

Poly(ether ether ketone) with pendent methyl groups as a toughening agent for amine cured DGEBA epoxy resin

Bejoy Francis · V. Lakshmana Rao · Seno Jose ·
Bina K. Catherine · R. Ramaswamy ·
Jesmy Jose · Sabu Thomas

Received: 18 July 2005 / Accepted: 21 October 2005 / Published online: 13 June 2006
© Springer Science+Business Media, LLC 2006

Abstract A diglycidyl ether of bisphenol-A (DGEBA) epoxy resin was modified with poly(ether ether ketone) with pendent methyl groups (PEEKM). PEEKM was synthesised from methyl hydroquinone and 4,4'-difluorobenzophenone and characterised. Blends of epoxy resin and PEEKM were prepared by melt blending. The blends were transparent in the uncured state and gave single composition dependent T_g . The T_g -composition behaviour of the uncured blends has been studied using Gordon–Taylor, Kelley–Bueche and Fox equations. The scanning electron micrographs of extracted fracture surfaces revealed that reaction induced phase separation occurred in the blends. Cocontinuous morphology was obtained in blends containing 15 phr PEEKM. Two glass transition peaks corresponding to epoxy rich and thermoplastic rich phases were observed in the dynamic mechanical spectrum of the blends. The crosslink density of the blends calculated from dynamic mechanical analysis was less than that of unmodified epoxy resin. The tensile strength, flexural strength and modulus were comparable to that of the unmodified epoxy resin. It was found from fracture toughness measurements that PEEKM is an effective toughener for DDS cured epoxy resin. Fifteen phr PEEKM

having cocontinuous morphology exhibited maximum increase in fracture toughness. The increase in fracture toughness was due to crack path deflection, crack pinning, crack bridging by dispersed PEEKM and local plastic deformation of the matrix. The exceptional increase in fracture toughness of 15 phr blend was attributed to the cocontinuous morphology of the blend. Finally it was observed that the thermal stability of epoxy resin was not affected by the addition of PEEKM.

Introduction

Epoxy resins are used for multitudes of applications in aerospace, electrical and electronic industries and automobile industries as structural adhesives, matrices for composite materials, insulating materials, moulded articles etc. They are widely used because of the ability of the epoxy group to react with a wide range of reactive functional groups, easy processability, wide range of attainable properties, low cost etc. Another feature of epoxy curing is that no volatiles are given off during cure [1–3]. This makes it a good choice as matrix material in advanced composites.

Epoxy resins can be cured by catalytic or coreactive curing agents. The ultimate properties of cured resins can be controlled according to end use by proper choice of curing agent and curing conditions. Although epoxy resins are used for a wide range of applications, their inability to withstand impact is a serious drawback for several advanced applications. There are several methods to improve the fracture toughness of epoxy resins. They include improving the flexibility of the system by chemical

B. Francis · V. Lakshmana Rao (✉) · B. K. Catherine ·
R. Ramaswamy

Polymers and Special Chemicals Division, Analytical and Spectroscopy Division, Propellants and Special Chemicals Group, Propellants Chemicals and Materials Entity, Vikram Sarabhai Space Centre, Thiruvananthapuram, Kerala 695 022, India
e-mail: rao_vl@rediffmail.com

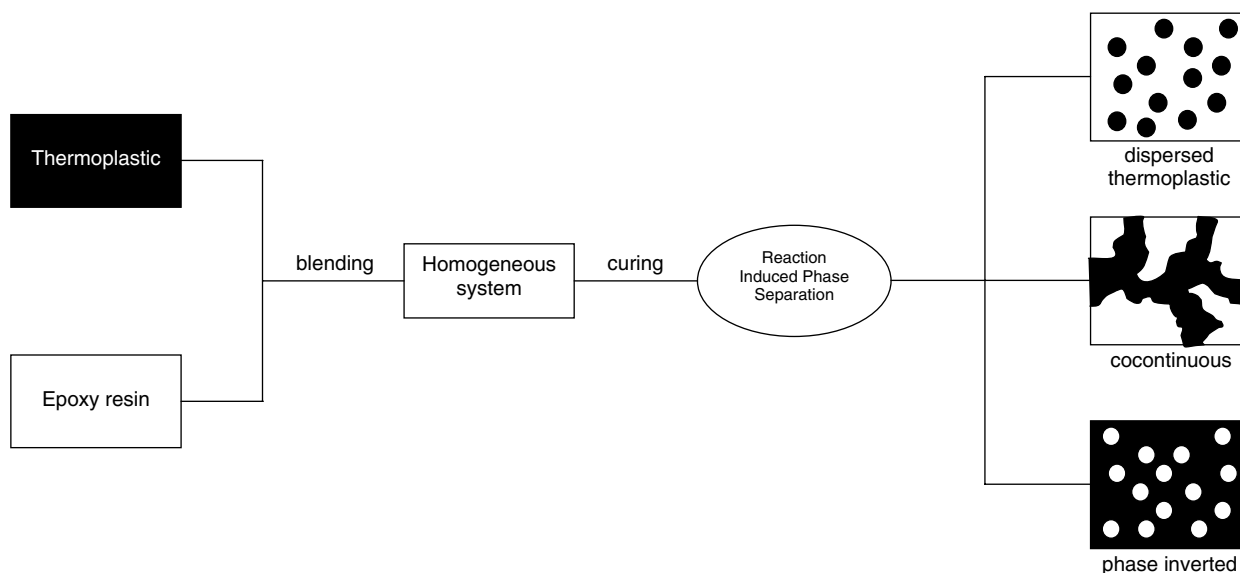
S. Jose · J. Jose · S. Thomas
School of Chemical Sciences, Mahatma Gandhi University,
Priyadarshini Hills, Kottayam, Kerala 686 560, India

modification of rigid epoxy to give flexible backbone structure, increasing epoxy monomer molecular weight, lowering of crosslink density of cured resin and incorporation of dispersed toughener phase. Among these addition of dispersed toughener phase was found to be the most effective method. Addition of rubbers like carboxy terminated butadiene acrylonitrile (CTBN) [4, 5], amine terminated butadiene acrylonitrile (ATBN) [6, 7] etc. are found to increase the fracture toughness. The elastomers form homogeneous systems with epoxy resin in the uncured state and phase separates into fine droplets on curing. Often elastomer toughening results in lower modulus and reduction in elevated temperature properties. Also elastomers failed to toughen highly crosslinked epoxy resin systems like triglycidyl *p*-amino phenol (TGAP) and tetraglycidyl diaminodiphenyl methane (TGDDM) because the important mechanisms responsible for improved fracture toughness in rubber toughened epoxy system are due to rubber particle cavitation and matrix shear yielding, which do not occur in highly crosslinked systems [8, 9].

