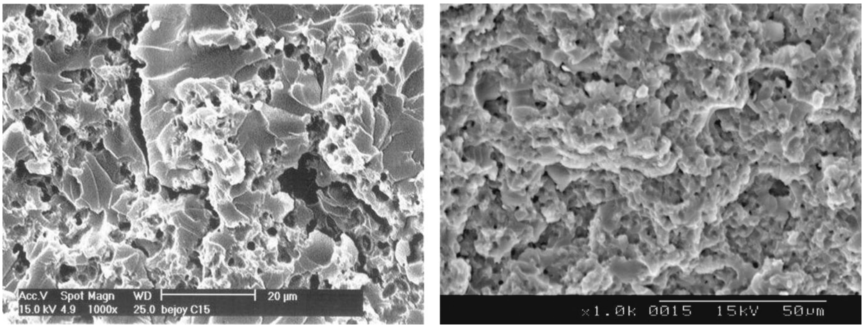


FIGURE 5 Scanning electron micrographs of 15 phr blends of DGEBA/PEEKDTF and DGEBA/PEEKDT.

TABLE 2 $\overline{D_n}$, $\overline{D_w}$ and PDI of DGEBA/Ditert-Butyl PEEK Blends

Composition (phr)	$\overline{D_n}$ (μm)	$\overline{D_w}$ (μm)	PDI
DGEBA/PEEKDTOH			
5	1.49	1.55	1.04
10	1.35	1.40	1.03
15	1.70	1.75	1.03
DGEBA/PEEKDTF			
15	1.85	2.05	1.11
DGEBA/PEEKDT			
15	1.96	2.04	1.04

Dynamic Mechanical Thermal Analysis

The viscoeleastic properties of the blends were studied using dynamic mechanical thermal analysis. The tan δ against temperature plot for DGEBA/PEEKDT and DGEBA/PEEKDTF blends are shown in Figures 6 and 7, respectively. A single relaxation was observed for

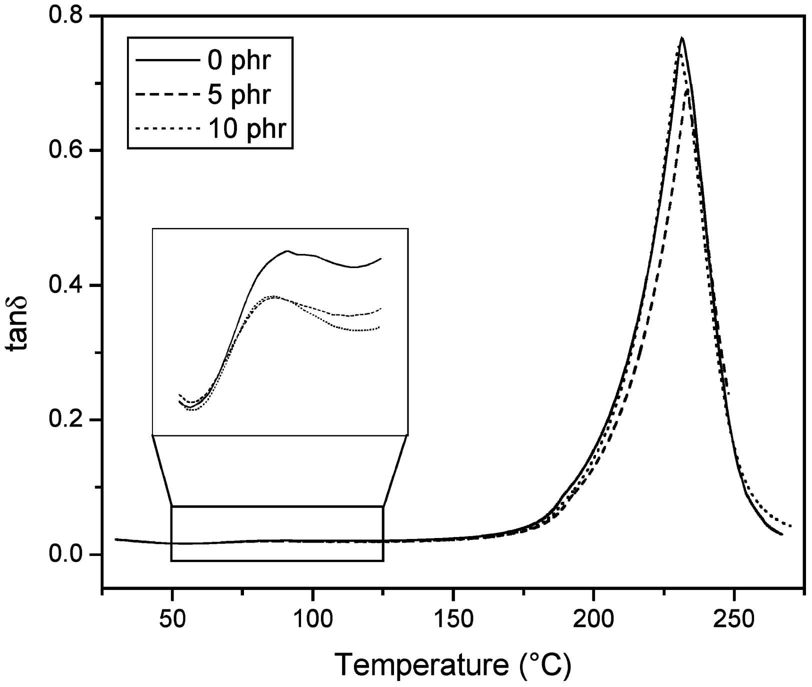


FIGURE 6 tan δ against temperature plot of DGEBA/PEEKDT blends.

