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Hydroxyl terminated poly(ether ether ketone) with pendent methyl group toughened epoxy resin: miscibility, morphology and mechanical properties

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Abstract

The synthesis, processing, thermal and mechanical properties and fracture toughness of epoxy resin formulated with hydroxyl terminated poly(ether ether ketone) with pendent methyl group are reported. Hydroxyl terminated poly(ether ether ketone) oligomers based on methyl hydroquinone (PEEKMOH) were synthesised from methylhydroquinone and 4,4′-difluorobenzophenone in *N*-methyl-2-pyrrolidone. PEEKMOH oligomers with different molecular weights were synthesised and characterised. Blends of diglycidyl ether of bisphenol-A epoxy resin with PEEKMOH were prepared by melt mixing. The uncured blends were homogeneous and the T_g-composition behaviour was predicted using Fox, Gordon–Taylor and Kelley–Bueche equations. Reaction induced phase separation occurred in the blends on curing with 4,4′-diaminodiphenyl sulfone. Scanning electron microscopy studies revealed the two-phase morphology of the blends. Domain size of the blends increased with increase in PEEKMOH8 in the blends. Phase separation in the blends occurred by nucleation and growth mechanism. Infrared spectroscopic studies revealed that some of the epoxy groups were opened up by hydroxyl group of PEEKMOH. The tensile and flexural properties of the blends were comparable to that of neat epoxy resin and the properties were dependent on the composition of the blend and molecular weight of PEEKMOH used. Dynamic mechanical analysis revealed two glass transition temperatures corresponding to epoxy rich and thermoplastic rich phases. The crosslink density of epoxy resin decreased with the addition of PEEKMOH to epoxy resin. The blends exhibited superior fracture toughness compared to unmodified epoxy resin. The increase in fracture toughness was due to local plastic deformation of the matrix, crack path deflection and crack pinning. The thermal stability of amine cured epoxy resin was not affected by the incorporation of PEEKMOH into the epoxy resin.

Keywords: Epoxy resin; PEEKMOH; Morphology

1. Introduction

Thermosetting resins are widely used in composite industry because of their high modulus and easy processability. Among the various thermosetting resins, epoxy resins are extensively used as matrices for high performance composites in aerospace and automotive industry due to their high modulus, corrosion resistance and low shrinkage on curing. The excellent properties arises from the highly crosslinked structure of the cured epoxy resins [1,2]. A practical disadvantage of highly crosslinked materials is their poor resistance to crack propagation. These materials are brittle and cannot be used for damage tolerant applications. There had been a large amount of literature regarding the improvement of toughness of epoxy resin. The most common method to increase the fracture toughness is to incorporate rubber to epoxy resin [3–6]. Various reactive functionalised butadiene-*co*-acrylonitrile rubbers like carboxy terminated butadiene acrylonitrile (CTBN) [7–10], amine terminated butadiene acrylonitrile (ATBN) and epoxy terminated butadiene acrylonitrile (ETBN) [11–13] were widely used as modifiers for epoxy resin, especially diglycidyl ether of bisphenol-A (DGEBA) resin. The advantage of reactive functionalised elastomers is that the blends are homogeneous in the uncured state and will undergo phase separation on curing giving rise to a uniform distribution of rubber particles in epoxy matrix at low rubber concentrations [14]. The dispersed rubber particles initiate different toughening mechanisms, the important

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mechanisms being rubber particle cavitation and matrix shear yielding. Even though rubber toughening is effective in DGEBA resins, it is ineffective in highly crosslinked epoxy resins like tetraglycidyl diaminodiphenyl methane (TGDDM). The inability of rubber to toughen multifunctional epoxy system is due to the high crossslink density of epoxies by which shear deformation of the matrix was prevented; apart from that rubber-toughened system have low modulus and decreased thermal stability.

In order to get improved toughness without loosing thermal and mechanical properties, engineering thermoplastics are often used for toughening epoxy resins. The advantage of using thermoplastic is that the mechanical and thermal properties of epoxy resin are retained even after blending. The frequently used thermoplastics are poly(ether sulfone) PES, poly(ether imide) PEI, poly(aryl ether ketone), poly(phenylene oxide), polyamide etc. [15–23]. They have been reported as good toughening agents for epoxy resins. The thermoplastic toughened epoxies form homogeneous blends in the uncured state and undergo phase separation on curing. The curing and phase separation process was well studied in these blends [24–35]. As in the case of rubber modified epoxy resins, functional groups in the polymer enhances the initial miscibility and interfacial adhesion between the phases in the cured state [36–38]. For example, the toughening of epoxy resins using functionalised polyesters has been reported by several researchers [39,40].

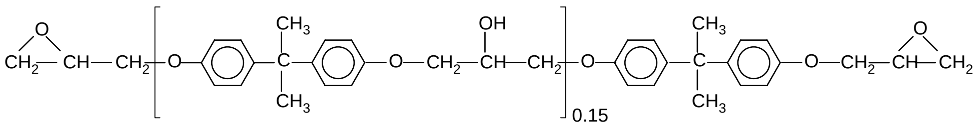
Poly(ether ether ketone) (PEEK) is an engineering thermoplastic with excellent properties. But commercially available PEEK is immiscible with epoxy resin even at high temperatures. Hence, other alternatives like introducing bulky pendent groups or reactive functional groups on the PEEK backbone were investigated to improve the processability. Amorphous PEEK like phenolphthalein poly(ether ether ketone) (PEK-C) was synthesised and used to modify epoxy resin. PEK-C was miscible with epoxy resin and the ultimate morphology of the blends was dependent on the curing agent and curing conditions used [41,42]. Bennet et al. [19] investigated the fracture toughness and mechanical properties of blends of DGEBA epoxy resin with amine terminated *tert*-butyl hydroquinone, methyl hydroquinone and bisphenol-A based PEEK oligomers. The blends exhibited enhanced fracture toughness and morphology ranging from dispersed thermoplastic to continuous thermoplastic depending on the composition. The morphology of the blends was dependent on the curing agent and curing conditions employed for preparing the blends [43]. Iijima et al. [44] observed similar results with methyl hexahydrophthalic anhydride cured bisphenol-A epoxy resin modified with poly(aryl ether ketone) prepared from phthaloyl chloride and diphenyl ether.

We have earlier reported the kinetics of cure of blends of DGEBA epoxy resin and PEEK with pendent *tert*-butyl groups cured with DDS [45]. The present study is devoted to the synthesis of PEEKMOH oligomers and modification of epoxy resin using PEEKMOH. The prime objective of the investigation is to find out the effect of molecular weight of PEEKMOH on morphology, mechanical properties and fracture toughness of DDS cured DGEBA epoxy resin. The thermal stability of a selected blend system was also investigated. Finally attempts have been made to correlate the morphology with the fracture toughness of the blends.

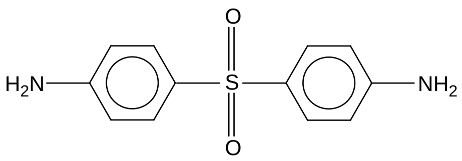
2. Experimental

2.1. Materials used

High purity methylhydroquinone (MeHQ) (Lancaster), 4,4′-difluorobenzophenone (DFBP) (Spectrochem), potassium carbonate (Qualigens), *N*-methyl-2-pyrrolidone (NMP) (SRL) and toluene (Qualigens) were used for the synthesis. MeHQ and DFBP were vacuum dried at 50 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) epoxy resin (LY 556, Ciba Geigy) with epoxide equivalent weight 188.68 was used. The hardener used was 4,4′-diaminodiphenylsulfone (DDS) (Merck). All the materials were used as received unless specified. The chemical structures of epoxy resin and DDS are given in Fig. 1.



Diglycidyl ether of bisphenol-A



4,4’-diaminodiphenyl sulfone

Fig. 1. Chemical structures of epoxy resin and DDS.