High performance engineering thermoplastics are often used to toughen highly crosslinked systems [10]. Even a mixture of thermoplastics were used to modify epoxy resin [11, 12]. Due to high modulus and high T_g , the thermal properties and modulus are retained in the cured blend. Thermoplastics are used to toughen both difunctional and multifunctional epoxy resins. As in the case of rubber-modified epoxies, thermoplastic toughened systems form homogeneous blends in the uncured state. Most of the systems undergo phase separation upon curing. Depending on the concentration and molecular weight of the thermoplastic, different morphologies are formed. The evolution of phase morphology is shown in Scheme 1. The

morphology of the blends changed with respect composition of the blends. At low levels of modifier, droplet matrix morphology with the modifier dispersed in the epoxy matrix will be obtained and at higher modifier concentrations phase inverted morphology will be obtained. At intermediate composition cocontinuous morphology is often observed. While curing, two factors are competing viz rate of curing reaction and rate of phase separation. Depending on the rate of phase separation either a homogeneous or a heterogeneous morphology is formed [13–15]. In phenoxy/DGEBA system cured with diaminodiphenyl sulfone (DDS), a homogeneous morphology was formed when the accelerator 1-cyanoethyl-2-ethyl-4-methylimidazole (CEMI) was used at high concentration. Here the rate of reaction is very fast compared to rate of phase separation [16]. Another factor, which can influence the morphology, is the curing agent. In phenolphthalein poly(ether ether ketone) (PEK-C) modified epoxy resin cured with anhydrides, homogeneous morphology was obtained when maleic anhydride or hexahydrophthalic anhydride (HHPA) was used as the curing agent [17]. The fracture toughness of epoxy/thermoplastic blends was also influenced by the morphology of the system. Usually phase separated or cocontinuous morphology gave maximum toughness. In few cases like low molecular weight poly(ethylene phthalate) (PEP) [18] and phenoxy [16] modified epoxies, homogeneous morphology gave more toughness than the phase separated counterparts.

Not only homogeneous morphology but also the interfacial adhesion between components also affects the fracture toughness. Good interfacial adhesion is a necessary condition for obtaining toughness enhancement. Oligomers like hydroxy polyethersulfone [19, 20], polyesters [21],



Scheme 1 Morphology evolution of thermoset/thermoplastic blends upon curing

amino polyethersulfone [22, 23], etc. were used successfully for modifying the epoxy resin.

Poly(ether ether ketone) (PEEK) though has excellent mechanical properties is immiscible in epoxy resin. Even solution casting is difficult due to its immiscibility in low volatile solvents. As an alternative for commercial semi-crystalline PEEK, amorphous PEEK like PEK-C have been developed and found to be miscible with epoxy resin [17, 24]. Another alternative is the use of functionalised polymers with low molecular weight as modifiers for epoxy resin. Amine terminated PEEK based on tert-butyl hydroquinone (TBHQ), methyl hydroquinone (MeHQ), hydroquinone (HQ), bisphenol-A etc were found to be miscible with epoxy system and enhanced the fracture toughness of epoxy resin [25]. These oligomers were amorphous. From these discussions it is clear that amorphous oligomers are capable of increasing the toughness of epoxy resins. Recently, in this laboratory we had synthesised a series of PEEK polymers with pendent alkyl groups. These polymers were used as toughening agents for epoxy resin. In our earlier study we had reported the cure kinetics of an epoxy-DDS system blended with PEEK with pendent tert-butyl groups [26]. As mentioned earlier, PEEK with pendent methyl groups was synthesised from methyl hydroquinone and difluorobenzophenone. This polymer was blended with epoxy resin and cured with DDS. The mechanical properties, fracture toughness and dynamic mechanical properties were investigated in detail. The properties were correlated with the morphology of the blends and various toughening mechanisms responsible for the toughness enhancement were identified. Finally the thermal stability of the blends was investigated using thermogravimetric analysis.

Experimental

Materials

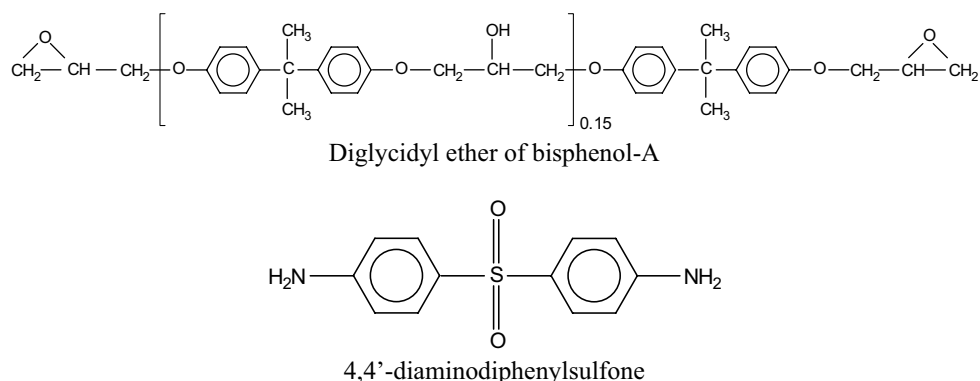
High purity methyl hydroquinone (MeHQ) (Fluka), 4,4'-difluorobenzophenone (DFBP) (Spectrochem), potassium carbonate (Qualigens), *N*-methyl-2-pyrrolidone (NMP)

(SRL) and toluene (Qualigens) were used for the synthesis of PEEKM. 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 P₂O₅ 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. The chemical structure of DGEBA and DDS are given in Fig. 1.