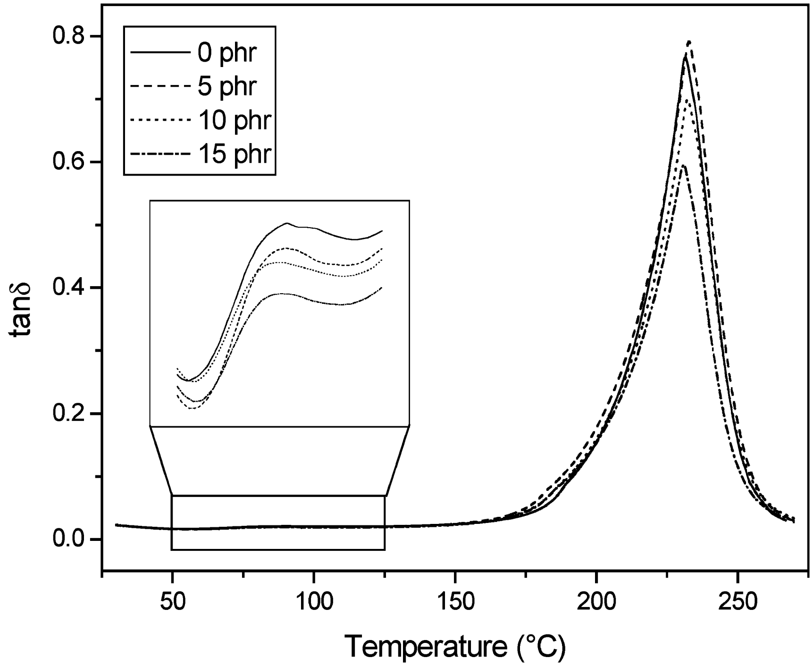


FIGURE 7 tan δ against temperature plot of DGEBA/PEEKDTF blends.

unmodified epoxy resin and the blends. Even though the blends showed two-phase morphology, single glass transition peak was observed in the dynamic mechanical spectrum due to the proximity of T_g of ditert-butyl PEEK polymers and cured epoxy resin. The tan δ values of the blends between 50 and 125°C are shown as inset in the figures. A small relaxation termed ω-relaxation was observed in the spectrum. The ω-relaxation was either due to the lower crosslink density sites in the epoxy network or due to the β-relaxation overtones in the regions of higher crosslink density matrix that are occluded in the lower crosslink density matrix [31–32]. The T_g did not show any shift toward lower temperature indicating no change in the crosslink density of epoxy resin. In PEEKDT modified epoxy resin, peak height remained close to that of neat epoxy resin. In PEEKDTF-modified epoxy resin, peak height decreased slightly. The variation of storage modulus of PEEKDTF and PEEKDT modified epoxy resin are shown in Figures 8 and 9, respectively. A sharp decrease in modulus is seen near the glass transition region. The modulus of the blends was higher than that of neat epoxy resin till the glass transition and thereafter slightly lower values than epoxy resin was observed. The loss modulus