2.2. Synthesis of oligomers

Hydroxyl terminated PEEK oligomers having pendent methyl group with different molecular weights were synthesised by the nucleophilic substitution reaction of DFBP with MeHQ as per Scheme 1. The molecular weight was controlled by taking specified amount of monomers calculated using Carother's equation. The hydroxyl functional group was maintained by taking calculated excess of the dihydroxy monomer MeHQ. A typical procedure for the synthesis of hydroxyl terminated oligomer with number average molecular weight ($\overline{M}_n$) 8000 is as follows. The 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. The flask was charged with 32 g (0.26 mol) of MeHQ and 44 g (0.32 mol) of potassium carbonate. The compounds were carefully washed into the flask using NMP. 150 ml toluene was added to the solution as azeotroping agent. The reaction mixture was heated at 160 °C for 4 h with constant stirring. Water formed during reaction formed an azeotrope with toluene and was effectively removed through the Dean-Stark trap. After 4 h the reaction temperature was brought down to 100 °C and 54 g (0.25 mol) 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 solution at 60 °C with constant stirring. The precipitated oligomer was filtered, purified and dried under vacuum at 120 °C for 24 h. Oligomers with number average molecular weights 3000, 6000 and 8000 were synthesised and were designated as PEEKMOH3, PEEKMOH6 and PEEKMOH8, respectively.

2.3. Blend preparation

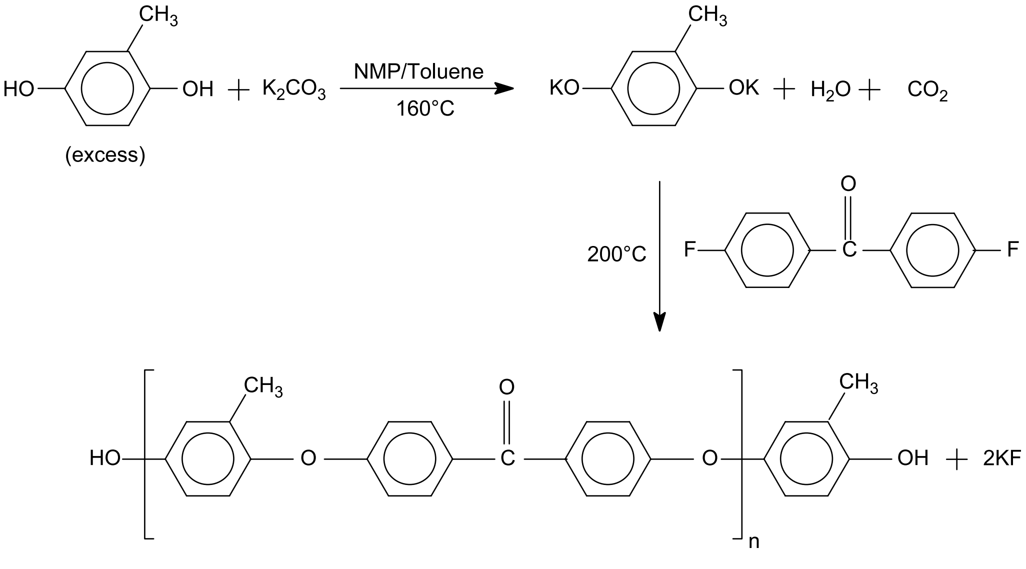
The blends were prepared by melt mixing. The oligomer was dissolved in epoxy resin at 180 °C with constant stirring. 0.5 phr triphenylphosphine (TPP) was added as catalyst in the blends. After complete dissolution stoichiometric amount of DDS was added and dissolved completely. The ternary solution was evacuated in a vacuum oven at 180 °C. After evacuation the mixture was transferred into an open mould 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 PEEKMOH were prepared.

3. Characterisation

The molecular weight and molecular weight distribution of PEEKMOH was determined using gel permeation chromatography (GPC). A Waters Alliance separation module in conjunction with Waters 410 differential refractive index detector was used. The machine was calibrated using polystyrene standard. The analysis was done using chloroform as solvent at a flow rate of 1 ml/min. The inherent viscosity of the oligomer was determined for 0.4% polymer solution in concentrated sulphuric acid at room temperature using Ubbelhode suspended level viscometer. The ^{13}C NMR spectrum of the oligomer 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.

3.1. DSC analysis

The glass transition temperature of pristine epoxy resin, PEEKMOH oligomers and the binary DGEBA/PEEKMOH8 blends were determined using TA instruments model 2920



Scheme 1. General reaction scheme for the synthesis of hydroxyl terminated PEEK with pendent methyl group.

differential scanning calorimeter. In order to determine the T_g of the oligomers, they were heated from 0 to 200 °C at a heating rate of 10 °C/min in nitrogen atmosphere and to determine the T_g of pristine epoxy and binary epoxy/PEEKMOH8 blends, the samples were heated from -50 to 200 °C at a heating rate of 10 °C/min in nitrogen atmosphere.

3.2. FTIR analysis

Infra red studies were conducted to investigate the completion of curing reaction. Fully cured samples were powdered and the spectra of these samples in KBr pellets was recorded using a Perkin–Elmer Spectrum GXA FTIR spectrometer.

3.3. Tensile and flexural properties

Tensile and flexural properties were determined as per ASTM D638 and ASTM D790, respectively. The measurements were done using a universal testing machine (model TNE 5000) at a crosshead speed of 10 mm/min. Rectangular specimens of $100\times10\times3\ \mathrm{mm}^3$ were used for determining flexural strength. Flexural strength was calculated using the equation

$$\text{Flexural strength} = \frac{3PL}{2bd^2} \tag{1}$$

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

3.4. Fracture toughness

Fracture toughness of the blends was determined according to ASTM STP410. Rectangular specimens of $100\times35\times 3\ \mathrm{mm}^3$ were used for fracture toughness measurements. A notch of 5 mm was made at one edge of the specimen. A natural crack was made by pressing a fresh razor blade into the notch. The analysis was done in tension mode. The fracture toughness expressed as stress intensity factor was calculated using Eq. (2).

$$\text{Stress intensity factor, } K_{\mathrm{Ic}} = \frac{QPa^{1/2}}{bd} \tag{2}$$

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 was calculated using Eq. (3).

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

3.5. Scanning electron microscopy

The fracture surfaces of cryogenically fractured specimens and failed specimens from fracture toughness measurement were analysed 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.

3.6. Dynamic mechanical thermal analysis

The viscoelastic properties of the unmodified resin as well as the blends were measured using TA Instruments DMA 2980 dynamic mechanical thermal analyser. Rectangular specimens of $60\times10\times3\ \mathrm{mm}^3$ 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.

3.7. Thermogravimetric analysis

The thermal stability of the blends was analysed by thermogravimetric studies. A TA Instruments model SDT 2960 thermal analyser was used for thermogravimetric analysis. The samples were heated from room temperature to 900 °C at a heating rate of 20 °C/min in nitrogen atmosphere.

4. Results

The FTIR spectrum of PEEKMOH is shown in Fig. 2. The peak due to carbonyl stretching vibration was observed at 1651 cm^{-1} and the symmetrical stretching vibration of C–H bonds in the methyl group was observed at 2922 and 3038 cm^{-1}. The O–H stretching vibration was observed as a broad peak at 3465 cm^{-1}. The symmetrical stretching vibration of ϕ-O bond, stretching and bending vibrations of C–CO bonds were observed at 1227 and 1277 cm^{-1}, respectively. The C–C stretching vibrations of benzene ring was observed at 1599 and 1487 cm^{-1}. The ring hydrogen

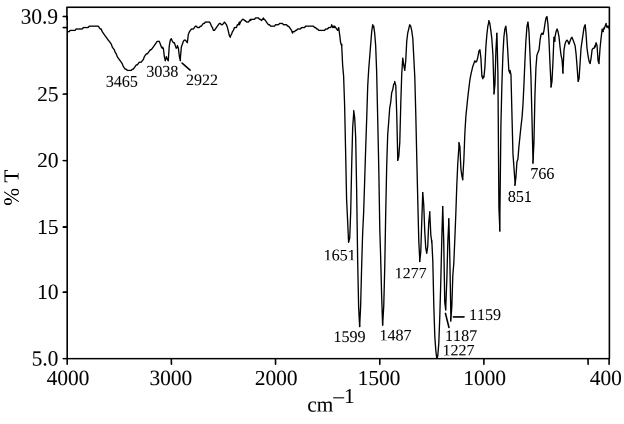


Fig. 2. FTIR spectrum of PEEKMOH8.