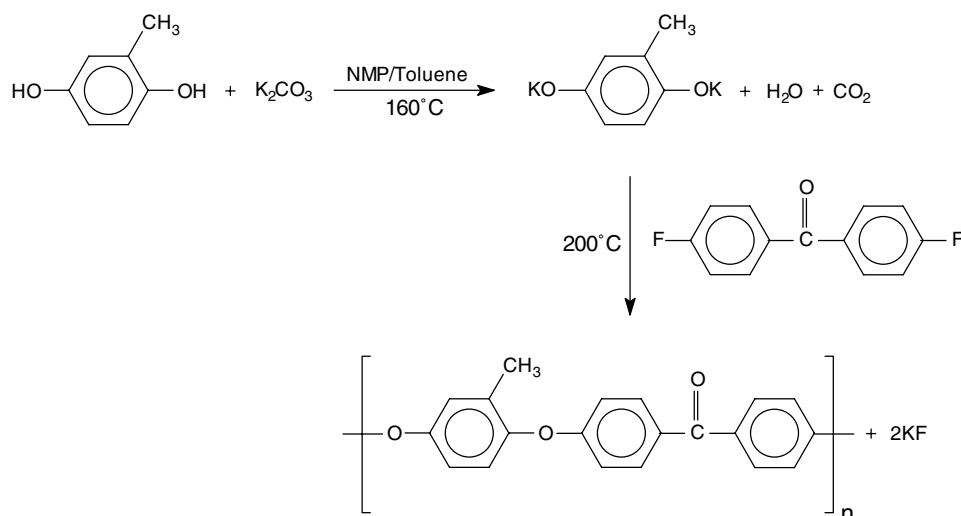
Synthesis of PEEKM

Poly(ether ether ketone) with pendent methyl group (PEEKM) was synthesised by the nucleophilic substitution reaction of DFBP with MeHQ as shown in Scheme 2. A typical procedure for the synthesis of PEEKM 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 40 g (0.24 mol) of MeHQ, 39.9 g (0.29 mol) of potassium carbonate, 360 ml NMP and 150 ml toluene. The reaction mixture was refluxed at 120–160°C for 4 h with constant stirring under nitrogen atmosphere. Water formed during reaction was removed as azeotrope with toluene through the Dean-Stark trap. After 4 h the reaction temperature was brought down to 100°C and 52.5 g (0.24 mol) of DFBP and 100 ml NMP were added to the flask. The reaction mixture was further heated at 200°C for 3 h and cooled to room temperature. The viscous polymer solution was precipitated in large excess of water at room temperature with constant stirring. The precipitated polymer was filtered and purified by refluxing with water repeatedly followed by soxhlet extraction with acetone. The resultant product was dried under vacuum at 120°C for 24 h and characterised using various analytical techniques.

Fig. 1 Chemical structure of epoxy resin and DDS



Scheme 2 Reactions involved in the synthesis of PEEK with pendent methyl group



Blend preparation

The blends were prepared by melt mixing. PEEKM was dissolved in epoxy resin at 180°C with constant stirring. 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 PEEKM were prepared.

Characterisation of PEEKM

The molecular weight and molecular weight distribution of PEEKM 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 PEEKM was determined for 0.4% polymer solution in concentrated sulphuric acid at room temperature using Ubbelohde suspended level viscometer. The ^{13}C NMR spectrum of PEEKM 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.

DSC analysis

The glass transition temperature of pristine epoxy and the binary epoxy/PEEKM blends were determined using TA

instruments model 2920 differential scanning calorimeter. In order to determine the T_g of PEEKM, the sample was heated to 350°C at 10°C/min, cooled to 0°C and reheated to 250°C at 10°C/min in nitrogen atmosphere. The T_g was taken from the second heating and to determine the T_g of pristine epoxy and the binary DGEBA/PEEKM blends, the samples were heated from -50 to 200°C at a heating rate of 10°C/min in nitrogen atmosphere.

Tensile and flexural 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 using a universal testing machine (model TNE 5000) at a crosshead speed of 10 mm/min. Rectangular specimens of 100 × 10 × 3 mm were used for determining flexural strength. The flexural measurements were done at a crosshead speed of 10 mm/min as per ASTM D790. Flexural strength was calculated using the equation

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

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

Fracture toughness

Fracture toughness of the modified and unmodified epoxy resin was determined according to ASTM STP410. Rectangular specimens of 100 × 35 × 3 mm 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 was calculated using Eq. 2.

$$K_{Ic} = \frac{QPa^{1/2}}{bd} \quad (2)$$

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.

$$Q = 1.99 - 0.41(a/b) + 18.7(a/b)^2 - 38.48(a/b)^3 + 53.85(a/b)^4 \quad (3)$$

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.

Dynamic mechanical thermal analysis

The viscoelastic properties of the neat resin as well as the blends were measured using TA Instruments DMA 2980 dynamic mechanical thermal analyser. Rectangular specimens of $60 \times 10 \times 3$ 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.

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.

Results and discussion

The synthesis of PEEKM was carried out in NMP in the presence of anhydrous potassium carbonate. PEEKM was characterised by various physico-analytical techniques.

The number average molecular weight (\bar{M}_n), weight average molecular weight (\bar{M}_w) and polydispersity index were found to be 22000, 65500 and 2.97 respectively from GPC measurements. The inherent viscosity was found to be 0.96 dl/g for 0.4% polymer solution in concentrated sulphuric acid at ambient conditions. The glass transition temperature of PEEKM was found to be 151°C from DSC measurements. The properties are summarised in Table 1.

The FTIR spectrum of PEEKM gave absorption in the range 1220–1225 cm^{-1} corresponding to the ϕ -O skeletal vibrations. Carbonyl stretching vibration was observed in the range 1600–1670 cm^{-1} . The C–H stretching vibration of the methyl groups was observed at 2960 cm^{-1} . The ^{13}C NMR spectrum of PEEKM along with the assignments is shown in Fig. 2. The spectrum showed 12 peaks corresponding to 12 distinguishable carbon atoms indicated in the structure. 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 ppm. The methyl carbon gave peak at 16.4 ppm. The other peaks are due to the aromatic ring carbons of the polymer.

Miscibility of DGEBA/PEEKM blends

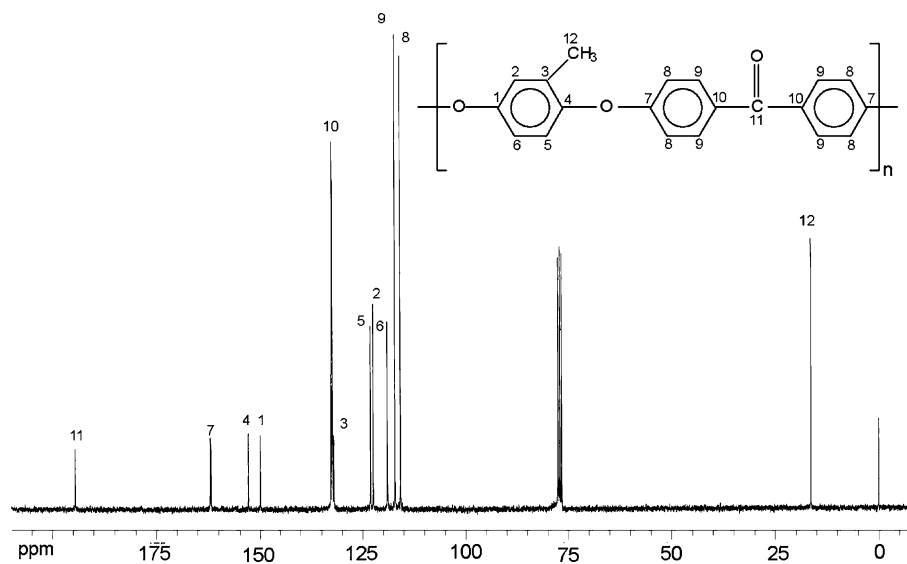
The basic idea behind the use of functionally terminated polymers or polymers with pendent groups is to improve the processing. PEEK being a semicrystalline engineering plastic was immiscible in epoxy resin. On introducing methyl group to PEEK backbone, the processability was improved. Epoxy resin was blended with PEEKM by melt mixing at 180°C. The binary DGEBA/PEEKM blends were transparent at room temperature. Even after heating at 200°C, the blends remained clear and transparent. Therefore, there was no visual evidence for heterogeneity in the blends before the addition of curing agent. The miscibility was further investigated using DSC. The blends exhibited single composition dependent T_g , which is characteristic of miscible systems. From visual transparency and DSC studies, it was concluded that the blends were homogeneous.