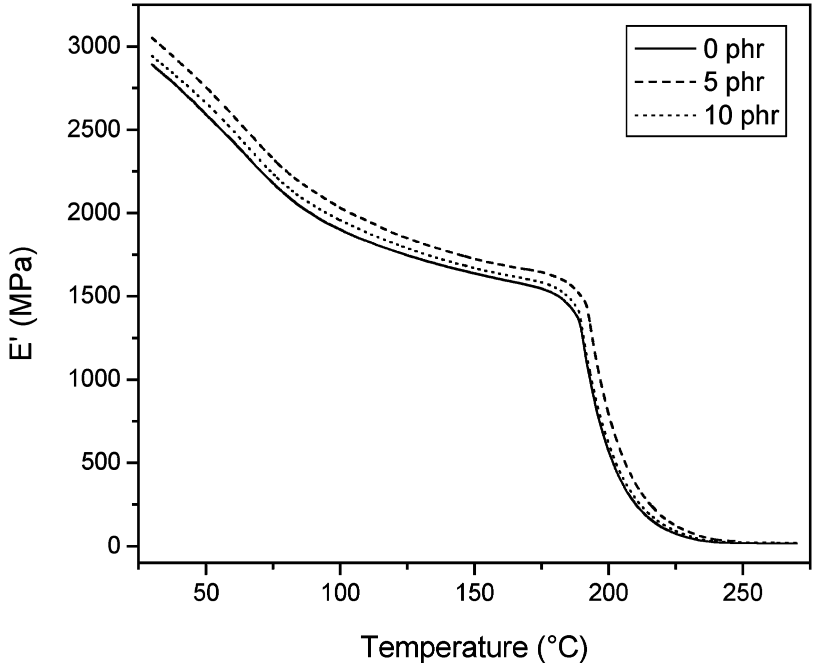


FIGURE 8 Storage modulus vs. temperature plot for DGEBA/PEEKDT blends.

of the blends are shown in Figures 10 and 11, respectively. The loss modulus of the blends were higher than that of neat epoxy resin at room temperature.

Mechanical Properties

The tensile and flexural properties of ditert-butyl PEEK-modified epoxy resin are summarized in Table 3. The tensile strength decreased with increase in ditert-butyl PEEK in the blends. The Young's modulus of the blends decreased with addition of ditert-butyl PEEK except for PEEKDTOH blends, where the reduction in modulus was only marginal. The flexural strength decreased whereas the flexural modulus was unaffected by blending with ditert-butyl PEEK. The decrease in properties was due to the immiscibility of the thermoplastic in epoxy resin and lack of good interfacial adhesion between epoxy and ditert-butyl PEEK polymers. It is to be noted that among the different blend systems investigated, PEEKDTOH blends showed less decrease in properties. During the preparation of blends, epoxy/PEEKDTOH

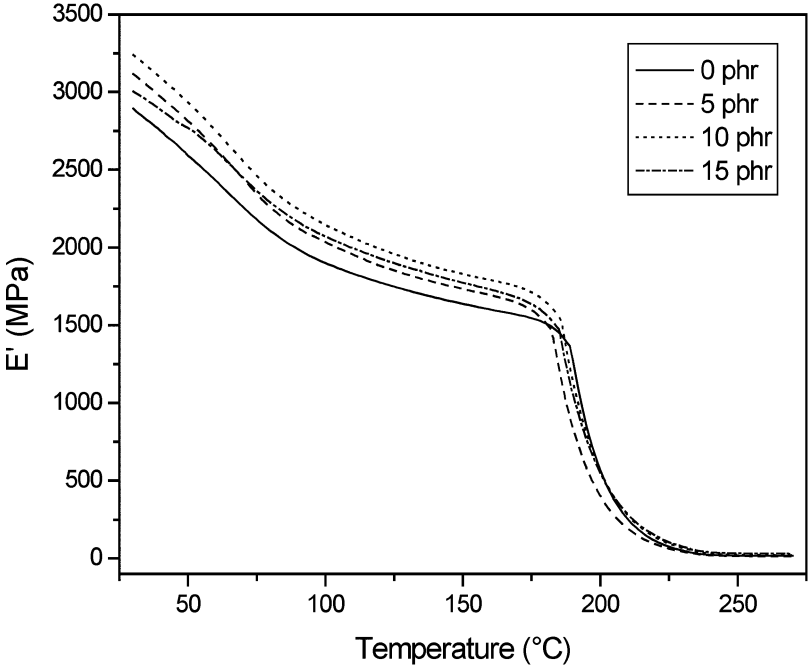


FIGURE 9 Storage modulus vs. temperature plot for DGEBA/PEEKDTF blends.

blends were heated with TPP. Some of the hydroxyl groups might have reacted with the epoxy groups thereby incorporating PEEKDTOH chains in the epoxy network. Therefore, the properties of PEEKDTOH blends were better than that of PEEKDTF and PEEKDT blends.