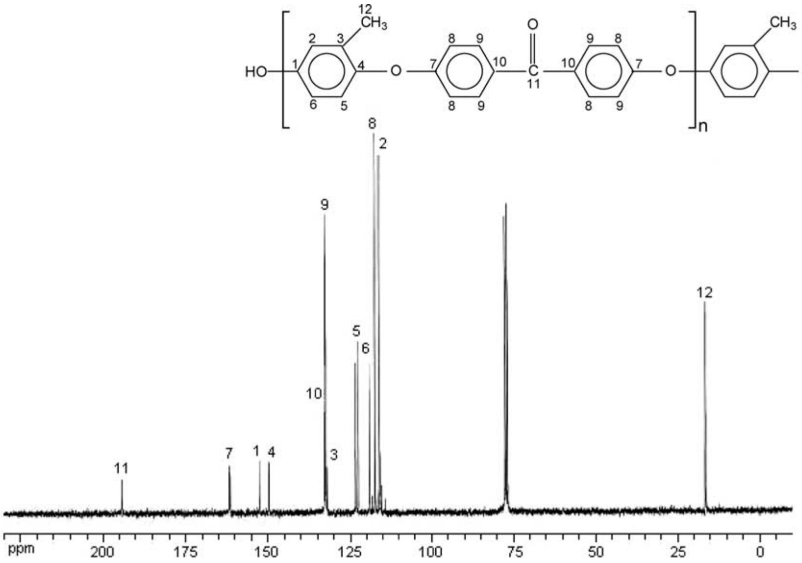


Fig. 3. ^{13}C NMR spectrum of PEEKMOH8.

rocking vibration was observed at 1187 and 1127 cm^{-1} and out of plane bending vibrations of C–H bonds in benzene ring was observed at 766 and 851 cm^{-1}.The ^{13}C NMR spectrum of PEEKMOH8 along with the peak assignments is shown in Fig. 3. The spectrum revealed twelve peaks corresponding to twelve distinguishable carbon atoms in the oligomer. The chemical shift assignments of various carbon atoms were based on the additivity constants for substituted benzene. The peak due to carbonyl carbon was observed at 194.2 ppm and the methyl carbon peak was observed at 16.3 ppm. The other peaks in the spectrum were due to aromatic ring carbons of the polymer. The number average molecular weights, inherent viscosity and T_g of the oligomers are given in Table 1. The inherent viscosity and glass transition temperature was found to increase with increase in molecular weight of the oligomers.

4.1. Miscibility of DGEBA/PEEKMOH blends

The melt mixed blends were transparent and no visual heterogeneity was observed. Among the different blend systems, DGEBA/PEEKMOH8 blend was chosen for differential scanning calorimetric studies. Only a single glass transition temperature was observed for the binary DGEBA/-PEEKMOH8 blends. The glass transition temperature increased with increase in PEEKMOH content in the blend. The T_g lies between those of pure DGEBA and PEEKMOH8. The presence of single T_g confirmed the fact that the blends were homogeneous before curing.

Table 1
Properties of PEEK oligomers with pendent methyl groups

Oligomer	$\overline{M}_n$ (g/mol)	Inherent viscosity (dl/g)	T_g (°C)
PEEKMOH3	2500	0.17	132
PEEKMOH6	5200	0.26	140
PEEKMOH8	7400	0.36	143

4.2. FTIR studies

The maximum properties of epoxy resin were attained by fully crosslinked systems. FTIR studies were conducted to investigate the completion of curing reaction. The IR spectrum of the blends is given in Fig. 4. The epoxy peak at 915 cm^{-1} vanished after curing indicating that the curing reaction reached completion.

4.3. Fracture toughness

The fracture toughness of DDS cured epoxy resin as well as its blends with PEEKMOH are given in Table 2. The fracture toughness increased with the addition of PEEKMOH to epoxy resin. All the blends exhibited varying degrees of enhanced fracture toughness. In general the fracture toughness was dependent on the molecular weight of the oligomer (Table 2) used to modify epoxy resin. Maximum increase in toughness (122%) was attained by the addition of 10 phr PEEKMOH8.

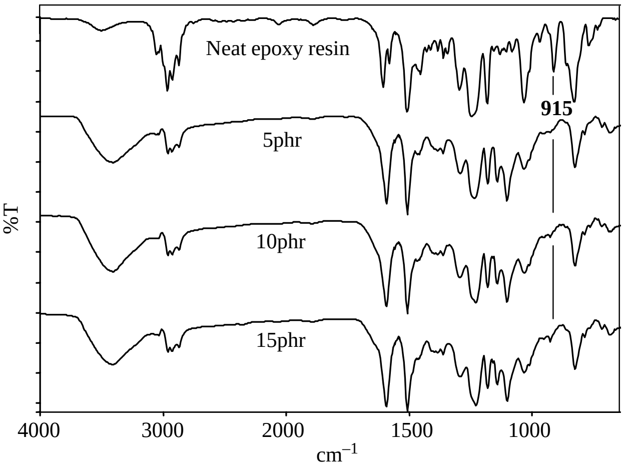


Fig. 4. FTIR spectrum of fully cured DGEBA/PEEKMOH8 blends.

Table 2
Fracture toughness of DGEBA/PEEKMOH blends

PEEKMOH content (phr)	K_{Ic} (M N $m^{-3/2}$)
0	1.46±0.08
PEEKMOH3	
5	2.74±0.13
10	2.64±0.08
15	2.92±0.13
PEEKMOH6	
5	2.63±0.17
10	2.79±0.09
15	3.06±0.15
PEEKMOH8	
5	2.74±0.17
10	3.24±0.09
15	2.52±0.15

All the other blends gave 80% or more improvement in fracture toughness compared to the unmodified resin.

4.4. Morphological analysis

Scanning electron microscopy is an excellent tool for studying the morphology of polymer blends. Preferential extraction of the minor component was helpful in getting a clear picture of the morphology of the blends. The scanning electron micrographs of cryogenically fractured surfaces of DGEBA/PEEKMOH8 and DGEBA/PEEKMOH6 blends are shown in Figs. 5 and 6, respectively. All the blends showed two-phase morphology in which PEEKMOH rich domains are dispersed in a continuous epoxy matrix. The cavities in the micrographs represented the space occupied by PEEKMOH domains before extraction. The domains are uniformly distributed in the blend. No phase inversion was observed in the compositions we studied. The domain size was determined using image analysis technique. The number average and weight average domain diameters and polydispersity index were calculated using the following equations.

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

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

$$\text{Polydispersity index, PDI} = \frac{\overline{D}_w}{\overline{D}_n} \tag{6}$$

where, n_i is the number of domains having diameter d_i

The number average and weight average domain diameters and polydispersity index calculated using the above equations for DGEBA/PEEKMOH8 blends are summarised in Table 3. It was observed that the domain size and polydispersity index increased with increase in PEEKMOH8 content in the blends.