The T_g of miscible systems can be theoretically calculated using Fox [27], Gordon–Taylor [28] and Kelley–Bueche [29] equations, which are given by Eqs. 4, 5 and 6 respectively.

Table 1 Properties of PEEKM

Number average molecular weight	22000 g/mol
Weight average molecular weight	65500 g/mol
Polydispersity index	2.97
Inherent viscosity	0.96 dl/g
Glass transition temperature	151°C

Fig. 2 ^{13}C NMR spectrum of PEEKM



$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \quad (4)$$

where T_g is the glass transition temperature of the blend, T_{g1} and T_{g2} are the glass transition temperatures and w_1 and w_2 are the weight fractions of components 1 and 2 respectively

$$T_g = \frac{w_1 T_{g1} + k w_2 T_{g2}}{w_1 + k w_2} \quad (5)$$

where, k is an adjustable parameter and the other terms are the same as that of Fox equation

$$T_g = \frac{v_1 T_{g1} + k v_2 T_{g2}}{v_1 + k v_2} \quad (6)$$

Kelley–Bueche equation is similar to Gordon–Taylor equation but it utilises volume fraction instead of weight fraction.

A comparison of theoretically calculated T_g and experimental values from DSC measurements is shown in Fig. 3. Gordon–Taylor and Kelley–Bueche equations agreed well with the experimental values but Fox equation showed large deviations from experimental values. Prud'homme et al. [30, 31] suggested that the k value in Gordon–Taylor equation is an indication of the interaction between the blend components. In epoxy/PEEKM blends, a k value of 0.21 gave good correlation between experimental and theoretical values. The low value of k indicated weak interactions between uncrosslinked epoxy resin and PEEKM. Hence the miscibility was mainly due

to the entropy contribution to the free energy of mixing owing to the low molecular weight of uncrosslinked epoxy resin.

FTIR analysis

In order to attain the end use properties, epoxy resins were cured using suitable curing agents. In our studies on DGEBA/PEEKM blends, we used DDS as the curing agent. The DDS cured epoxy resins have excellent mechanical properties, adhesive strength and high T_g . The properties of the cured resins were strongly dependent on the extent of curing and usually a fully crosslinked system gave maximum properties [32]. In epoxy resin/thermoplastic blends, the morphology and ultimate properties were influenced by the curing conditions employed. Usually complete conversion was achieved for these systems by post curing [33]. In epoxy/PEEKM blends, after curing at 180°C, post curing was done at 200°C for ensuring complete reaction. FTIR studies were conducted to examine the completion of cure reaction [34]. The IR spectrum of uncured epoxy resin and the cured blends are depicted in Fig. 4. The spectra of the blends did not show any absorption characteristic of epoxy group at 915 cm^{-1} . This observation revealed that no free epoxy group was present in the cured blends.

Scanning electron microscopy studies

The transparent binary DGEBA/PEEKM blends became opaque on curing with DDS indicating the formation of a phase separated system. The morphology of the blends

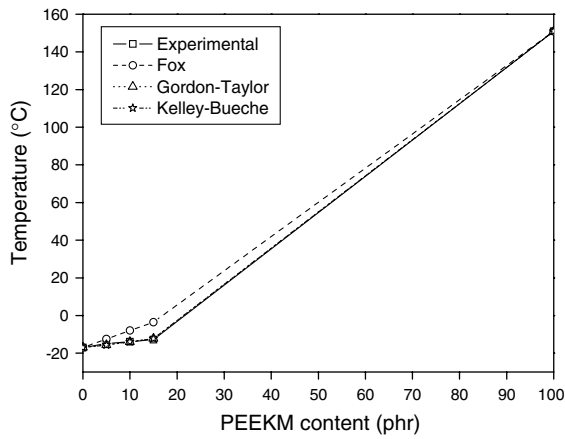
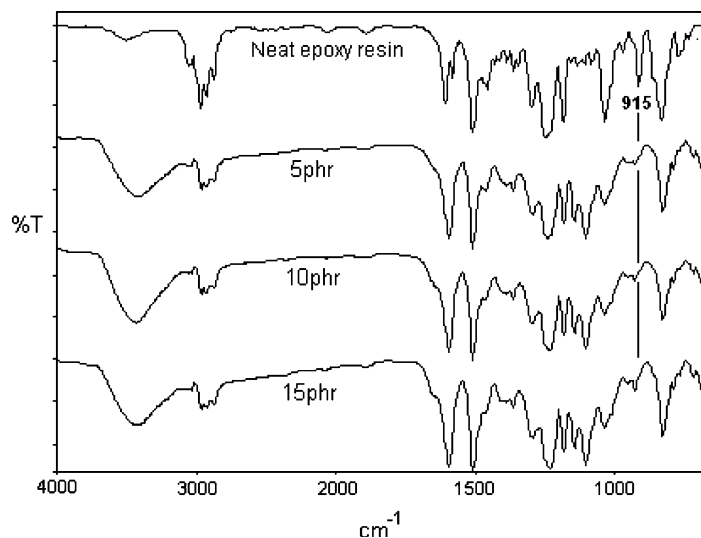


Fig. 3 Comparison of experimental and theoretical values of glass transition temperatures of DGEBA/PEEKM blends

was investigated using SEM. The SEM pictures of cryogenically fractured surfaces of 5, 10 and 15 phr blends are shown in Fig. 5a–c. The fracture surfaces of 5 and 10 phr blends were extracted with chloroform before taking the micrographs. The holes seen in Fig. 5a, b represent dispersed PEEKM etched by chloroform. Figure 5c represents the unetched fracture surface of 15 phr blend and it exhibited cocontinuous morphology. The darker regions represent epoxy rich phase and lighter region represents thermoplastic rich phase. As mentioned earlier, the initial miscibility was attributed to the low molecular weight of epoxy resin. Upon curing the molecular weight of epoxy resin increased as a result of crosslinking reaction. Hence the entropy contribution towards miscibility decreased as a result of crosslinking and the system became phase separated.

Fig. 4 FTIR spectrum of cured DGEBA/PEEKM blends



The domain diameters and polydispersity index were calculated for 5 and 10 phr blends using the following equations and are summarised in Table 2.

$$\text{Number average diameter, } \bar{D}_n = \frac{\sum n_i d_i}{\sum n_i} \quad (7)$$

$$\text{Weight average diameter, } \bar{D}_w = \frac{\sum n_i d_i^2}{\sum n_i d_i} \quad (8)$$

$$\text{Polydispersity index, } PDI = \frac{\bar{D}_w}{\bar{D}_n} \quad (9)$$

where, n_i is the number of domains having diameter d_i .

The interparticle distance and interfacial area per unit volume were calculated using Eqs. 10 and 11 respectively.

$$\text{Interparticle distance} = d_{TP} \left[\left(\frac{\pi}{6\phi_{TP}} \right)^{1/3} - 1 \right] \quad (10)$$

$$\text{Interfacial area per unit volume} = \frac{3\phi_{TP}}{r} \quad (11)$$

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.