The tensile stress-strain curves of DGEBA/PEEKDTOH blends are shown in Figure 12. No yielding was observed in the stress-strain curves. This is typical of brittle materials. The strain decreased with increase in PEEKDTOH content in the blends. The stress-strain curves for 5 phr blends of all the blend systems are shown in Figure 13. All the blend systems showed similar behavior. The strain varied slightly among the different systems and was dependent on the modifier used. The flexural stress-strain curves of 5 phr blends are shown in Figure 14. The flexural strain of the blends was lower than that of neat epoxy resin and changed with the modifier used. The mechanical properties of the ditert-butyl PEEK were lower than that of PEEK with pendent tert-butyl groups [30]. The reduction in mechanical properties was due to the fact that the ditert-butyl PEEK-modified epoxy resin was heterogeneous before curing. In other cases

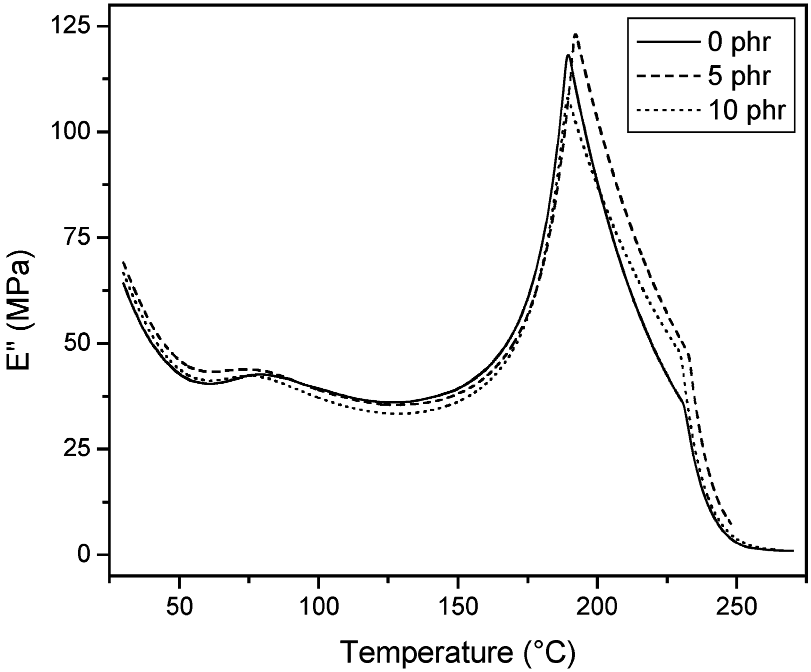


FIGURE 10 Loss modulus vs. temperature plot for DGEBA/PEEKDT blends.

reaction-induced phase separation occurred, resulting in a fine dispersion of the domains in the epoxy matrix.

The fracture toughness of the blends expressed as stress intensity factor (K_{Ic}) is given in Table 4. Blending of epoxy resin with ditert-butyl PEEK increased the fracture toughness of the product. The fracture toughness was dependent on the type and amount of ditert-butyl PEEK used to modify epoxy resin. In PEEKDTOH and PEEKDT modified epoxy resin, the fracture toughness decreased on increasing their concentration from 5 phr to 15 phr. PEEKDTF toughened epoxy resin did not show much change with respect to composition. Maximum toughness was attained by the addition of 5 phr PEEKDTOH to epoxy resin. The fracture toughness of blends with hydroxyl and fluorine terminated polymers were higher than that of the randomly terminated polymer (PEEKDT)-modified epoxy resin. The higher fracture toughness was due to the presence of intermolecular interactions between the thermoplastic and the epoxy resin. Even though randomly terminated polymer also had functional groups, the number of chain ends was less due to the high molecular weight compared to that of the