4.5. Dynamic mechanical thermal analysis

The dynamic mechanical analysis of the blends gave insight into the viscoelastic properties as well as the morphology of the blends. The tan δ against temperature plot for DGEBA/PEEKMOH8 blends given in Fig. 7 revealed two peaks. The peak between 130 and 160 °C corresponds to the T_g of PEEKMOH8 rich phase and the peak at higher temperature corresponds to epoxy rich phase. The storage modulus of the blends at room temperature was the same as that of neat epoxy except for 15 phr, which showed higher values (Fig. 8). Two inflections were seen in the plot of storage modulus, one near the T_g of thermoplastic and the second near the T_g of epoxy. The storage modulus was lower than that of epoxy resin near glass transition and continued to be the same in the plateau region. The loss modulus of the blends and the neat resin with respect to temperature are given in Fig. 9. The loss modulus was higher for the blends than the neat resin. The higher values of loss

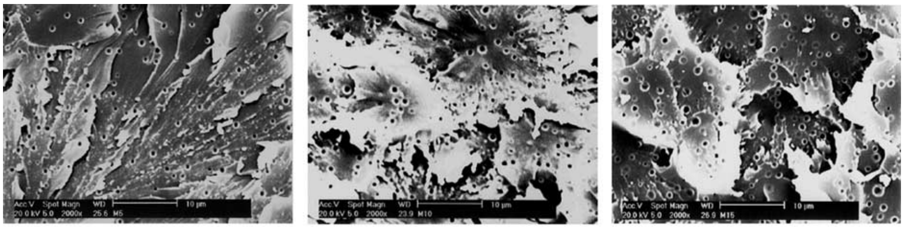

5phr 10phr 15phr

Fig. 5. Scanning electron micrographs of DGEBA/PEEKMOH8 blends etched with chloroform.

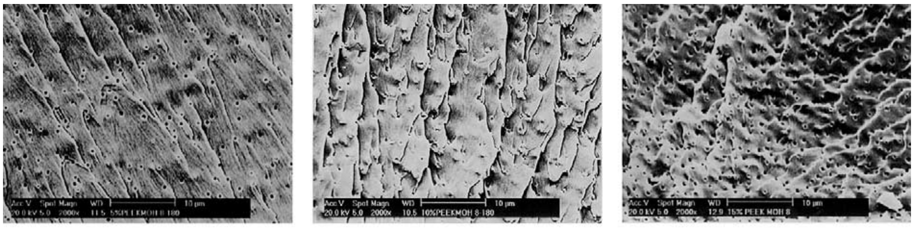

5 phr 10 phr 15 phr

Fig. 6. Scanning electron micrographs of DGEBA/PEEKMOH6 blends etched with chloroform.

Table 3
Number average and weight average domain diameters of DGEBA/PEEKMOH8 blends

PEEKMOH8 content (phr)	$\overline{D}_n$ (μm)	$\overline{D}_w$ (μm)	PDI
5	0.41	0.43	1.07
10	0.45	0.50	1.09
15	0.52	0.58	1.12

modulus of the blends showed that the blends have better interaction between the phases.

4.6. Tensile and flexural properties

The results from tensile and flexural property measurements are summarised in Table 4. A small increase in tensile strength was observed for the blends. The tensile modulus calculated from the initial slope of the tensile stress strain curves showed a slight decrease in all the blend systems studied. The flexural strength of the blends was lower than that of the neat resin. The decrease in flexural strength was dependent on the molecular weight of PEEKMOH used to modify epoxy resin. The lowest molecular weight PEEKMOH modified epoxy resin showed nearly 50% reduction in flexural strength. The flexural modulus showed only a small decrease from that of the neat resin.

4.7. Thermogravimetric analysis

The thermal stability of the blends was analysed using TGA. The TGA thermograms of DGEBA/PEEKMOH8 blends are shown in Fig. 10. The initial decomposition temperature (IDT) and temperature at which the rate of decomposition is maximum ($T_{\max}$) remained the same as that of unmodified epoxy resin. Activation energy (E) for decomposition was calculated using non-isothermal integral equations viz; Coats-Redfern [46] equation. The main advantage of non-isothermal techniques is obtaining kinetic values from a single measurement for the whole temperature range. The Coats-Redfern equation given in Eq. (7) was used to compute the activation energy.

$$\ln\left[\frac{g(\alpha)}{T^2}\right] = \ln\left\{\left(\frac{AR}{\varphi E}\right)\left(1-\frac{2RT}{E}\right)\right\} - \frac{E}{RT} \tag{7}$$

where

$$g(\alpha) = \left\{\frac{1-(1-\alpha)^{1-n}}{1-n}\right\} \quad \text{for } (n \neq 1)$$

and

$$g(\alpha) = -\ln(1-\alpha) \quad \text{for } n = 1$$

where, α is the fraction decomposed at temperature T, ϕ is the heating rate, R is the gas constant and A is the Arrhenius factor. Best fit (correlation coefficient $r > 0.99$) was obtained for $n = 1$. The activation energy (E) was determined from the plot of $\ln[-\ln(1-\alpha)/T^2)]$ against reciprocal of absolute temperature ($1/T$). Activation energy was calculated from the slope of the kinetic plot. The calculated values of E along with correlation coefficient and other parameters from thermogravimetric analysis are given in Table 5. The parameters were comparable to that of neat epoxy resin.

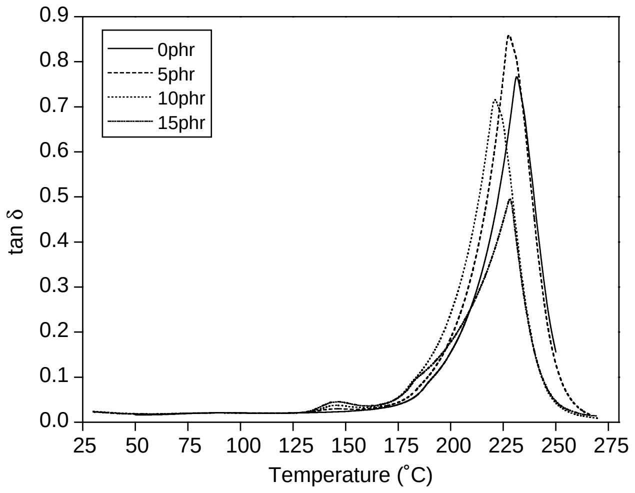


Fig. 7. tan δ vs. temperature plot of DGEBA/PEEKMOH8 blends.

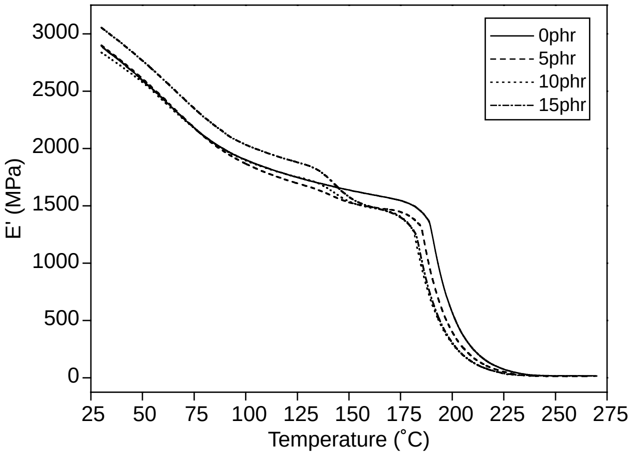


Fig. 8. Storage modulus of DGEBA/PEEKMOH8 blends.