From Table 2, it was found that the domain size increased with increase in PEEKM content in the blends. It is also observed that 5 phr blends exhibited a more uniform size distribution compared to 10 phr blends. The scanning electron micrographs in Fig. 5 clearly showed the increase

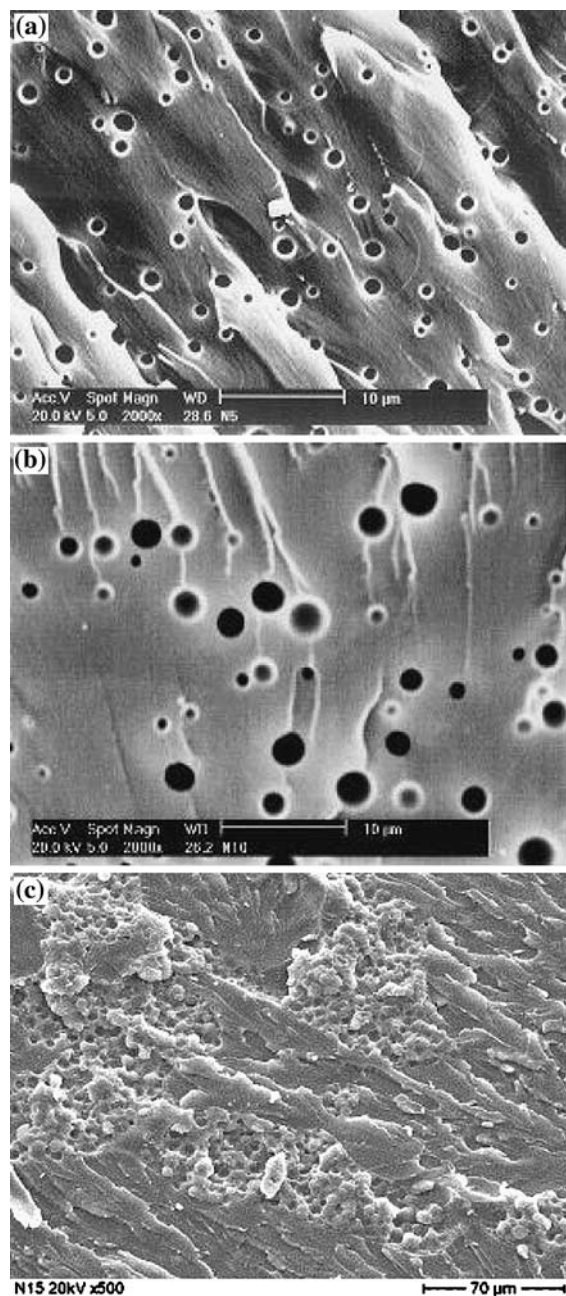


Fig. 5 Scanning electron micrographs of DGEBA/PEEKM blends (a) 5 phr DGEBA/PEEKM, (b) 10 phr DGEBA/PEEKM and (c) 15 phr DGEBA/PEEKM blend

in domain size and broader size distribution of 10 phr blend compared to 5 phr blend. The increase in domain size was due to the coalescence of the domains after phase

separation and also due to the proximity of this composition to cocontinuous morphology in 15 phr epoxy/PEEKM blend. It is to be noted that an appreciable amount of holes have a white circular diffuse zone between the epoxy matrix and the empty hole. These diffuse zones are probably transition zones of incomplete phase separation where both epoxy and PEEKM are present. Similar behaviour was reported by Teng and Chang [16] in epoxy/phenoxy blends cured with DDS. Hence it is inferred that the two phases are not pure.

Dynamic mechanical thermal analysis

The $\tan\delta$ curves for the modified and unmodified epoxy resin is shown in Fig. 6. The two peaks observed in Fig. 6 were due to epoxy rich and PEEKM rich phases with the thermoplastic peak becoming more prominent with increase in PEEKM content in the blends. The T_g of epoxy rich phase shifted to lower temperature side while that of PEEKM rich phase shifted towards high temperature side. It is possible that during phase separation, some lightly crosslinked epoxy may get trapped in the PEEKM phase and due to the increase in viscosity of the system with the progress of curing reaction and the trapped epoxy remains in PEEKM rich phase. This will result in a slightly higher T_g for PEEKM rich phase. PEEKM was synthesised using equimolar ratio of DFBP and MeHQ. As a result there was no control over the terminal functional group of the resulting polymer. The chain ends will be either hydroxyl or fluorine terminated. Hence due to the possible H-bonding interactions between these groups and epoxy resin, a small amount of PEEKM will remain in the epoxy phase. This will act as a plasticiser for the epoxy rich phase leading to reduction in epoxy T_g .

The storage modulus of the blends is shown in Fig. 7. For 5 phr blend, the storage modulus is same as that of neat resin below T_g but for 10 and 15 phr blends, the values were higher than that of neat epoxy. Two inflections were seen near the T_g of PEEKM and epoxy rich phases in Fig. 7. The increase in storage modulus at room temperature indicates increased stiffness of the system. The variation of loss modulus with temperature for the neat resin as well as the blends is shown in Fig. 8. The loss modulus of the blends was higher than that of neat resin near room temperature. This indicated better interaction between the blend components.

Table 2 Domain size, interparticle distance and interfacial area/unit volume for DGEBA/PEEKM blends

Composition (phr)	\bar{D}_n (μm)	\bar{D}_w (μm)	PDI	Interparticle distance (μm)	Interfacial area/unit volume (μm^{-1})
5	1.09	1.19	1.10	1.4	0.2428
10	1.79	2.13	1.19	1.5	0.2832

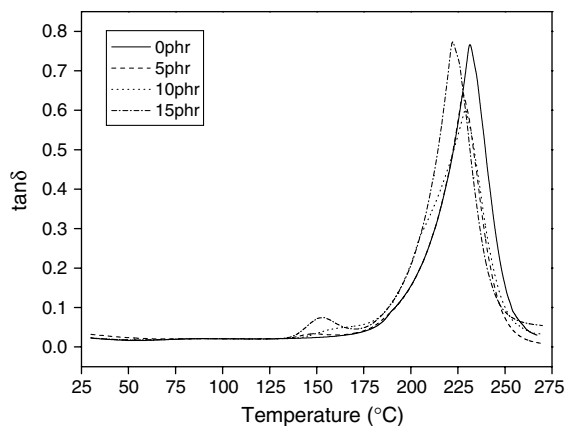


Fig. 6 $\tan\delta$ versus temperature plot of DGEBA/PEEKM blends cured with DDS

An approximate idea about the crosslink density can be obtained from the T_g of the blends. According to Nielsen [35], the number average molecular weight between crosslinks M_c is given by

$$M_c = \frac{3.9 \times 10^4}{T_g - T_{g0}} \tag{12}$$

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. According to Bellenger et al. [36] the value of T_{g0} was 91°C for DGEBA-DDS system. The effective crosslink density ν_e was calculated from M_c using the following equation [37]