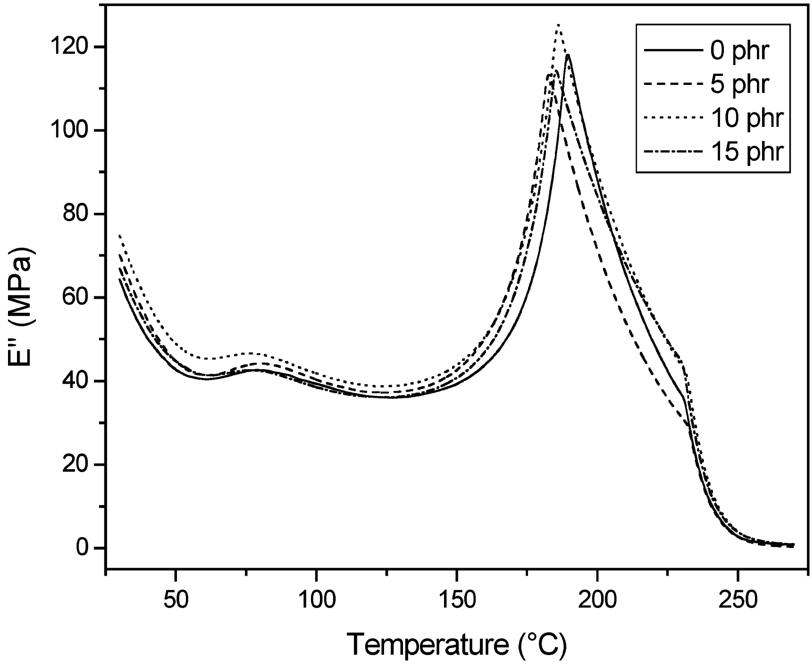


FIGURE 11 Loss modulus vs. temperature plot for DGEBA/PEEKDTF blends.

TABLE 3 Mechanical Properties of DGEBA/Ditert-Butyl PEEK Blends

Ditert-butyl PEEK content (phr)	Tensile strength (MPa)	Young's modulus (GPa)	Flexural strength (MPa)	Flexural modulus (GPa)
0	60 ± 4	1.70 ± 0.12	122 ± 6	2.95 ± 0.11
PEEKDTOH				
5	54 ± 4	1.55 ± 0.06	97 ± 2	2.93 ± 0.10
10	50 ± 2	1.57 ± 0.07	101 ± 2	3.05 ± 0.12
15	50 ± 3	1.72 ± 0.10	68 ± 1	2.89 ± 0.09
PEEKDTF				
5	63 ± 1	1.40 ± 0.05	96 ± 1	2.90 ± 0.07
10	54 ± 4	1.32 ± 0.03	75 ± 3	2.95 ± 0.08
15	51 ± 3	1.07 ± 0.02	76 ± 2	3.01 ± 0.12
PEEKDT				
5	58 ± 4	1.37 ± 0.07	92 ± 2	3.00 ± 0.13
10	56 ± 3	1.16 ± 0.03	88 ± 7	2.73 ± 0.09
15	49 ± 3	1.27 ± 0.05	83 ± 2	3.17 ± 0.10