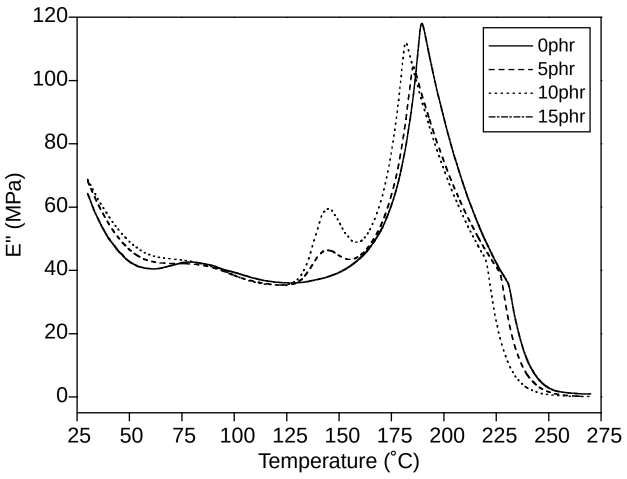


Fig. 9. Loss modulus of DGEBA/PEEKMOH8 blends.

Table 4
Mechanical properties of DGEBA/PEEKMOH blends

Composition (phr)	Tensile strength (MPa)	Young's modulus (GPa)	Flexural strength (MPa)	Flexural modulus (GPa)
0	60±4	1.7±0.12	122±6	2.95±0.11
PEEKMOH3				
5	67±4	1.5±0.08	62±2	2.90±0.19
10	65±3	1.3±0.06	70±3	2.64±0.16
15	66±6	1.4±0.05	62±4	2.98±0.09
PEEKMOH6				
5	73±5	1.5±0.09	114±10	2.85±0.16
10	73±3	1.6±0.11	123±8	2.92±0.14
15	78±1	1.6±0.07	117±7	3.02±0.15
PEEKMOH8				
5	70±1	1.7±0.07	112±6	2.86±0.12
10	70±5	1.6±0.09	113±4	2.85±0.13
15	67±3	1.4±0.05	127±4	2.97±0.15

5. Discussion

Improving the fracture toughness of epoxy resin without reduction in thermo-mechanical properties was the aim behind blending thermoplastics with epoxy resin. In order to achieve good toughness improvement, a homogeneous blend, which phase separated on curing, is required. A uniform dispersion of domains with good interfacial adhesion is essential for achieving a tough epoxy resin system. Reaction induced phase separation of the homogeneous blends on curing yields a uniform dispersion of domains of thermoplastic in epoxy/thermoplastic blends at low thermoplastic contents. The use of PEEK as a modifier is of immense potential since PEEK has good physico-mechanical properties. In general the immiscibility of PEEK in epoxy resin was overcome by using low molecular weight oligomers with reactive functional groups or PEEK with bulky pendent group [42,43]. The ultimate properties of the blends were dependent on the inherent properties of the oligomer used as well as the properties of the matrix. In the present work, we have used hydroxyl terminated PEEK oligomers with pendent methyl group to modify DGEBA epoxy resin cured with DDS. The oligomers with different molecular weights were synthesised from methylhydroquinone and difluorobenzophenone using NMP as solvent in the presence of anhydrous potassium carbonate. The hydroxyl functionality was maintained by reacting calculated excess of MeHQ with DFBP. The glass transition temperature and inherent viscosity were dependent on the molecular weight of the oligomers. It was possible to prepare the blends with epoxy resin by melt mixing at 180 °C. No heterogeneity was observed in DGEBA/PEEKMOH blends on visual inspection. Heating at 200 °C did not change the visual transparency of the blends.

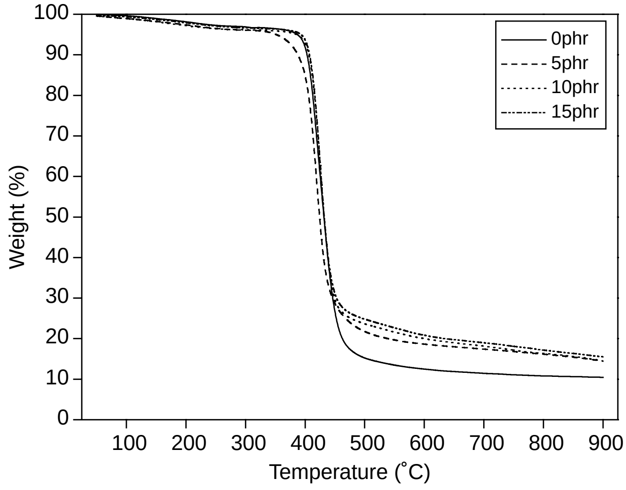


Fig. 10. TGA thermograms of DGEBA/PEEKMOH8 blends.

Table 5
IDT, T_{max}, activation energy for decomposition and correlation coefficient of DGEBA/PEEKMOH8 blends

PEEKMOH8 content (phr)	IDT (°C)	T_{max} (°C)	E (kJ mol^{-1})	Correlation coefficient
0	402	430	280	0.9972
5	399	419	244	0.9982
10	408	429	299	0.9970
15	405	425	316	0.9966

DSC studies of binary DGEBA/PEEKMOH8 blends gave only a single T_g, which increased with increase in PEEKMOH content in the blends, confirming the homogeneity of the blends. The glass transition temperature of homogeneous blend systems can be calculated theoretically using equations like Gordon–Taylor [47], Kelley–Bueche [48] and Fox equation [49]. They are given by Eqs. (8)–(10), respectively.

$$T_g = \frac{w_1 T_{g1} + k w_2 T_{g2}}{w_1 + k w_2} \tag{8}$$

$$T_g = \frac{v_1 T_{g1} + k v_2 T_{g2}}{v_1 + k v_2} \tag{9}$$

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \tag{10}$$

where T_g is the glass transition temperature of the blend, T_{g1} and T_{g2} are the glass transition temperatures, w_1 and w_2 are the weight fractions, v_1 and v_2 are the volume fractions of component 1 and 2, respectively, and k is an adjustable parameter.

The plot of experimental and theoretically calculated values of T_g is shown in Fig. 11. The T_g-composition behaviour up to 15 phr blend is shown in inset. It is seen from the figure that Fox equation deviated most from the experimental T_g determined using DSC and was always greater than the experimental value. Kelley–Bueche and Gordon–Taylor equations gave T_g's, which are in good correlation with the experimental values. Prud'homme and co-workers [50,51] suggested that the k value in Gordon–Taylor equation indicates the interaction between the blend components. In epoxy/PEEKMOH blends, a k value of 0.32 showed good agreement with the experimental T_g. The low value of k indicated weak interactions between uncrosslinked epoxy resin and PEEKMOH. Hence, the initial miscibility was mainly associated with the entropic contribution arising from the low molecular weight of uncrosslinked epoxy resin.

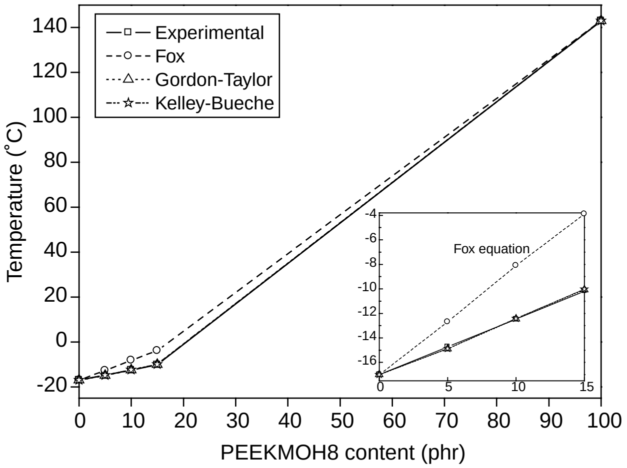
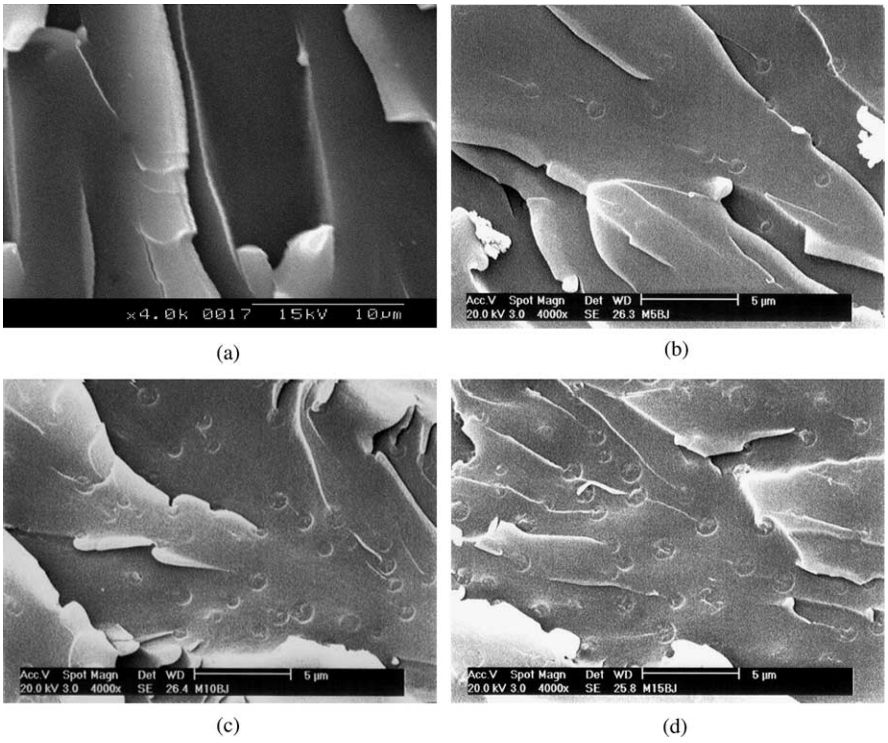