$$\text{Effective crosslink density, } \nu_e = \frac{\rho N_A}{M_c} \tag{13}$$

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

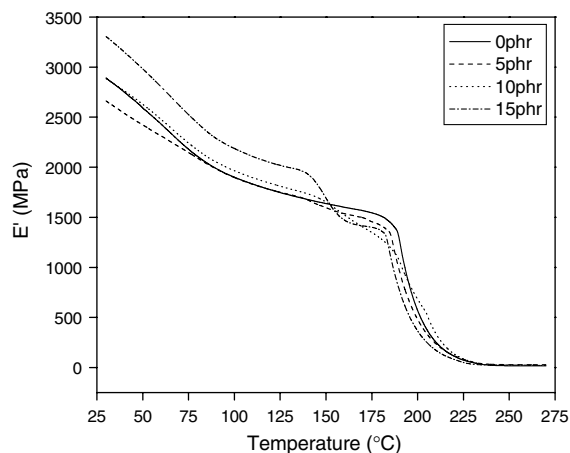


Fig. 7 Storage modulus of DGEBA/PEEKM blends cured with DDS

Table 3 gives the M_c and ν_e values for PEEKM modified epoxy resin. The decrease in crosslink density of the epoxy resin on blending with PEEKM is evident from the table.

Tensile and flexural properties

The tensile and flexural stress–strain curves are shown in Figs. 9 and 10 respectively. No yielding was observed in the tensile stress–strain curves. The tensile strain of the blends were higher than that of epoxy resin except for 10 phr blend. The slight increase in strain was due to the decrease in crosslink density of the blends. Among the blends, 15 phr blend showed maximum strain. This was due to the cocontinuous morphology of the blend. The flexural strain decreased slightly compared to that of neat resin. A slight reduction was observed but not much variation was observed with respect to composition of the blends.

The tensile and flexural properties of the blends are given in Table 4. The tensile strength of the blends was enhanced by the addition of PEEKM. Maximum increase was observed for 15 phr blend. The Young’s modulus of the blends was slightly lower than that of neat epoxy resin. The flexural strength and modulus of the blends were always less than that of neat epoxy resin. However, the decrease in flexural modulus observed was within acceptable limits.

Fracture toughness

Fracture toughness is the ability of a material to resist the propagation of crack. Highly crosslinked materials are prone to catastrophic failure on impact. Out of the many methods used to improve their toughness, blending with a second polymeric component was the most effective method. One of the primary requirements for obtaining improved toughness is phase-separated morphology for the final material. Other than few exceptions [38, 39], all the tough thermoset/thermoplastic blends had two-phase morphology. The blends usually undergo reaction induced phase separation to give two-phase systems with different morphologies depending on the concentration of the modifier. The dispersed domains in the blends will initiate processes, which will increase the energy required for the propagation of the crack.

The dependence of fracture toughness on the composition of the blends is shown in Fig. 11. It is seen from Fig. 11 that there is a significant improvement in the fracture toughness of epoxy resin on blending with PEEKM. The fracture toughness doubled with the addition of PEEKM and maximum increase was shown by 15 phr blend. The increase in fracture toughness was due to several reasons. One of the factors influencing fracture

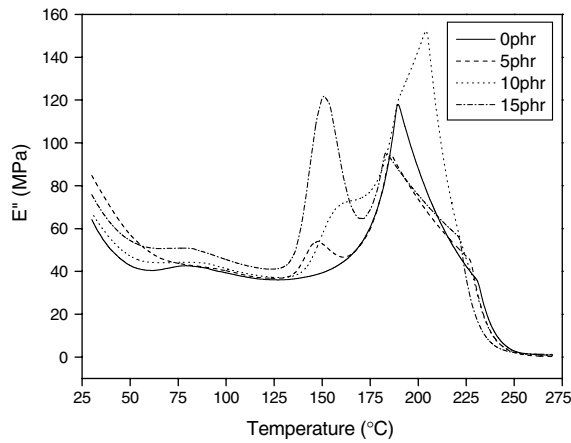


Fig. 8 Loss modulus of DGEBA/PEEKM blends cured with DDS

toughness is the crosslink density of the blends. A highly crosslinked system becomes less brittle with decrease in crosslink density. The crosslink density of the blends was calculated from dynamic mechanical analysis. The reduction in T_g and v_e of the epoxy phase showed that there is a decrease in the crosslink density on blending epoxy resin with PEEKM.

In order to understand the various toughening mechanisms, the scanning electron micrographs of the failed specimens from fracture toughness measurements were taken. The micrographs of the failed surfaces are given in

Table 3 M_c and v_e values of DGEBA/PEEKM blends

PEEKM content (phr)	$M_c \times 10^{-4}$ (kg/mol)	$v_e \times 10^{27}$ chains/m ³
0	279	2.59
5	285	2.54
10	283	2.56
15	298	2.43

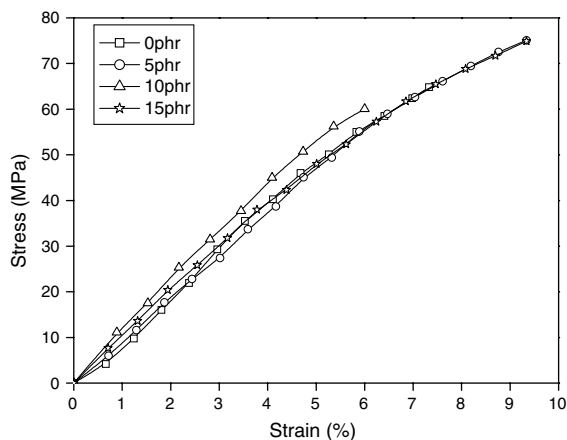


Fig. 9 Tensile stress–strain curves of DDS cured DGEBA/PEEKM blends

Fig. 12a–d. The fracture surface of the neat resin revealed typical features of brittle fracture (Fig. 12a). The fracture surfaces of the blends (Fig. 12b–d) were rough and ridge like patterns and river marks could be seen on the fracture surface. The roughness of the fracture surface is associated with the ductile nature of the crack. The ductile nature of the crack was due to the decrease in crosslink density of the blends. Another important factor influencing the fracture toughness was the strength of interfacial adhesion between the matrix and dispersed domains. If there is good adhesion between the phases, vacant space left by the domains will not be seen in the micrographs. The fracture surfaces of the blends shown in Fig. 12b–d revealed no vacant space left by the removal of PEEKM domains from the fracture surface, i.e. there exists good interfacial adhesion between the dispersed domains and epoxy matrix. The scanning electron micrographs of etched surfaces revealed a diffuse zone, where both phases coexisted. Both these factors showed that there was good interfacial adhesion between the phases.