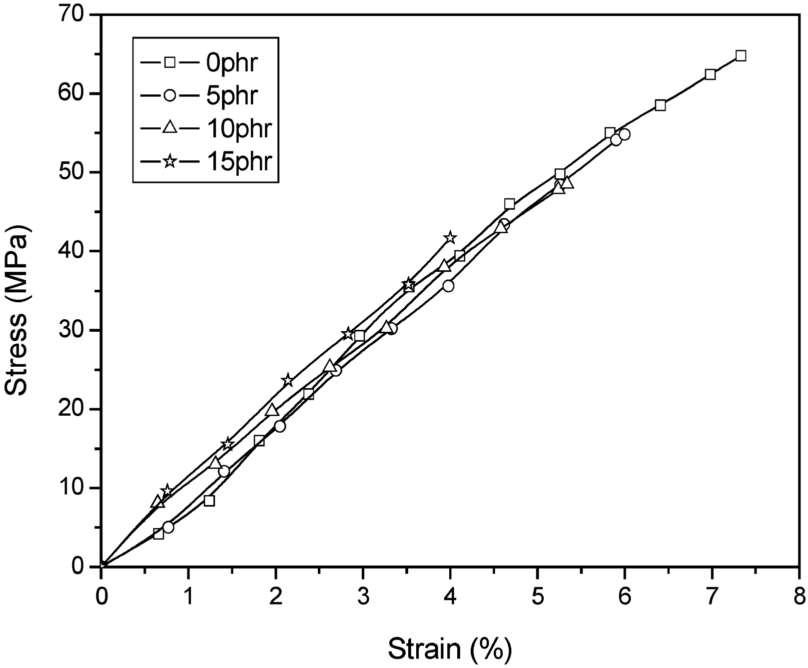


FIGURE 12 Tensile stress-strain curve for DGEBA-PEEKDTOH blends.

functionally terminated polymers, leading to less interaction between the matrix and the dispersed domains. Thermoplastics like polybutyleneterephthalate (PBT), polyvinyledenefluoride (PVDF), polyamide 6 (PA6), and polyamide 12 (PA12) were used to toughen epoxy resin by dispersing them in epoxy resin in particulate form. PA12 and PVDF [33–34] did not give improvement in fracture toughness due to lack of interfacial adhesion between the dispersed particles and epoxy resin. But in PBT modified system the fracture toughness increased by more than 100% due to phase transformation toughening. In the present systems, these mechanisms are not applicable. Unlike most of the other thermoplastic-modified epoxy resins, no reaction-induced phase separation occurred in ditert-butyl PEEK modified epoxy resin because the polyethers were immiscible in epoxy resin. Therefore, the ditert-butyl PEEK polymers acted like filler. In order to have good toughness, there should be effective stress transfer between the matrix and dispersed phase. Good interfacial adhesion is necessary to obtain effective stress transfer. In PEEKDTOH-toughened epoxy resin, the hydroxyl groups reacted with epoxy group giving rise to good

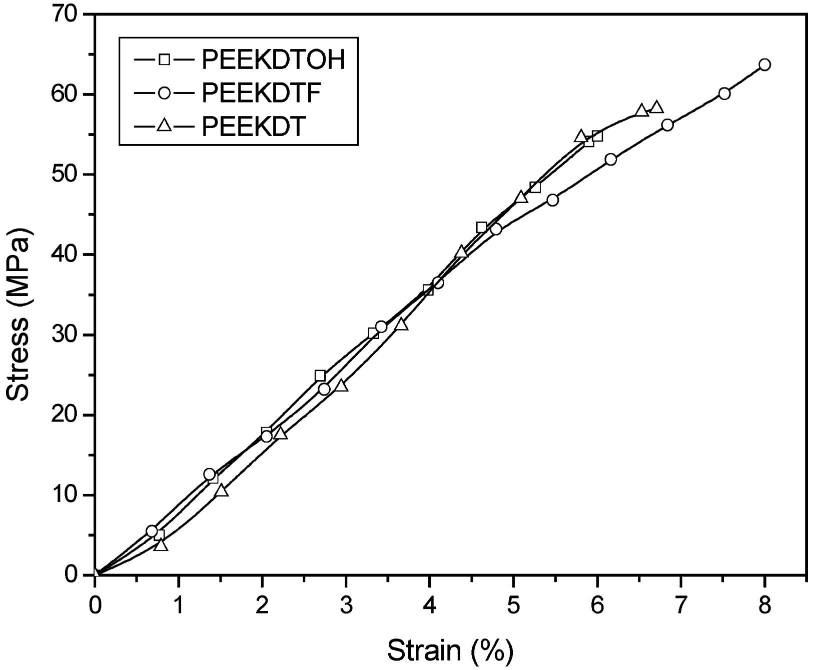


FIGURE 13 Tensile stress-strain curves for different blend systems.

interaction between the crosslinked network and the dispersed polymer. H-bonding interactions occur between PEEKDTF and epoxy resin. Due to these interactions stress transfer occurred between the dispersed domains and epoxy matrix giving rise to improvement in fracture toughness.