Fig. 11. Comparison of experimental and theoretical values of glass transition temperatures for DGEBA/PEEKMOH8 blends.

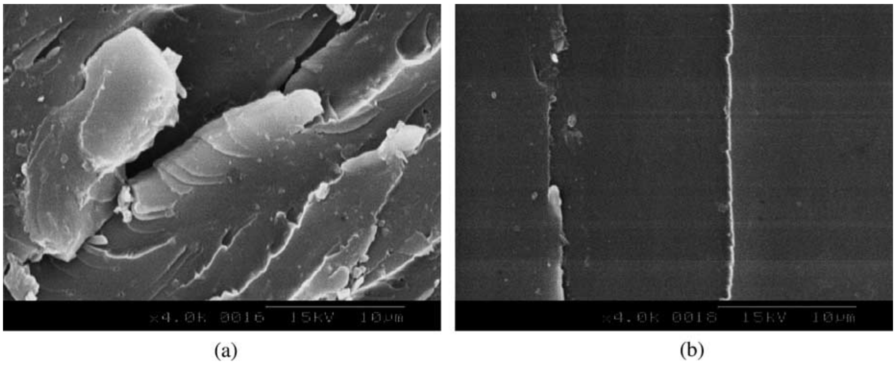
The extent of crosslinking plays a crucial role in determining the ultimate properties of the cured resin. Also the properties were dependent on the amount of curing agent used. If there is not sufficient curing agent to crosslink all the epoxy groups, the ultimate properties will be reduced. A stoichiometric amount of curing agent gave maximum T_g for DDS cured DGEBA resin [52]. In epoxy/thermoplastic blends, the presence of thermoplastic was reported to hinder the curing reaction. For example, in DDM cured DGEBA/PEK-C blends cured with anhydride, absorption due to unreacted epoxy group was present in the IR spectrum of the cured blends [41]. But in the present system, the spectra of the blends in Fig. 4 did not show any characteristic absorption of epoxy group at 915 cm^{-1}. This observation revealed that no free epoxy group was present in the cured blends indicating a fully crosslinked system.

All the blends exhibited higher fracture toughness compared to the unmodified resin. The extent of improvement in fracture toughness was dependent on the molecular weight of the oligomer and the composition of the blends. Two-phase morphology was one of the important criteria for enhancement of fracture toughness. Although few exceptions are there [53,54], heterogeneous blends gave higher fracture toughness compared to homogeneous blends. From the scanning electron micrographs it was clear that all the DGEBA/PEEKMOH blends were heterogeneous and the frequency of the domains increased with PEEKMOH content in the blends. The dispersed PEEKMOH in the blends initiated various energy absorbing mechanisms resulting in increased fracture toughness. The scanning electron micrographs of the failure surfaces could give more information about the fracture mechanisms in the blends. Fig. 12(a)–(d) reveals the failed fracture surface of DDS cured epoxy resin and its blends with PEEKMOH8. The fracture surface of neat epoxy resin showed typical characteristics of brittle fracture. The surface was smooth and the crack propagated uninterrupted. The fracture surfaces of the blends were rough and ridge patterns and river marks could be seen on the fracture surface. The roughness of the fracture surface was due to two reasons. First it is an indication of crack path deflection i.e. the crack deviated from its original plane, increasing the area of the crack. Hence, the energy required for the propagation of



(a) (b) (c) (d)

Fig. 12. Scanning electron micrograph of failed surfaces of (a) neat epoxy resin, (b) 5 phr, (c) 10 phr and (d) 15 phr DGEBA/PEEKMOH8 blends.



(a) (b)

Fig. 13. Scanning electron micrographs of failed surfaces of (a) DGEBA/PEEKMOH6 and (b) DGEBA/PEEKMOH3 blends.

the crack increased. Second the roughness indicated the ductile nature of the crack.

As described above two phase morphology is desirable for increase in fracture toughness. At the same time, good interaction between the dispersed phase and epoxy matrix is also essential for enhancing the fracture toughness. This is often achieved by incorporating reactive groups in the modifier [36–40]. Dispersed PEEKMOH domains have good adhesion with epoxy matrix due to the presence of hydroxyl groups. We have added TPP to catalyse the reaction between epoxy and hydroxyl group. Further, from the micrographs in Fig. 12(b)–(d) it is seen that no vacant spaces were there on the fracture surface due to removal of domains from the fracture surface. The ductile tearing of the domains indicated that there exists strong interfacial adhesion between the matrix and the domains. This is due to the opening up of epoxy ring by hydroxyl groups or due to the H-bonding interactions between the two.

FTIR analysis of binary epoxy/PEEKMOH8 blends revealed that some of the epoxy groups were opened up by the hydroxyl group and hence PEEK chains are incorporated into the crosslinked network structure. Since TPP can catalyse the polyetherification of epoxy resin and reaction between hydroxyl and epoxy groups, the decrease intensity can be due to either of them or both. Hence, the FTIR spectra of epoxy resin heated with and without TPP were taken and quantitative analysis demonstrated a decrease in the intensity of the epoxy peak. But the decrease in intensity was less than that in the case of blends. Therefore, it was concluded that TPP catalyses both the reaction between hydroxyl and epoxy groups and polyetherification of epoxy resin. Hence, it is clear that there exist good adhesion between the two phases. Also in the scanning electron micrographs white rings were seen round the domains. This meant that there existed a diffuse layer in which both thermoplastic and epoxy were present. When an external load was applied, the dispersed domains acted as stress concentrators leading to the plastic deformation of the local area surrounding the domains. The river marks on the fracture surface also indicated plastic deformation and ductile nature of the crack. On close observation of the micrographs, tail marks could be seen behind the domains indicating crack pinning mechanism. Crack pinning was reported in epoxy/PPO blends, which improved the fracture toughness of the blends [55]. All these factors contributed to the increase in fracture toughness of the blends. The fracture surface of PEEKMOH6 and PEEKMOH3 blends are shown in Fig. 13. The fracture surface of PEEKMOH6 blend showed similar features as that of PEEKMOH8 modified epoxy resin whereas the fracture surface of PEEKMOH3 modified system appeared smooth and very little features could be seen. This is due to the better miscibility of PEEKMOH3 with epoxy resin. It was found from FTIR investigations that there were interactions between the hydroxyl and epoxy groups. As the molecular weight decreases the number of terminal hydroxyl groups will increase proportionally. As a result the extent of miscibility will be high in the case of PEEKMOH3 modified epoxy resin.