The domains on the failed surfaces were not completely pulled off from the fracture surface, but they are torn up on fracture. The ductile tearing of domains indicated good interfacial adhesion and it increased the fracture toughness by bridging the advancing crack to a certain extent. The roughness of fracture surface indicated that the crack deviated from the original plane i.e. the domains acted as obstacles in the crack path. As a result the surface area of the crack was increased and more energy is required for the propagation of the crack. The tail marks behind the domains in the micrographs indicate crack pinning mechanism as in rigid particle toughened epoxy systems. Another mechanism responsible for increase in fracture toughness was the local plastic deformation of the matrix. Plastic deformation occurred because the domains acted as stress concentrators. White ring marks seen around the domains

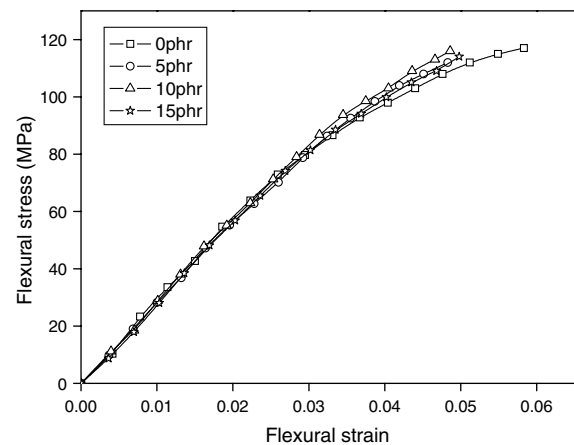


Fig. 10 Flexural stress–strain curves of DDS cured DGEBA/PEEKM blends

Table 4 Tensile and flexural properties of DGEBA/PEEKM blends

PEEKM content (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
5	73 ± 1	1.5 ± 0.05	113 ± 2	2.87 ± 0.10
10	64 ± 2	1.9 ± 0.09	119 ± 5	2.95 ± 0.15
15	74 ± 2	1.6 ± 0.07	114 ± 3	2.89 ± 0.13

were an indication of local plastic deformation of the matrix. The river marks of the fracture surface corroborated the plastic deformation of the matrix. The combined effect

of the above discussed mechanisms explains the increase in fracture toughness of the blends.

The fracture toughness of 5 and 10 phr blends were similar. This behaviour was explained on the basis of morphology of the blends. The fracture toughness of phase separated thermoset/thermoplastic blends depends on morphological parameters like interparticle distance, interfacial area per unit volume, domain size, domain size distribution, distribution of domains in the matrix etc. The interfacial area per unit volume and interparticle distance for 5 and 10 phr blends were similar (Table 2). Looking into the domain size distribution of the blends, it was found that 10 phr blend is having a broader size distribution than 5 phr blend and the domain size varied from 0.71 to 3.1 μm. Large domains are not much effective in improving the fracture toughness. As a result of all these factors, 5 and 10 phr blends exhibited similar fracture toughness. On examining the morphology of the blends, it was found that the 15 phr blend generated cocontinuous morphology. Hence, the advancing crack had to propagate through more

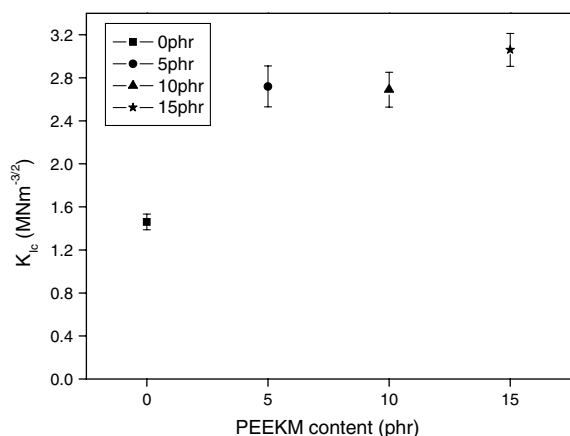
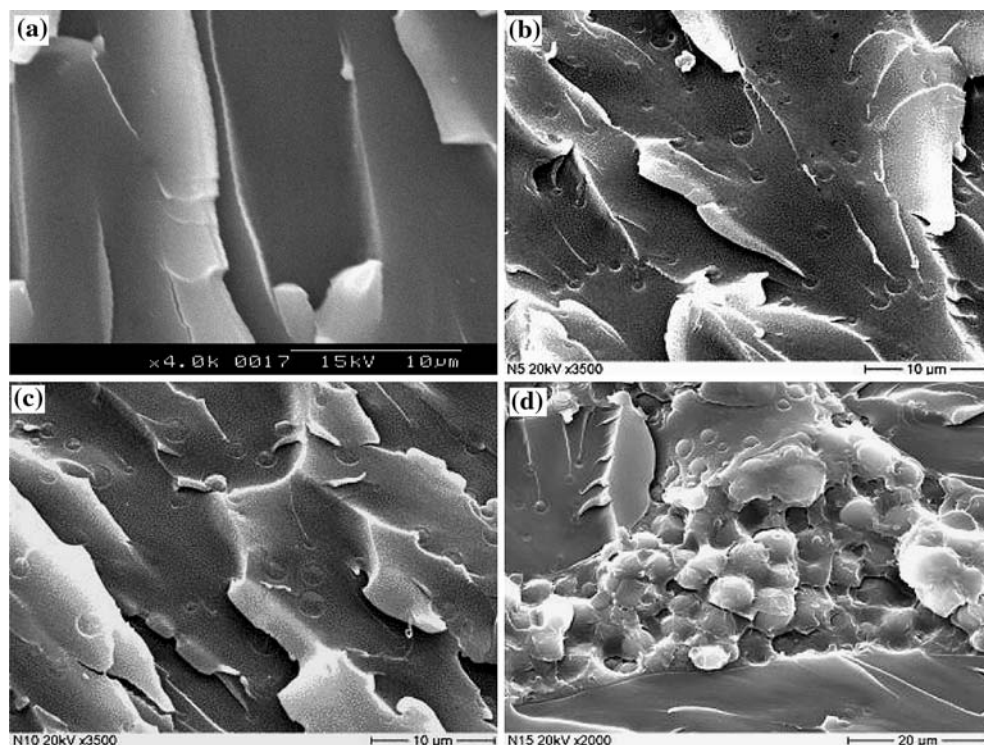


Fig. 11 Fracture toughness of DDS cured DGEBA/PEEKM blends

Fig. 12 Scanning electron micrographs of failed surfaces from fracture toughness measurements of (a) neat epoxy resin, (b) 5 phr DGEBA/PEEKM (c) 10 phr DGEBA/PEEKM and (d) 15 phr DGEBA/PEEKM blend



ductile continuous PEEKM phase, which offered more resistance to crack propagation. Min and Kim [40] reported that plastic deformation of the continuous thermoplastic rich phase was found to be more effective in enhancing the fracture toughness than crack pinning or crack path deflection observed in sea island morphology. The scanning electron micrograph of the epoxy rich phase of 15 phr DGEBA/PEEKM blend is shown in Fig. 13. Dispersed PEEKM phase was observed in the continuous epoxy phase. This observation supported the decrease in T_g of epoxy phase in the dynamic mechanical spectrum. Evi-