CONCLUSIONS

PEEKDTOH, PEEKDTF, and PEEKDT were synthesized by the nucleophilic substitution reaction of DFBP with DTBHQ using NMP as solvent, and then used as toughening agents for epoxy resin. Reaction-induced phase separation could not be obtained due to the immiscible behavior of blend components before curing. The mechanical properties of the blends were slightly lower than that of unmodified epoxy resin. The hydroxyl and fluorine terminated polymers were more effective in increasing the fracture toughness than the random polymer. Scanning electron micrographs revealed ditert-butyl PEEK domains dispersed in epoxy matrix. The domains

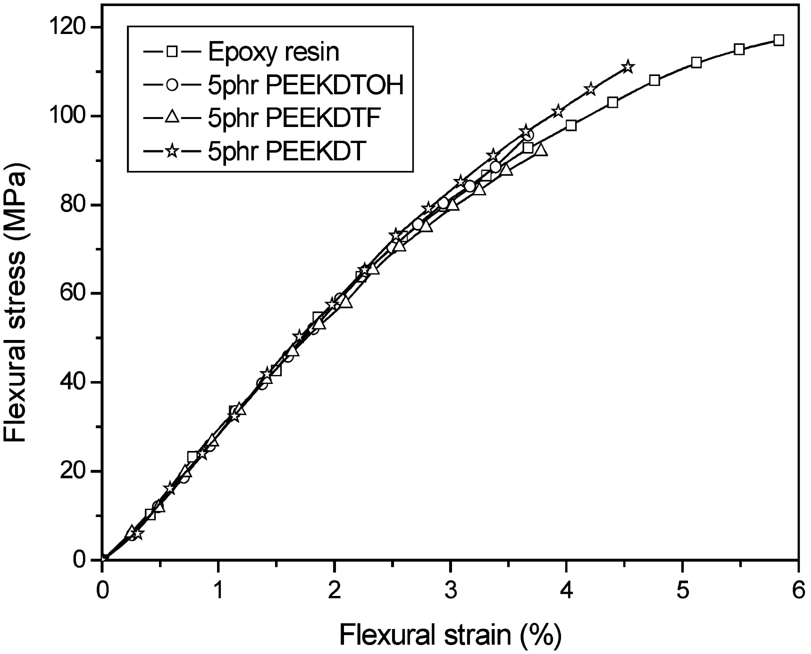


FIGURE 14 Flexural stress-strain curves for unmodified epoxy resin and 5 phr ditert-butyl PEEK modified epoxy resin.

TABLE 4 Fracture Toughness of DGEBA/ Ditert-Butyl PEEK Blends

Composition (phr)	K_{Ic} ($MNm^{-3/2}$)
Epoxy resin	1.46 ± 0.08
DGEBA/PEEKDTOH	
5	2.03 ± 0.12
10	1.53 ± 0.10
15	1.39 ± 0.06
DGEBA/PEEKDTF	
5	1.70 ± 0.08
10	1.65 ± 0.09
15	1.79 ± 0.07
DGEBA/PEEKDT	
5	1.59 ± 0.10
10	1.60 ± 0.04
15	1.21 ± 0.06

were irregularly shaped and the domain size of hydroxyl and fluorine terminated modified epoxy resin was lower than that of the random ditert-butyl PEEK modified epoxy resin. tanδ versus temperature plot shows a single relaxation near the glass transition of epoxy resin due to similar T_g of ditert-butyl PEEK and cured epoxy resin. The ω-relaxation due to the lower crosslink density sites in the epoxy network is observed above room temperature. The storage modulus and loss modulus of the blends were higher than that of neat resin up to the glass transition temperature.

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