From Table 2 it was found that the improvement in fracture toughness was dependent on the molecular weight and concentration of PEEKMOH in the blends. Addition of 10 phr PEEKMOH8 having the highest molecular weight gave the maximum improvement (122%) in fracture toughness. In the case of PEEKMOH6 and PEEKMOH3 toughened systems, 15 phr addition gave 100% increase in fracture toughness. In the above said blends fracture toughness increased with composition with 15phr giving maximum toughness. In DGEBA/PEEKMOH8 blend, 15 phr addition gave less fracture toughness than 10 phr blend.

There are several factors, which influence the fracture toughness of the blends. The interparticle distance, interfacial area per unit volume, domain size, domain size distribution etc. influence the extent of improvement in fracture toughness among the various blend systems. The interparticle distance and interfacial area per unit volume were calculated using Eqs. (11) and (12), respectively and are summarised in Table 6.

$$\text{Interparticle distance} = d_{\text{TP}}\left[\left(\frac{\pi}{6\phi_{\text{TP}}}\right)^{1/3} - 1\right] \tag{11}$$

Table 6
Interfacial area per unit volume and interparticle distance of DGEBA/PEEKMOH8 blends

PEEKMOH8 content (phr)	Interparticle distance (μm)	Interfacial area/unit volume (μm^{-1})
5	0.53	0.6454
10	0.38	1.1267
15	0.33	1.4031

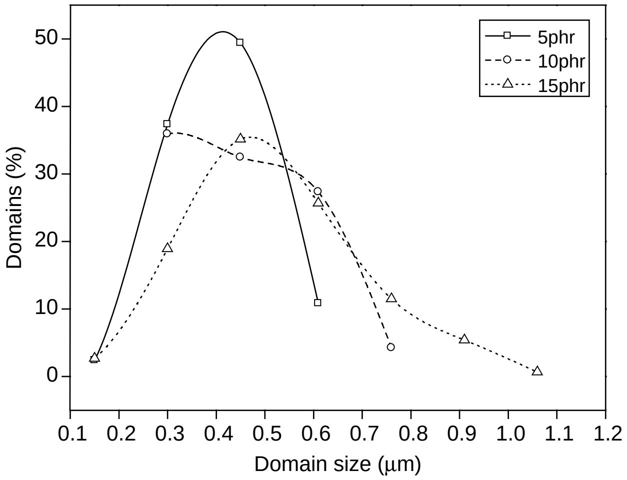


Fig. 14. Domain size distribution of DGEBA/PEEKMOH8 blends.

$$\text{Interfacial area per unit volume} = \frac{3\phi_{\text{TP}}}{r} \tag{12}$$

where, d_{TP} is the diameter of the domains, r is the radius of the domains and ϕ_{TP} is the volume fraction of the thermoplastic.

The interparticle distance decreased and the interfacial area per unit volume increased on increasing the PEEKMOH8 content in the blends from 5 to 15 phr. The domain diameter increased with the increase in oligomer content in the blends. All these factors favour improvement in fracture toughness with increase in concentration of PEEKMOH in the blends. But the fracture toughness of 15 phr blend was lower than that of 10 phr blend. This can be explained on the basis of domain size distribution of the blends. The domain size distribution of the blends is given in Fig. 14. The narrowest size distribution was shown by 5 phr blend and 15 phr showed the broadest distribution. In 10phr blend more than 90% of the domains have diameters between 0.25 and 0.7 μm. Also it is seen from the graph that both small and large domains are present in almost equal amounts in 10 phr blend. Very small and very large domains are less effective in improving the fracture toughness. These factors led to the lower fracture toughness of 15 phr blend compared to 10 phr blend.

Scanning electron micrographs of all the blends exhibited two phase morphology. The initially homogeneous blends phase separated upon curing due to increase in molecular weight of epoxy resin as a result of crosslinking. The phase separation mechanism in epoxy resin/thermoplastic blends was studied extensively [29,56]. The phase separation mechanism was found to be dependent on the composition of the blends, nature of curing agent, curing temperature and secondary phase separation was observed in some cases. When the composition of the blend was near the critical composition, phase separation occurred by spinodal decomposition and at off critical compositions phase separation occurred by nucleation and growth mechanism. For thermoplastic with average molar mass between 10,000–30,000 g/mol, the critical concentration of thermoplastic was 10–15 wt% in liquid epoxy and diamine monomer as calculated by Flory–Huggins model [57]. In the present study, PEEKMOH with lower molecular weights were used to modify epoxy resin. Hence, the critical concentration may be higher than the above mentioned range. Therefore, the phase separation was expected to occur by nucleation and growth mechanism.

Dynamic mechanical thermal analysis of the blends also supported the two-phase morphology of the blends. Two peaks corresponding to epoxy rich and thermoplastic rich phases appeared in the tan δ against temperature of the blends in Fig. 7. The T_g of the epoxy rich phase decreased with addition of PEEKMOH8. This is due to the presence of a small amount of PEEKMOH8 remaining in the epoxy matrix. The decrease may be also due to the decrease in crosslink density of the blends as result of the incorporation of PEEKMOH8 to epoxy. FTIR studies revealed that there exists reaction between epoxy and hydroxyl groups of PEEKMOH. The peak height, peak area and peak width at half height, M_c values and effective crosslink density of the blends are tabulated in Table 7. The peak height, peak width and peak area of DGEBA/PEEKMOH8 blends were higher than that of neat resin while PEEKMOH6 and PEEKMOH3 modified epoxy resin showed lower values. M_c was calculated using the following equation [58].

$$M_c = \frac{3.9 \times 10^4}{T_g - T_{g0}} \tag{13}$$

where, T_g is the glass transition temperature of the crosslinked epoxy resin and T_{g0} is the glass transition temperature of the uncrosslinked polymer having the same chemical composition as the crosslinked polymer. The value of T_{g0} was taken as 91 °C for DGEBA/DDS system [59]. The effective crosslink density

Table 7
Peak height, peak width at half height, peak area, T_g, M_c and effective crosslink density of the blends from dynamic mechanical thermal analysis

PEEKMOH content (phr)	Peak height	Peak width at half height (°C)	Peak area (cm^2)	T_g (°C)	M_c (g/mol)	$\nu_e \times 10^{27}$ chains/m^3
0	0.77	24.5	21.7	233	279	2.59
PEEKMOH8						
5	0.86	25.0	25.2	228	285	2.54
10	0.72	24.6	21.1	221	300	2.41
15	0.69	30.2	26.6	219	305	2.37
PEEKMOH6						
10	0.73	18.4	16.3	218	307	2.35
PEEKMOH3						
10	0.62	22.0	16.6	215	315	2.30

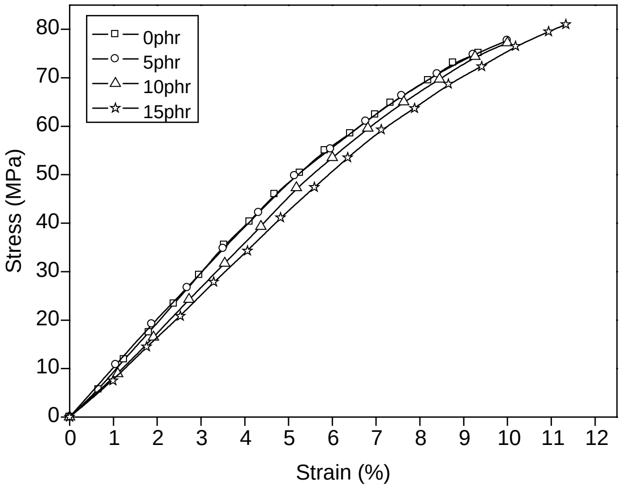


Fig. 15. Tensile stress–strain curve for DGEBA/PEEKMOH8 blends.

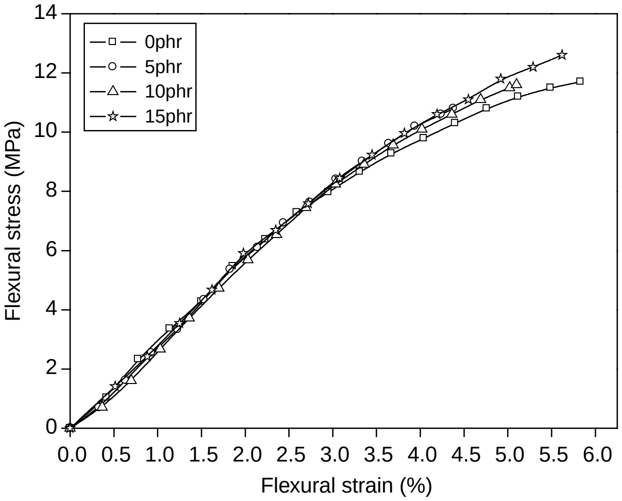


Fig. 17. Flexural stress–strain curves for DGEBA/PEEKMOH8 blends.

ν_e was calculated from M_c using the following equation.

$$\text{Effective crosslink density, } \nu_e = \frac{\rho N_A}{M_c} \tag{14}$$

where, ρ is the density and N_A is Avogadro's number.

It was found that the crosslink density decreased with the addition of PEEKMOH to epoxy resin. The decrease in crosslink density was due to the incorporation of PEEKMOH chains in the epoxy network as a result of the reaction between hydroxyl and epoxy groups.

The storage modulus of the blends decreased with increase in temperature. The blends showed two inflections in Fig. 8. The first inflection was near the T_g of PEEKMOH8 and the second one at the T_g of epoxy. The storage modulus of the blends was lower for the blends than that of neat epoxy after the first inflection point. This was an indication of the lower crosslink density of the blends. The loss modulus of the blends also gave two peaks in the dynamic mechanical spectrum corresponding to epoxy rich and thermoplastic rich phases. The loss modulus of the blends was always higher than that of the unmodified resin.

The tensile and flexural properties of the blends were dependent on the molecular weight of the oligomer used and composition of the blends. The tensile strength of the blends was higher than that of neat resin cured with DDS. The Young's modulus marginally decreased with the addition of PEEKMOH and DGEBA/PEEKMOH3 blends exhibited the lowest values. The plot of tensile stress-strain curves of epoxy/PEEKMOH8 blends and 10 phr blends with different molecular weight PEEKMOH are shown in Figs. 15 and 16, respectively. No yielding was observed in the tensile stress–strain curves of the DDS cured epoxy resin and all the blends showing that the DDS cured epoxy and its blends with PEEKMOH were basically brittle materials. The tensile strain of PEEKMOH8 blends increased with increase in concentration of PEEKMOH8 in the blends but the strain decreased with decrease in molecular weight of PEEKMOH.

Although the flexural strength decreased, the decrease was within acceptable limits. The flexural modulus of the blends

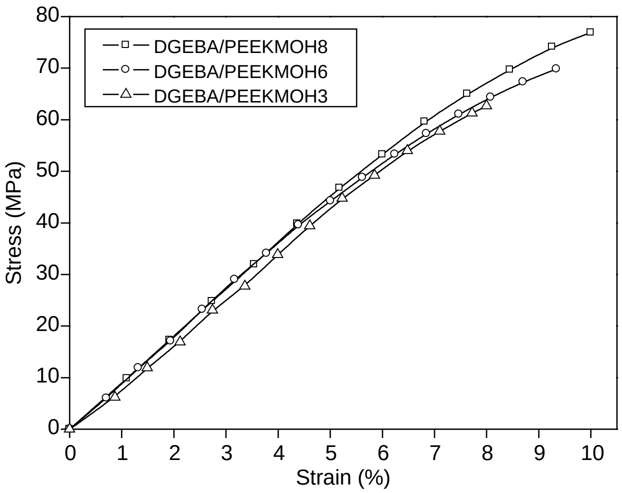


Fig. 16. Tensile stress–strain curves of DGEBA and 10 phr PEEKMOH with different molecular weights.

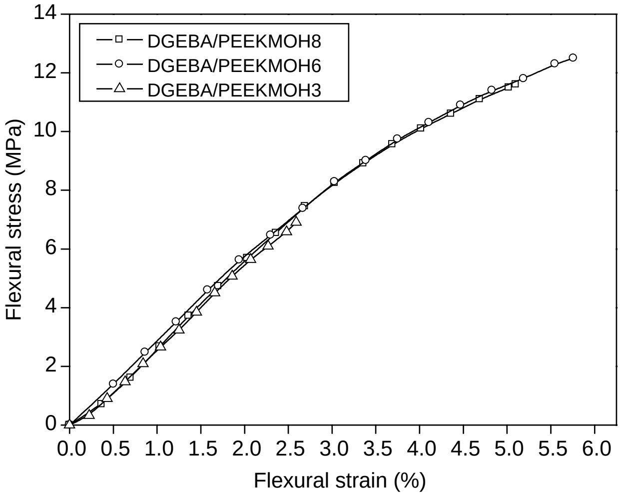


Fig. 18. Flexural stress–strain curves of DGEBA and 10 phr PEEKMOH with different molecular weights.

was comparable to that of neat epoxy resin. The flexural stress-strain curves of DGEBA/PEEKMOH8 blends are shown in Fig. 17. The flexural strain of the blends was comparable to that of neat epoxy resin. The flexural strain of all 10 phr PEEKMOH blends are shown in Fig. 18. The lower molecular weight PEEKMOH toughened epoxy resin showed the lowest strain. The decrease in tensile strain and flexural strain was maximum for DGEBA/PEEKMOH3 blends, which is to the inherently lower properties of PEEKMOH3 because of its low molecular weight.

From thermogravimetric analysis it was found that there was no decrease in the IDT and $T_{\max}$ of blends. Both PEEKMOH6 and PEEKMOH3 blends showed similar behaviour. The activation energy for decomposition remained the same or slightly higher than that of neat resin. This confirmed that the thermal stability was not affected by the presence of PEEKMOH in the blends.

6. Conclusions

A melt processable epoxy/PEEKMOH system was investigated for miscibility, fracture toughness, tensile and flexural properties and thermal properties. Hydroxyl terminated PEEK with pendent methyl groups was synthesised by the nucleophilic substitution reaction of DFBP and MeHQ. The blends in the uncured state were homogeneous and the glass transition temperature of the homogeneous systems was theoretically calculated. FTIR studies of the binary epoxy/PEEKMOH blends revealed that some of the hydroxyl groups reacted with epoxy group in the presence of TPP. Reaction induced phase separation occurred in all the blends upon curing with DDS. The blends exhibited two-phase morphology. A uniform dispersion of PEEKMOH domains in epoxy matrix was seen in DGEBA/PEEKMOH blends. The domain size and size distribution were dependent on the molecular weight and concentration of PEEKMOH in the blends. Substantial improvement in fracture toughness could be achieved by the incorporation of PEEKMOH in epoxy resin. The extent of improvement in fracture toughness was dependent on the domains size distribution, molecular weight of the oligomer and composition of the blends. Various toughening mechanisms like crack pinning, crack path deflection, ductile nature of crack and plastic deformation of the matrix were responsible for the increase in fracture toughness of the blends. The mechanical properties of the blends were comparable to that of the unmodified resin. The glass transition temperature of epoxy rich and thermoplastic rich phases was seen in the dynamic mechanical spectrum of the blends. The loss modulus of the blends was higher than that of neat resin indicating better interaction between the phases. No deterioration in the thermal stability of epoxy resin was observed on blending with PEEKMOH.

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