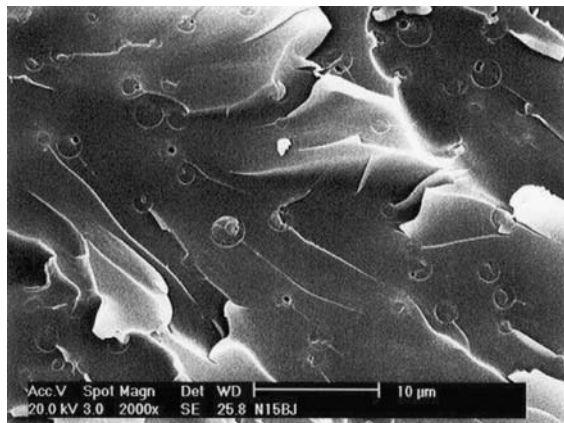


Fig. 13 Scanning electron micrograph of continuous epoxy region of 15 phr DGEBA/PEEKM blend

dences for various energy absorbing mechanisms like crack pinning, crack path deflection etc. are also observed in Fig. 13. Hence 15 phr blends exhibited maximum increase in fracture toughness.

Thermogravimetric analysis

The thermal stability of the blends was analysed using TGA. The parameters obtained from thermogravimetric analysis are summarised in Table 5. The initial decomposition temperature (IDT) and the temperature at which the rate of decomposition is maximum (T_{max}) for the blends remained the same as that of unmodified epoxy resin. T_{max} was taken as the maximum in the differential thermogravimetric curve. Activation energy (E) for decomposition

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

Composition (phr)	IDT (°C)	T_{max} (°C)	E (kJ/mol)	Corr. Coeff.
0	402	430	280	0.9971
5	401	430	271	0.9980
10	406	430	281	0.9975
15	404	431	269	0.9993

was calculated using non-isothermal integral equations viz; Coats-Redfern [41] equation. The main advantage of non-isothermal techniques is that the kinetic values for the whole temperature range could be obtained from a single measurement. The Coats-Redfern theory given in Eq. 4 was used to compute the activation energy.

$$\ln \left[\frac{g(\alpha)}{T^2} \right] = \ln \left\{ \left(\frac{AR}{\phi E} \right) \left(1 - \frac{2RT}{E} \right) \right\} - \frac{E}{RT} \quad (14)$$

where, $g(\alpha) = \left\{ \frac{1-(1-\alpha)^{1-n}}{1-n} \right\}$ for ($n \neq 1$) and

$$g(\alpha) = -\ln(1-\alpha)$$

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 was determined from the plot of $\ln[-\ln(1-\alpha)/T^2]$ against the reciprocal of absolute temperature ($1/T$). Activation energy was calculated from the slope of the kinetic plot. The kinetic parameters of the blends were comparable to that of neat epoxy resin. Although there was a slight decrease in the crosslink density of the blends, the thermal stability was unaffected by the addition of PEEKM.

Conclusions

A DGEBA epoxy resin cured with DDS was toughened using PEEK with pendent methyl groups; PEEKM. PEEKM was synthesised by the nucleophilic substitution reaction of DFBP with MeHQ. The polymer had a number average molecular weight of 22,000 and T_g of 151°C. Blends of DGEBA epoxy resin with PEEKM was prepared by melt mixing at 180°C. The binary blends were visually transparent and exhibited single composition dependent T_g indicating homogeneous behaviour. The T_g composition behaviour was theoretically calculated using Fox, Gordon-Taylor and Kelley-Bueche equations. The experimental and theoretical values were in close agreement for Gordon-Taylor and Kelley-Bueche equations. Reaction induced phase separation occurred on curing the blends with DDS. The scanning electron micrographs of the blends revealed that the morphology changed from droplet matrix to co-continuous on increasing the PEEKM concentration from 5 to 15 phr. In addition double phase separation was observed in 15 phr blends. Dynamic mechanical analysis of the blends showed that the T_g of the blends were lower than that of unmodified epoxy resin due to decrease in crosslink density and intermixing of the phases. The tensile strength of the blends showed a small increase while the flexural strength decreased slightly. The Young's modulus and flexural modulus remained unchanged.

Substantial improvement in fracture toughness was achieved by the incorporation of PEEKM to epoxy resin. The increase in fracture toughness was due to decrease in crosslink density and due to various energy absorbing mechanisms operating in the blends. Scanning electron micrographs of failed surfaces revealed evidences for toughening mechanisms like local plastic deformation of the matrix, crack pinning, crack path deflection, crack bridging by the dispersed domains and particle tearing. Five and ten phr blend exhibited similar fracture toughness and 15 phr blend exhibited higher fracture toughness than these two systems. The expected increase in fracture toughness on increasing the concentration of PEEKM from 5 to 10 phr was not observed because of the presence of large domains and broad domain size distribution. The large increase in fracture toughness of 15 phr blend was due to the cocontinuous morphology. In 15 phr blend, the crack propagated through more ductile thermoplastic phase and due to double phase separation, toughening mechanisms described in the case 5 and 10 phr blends also occurred in 15 phr blend giving rise to substantial improvement in fracture toughness. No deterioration in thermal stability was observed upon the addition of PEEKM to epoxy resin.

Acknowledgements The authors thank the authorities of Vikram Sarabhai Space Centre for giving permission to publish this article. One of the authors (Bejoy Francis) is thankful to CSIR, New Delhi for providing Senior Research Fellowship. Thanks are also due to Analytical and Spectroscopy Division, VSSC for analytical support.

References

- Ellis B (1993) Chemistry and technology of epoxy resins. Blackie Academic and Professional, London
- Lee H, Neville K (1967) Handbook of epoxy resin. McGraw Hill, New York
- Encyclopaedia of polymer science and engineering, vol 6, 2nd ed. Wiley Interscience, pp 322–382
- Kang BU, Jho JY, Kim J, Lee SS, Park M, Lim S, Choe CR (2001) *J Appl Polym Sci* 79:38
- Arias ML, Frontini PM, Williams RJJ (2003) *Polymer* 44:1537
- Hwang JF, Manson JA, Hertzberg RW, Miller GA, Sperling LH (1989) *Polym Eng Sci* 29:1466
- Butta E, Levita G, Marchetti A, Lazzeri A (1986) *Polym Eng Sci* 26:63
- Garg C, MAI YW (1988) *Compos Sci Technol* 31:179
- Pearson RA, Yee AF (1983) *J Mater Sci* 24:2571
- Blanco I, Cicala G, Faro CL, Recca A (2003) *J Appl Polym Sci* 89:268
- Giannotti MI, Foresti ML, Mondragon I, Galante MJ, Oyanguren PA (2004) *J Polym Sci Part B Polym Phys* 42:3953
- Giannotti MI, Mondragon I, Galante MJ, Oyanguren PA (2004) *J Polym Sci Part B Polym Phys* 42:3964
- Cao Y, Shao Y, Sun J, Lin S (2003) *J Appl Polym Sci* 90:3384
- Jasinski W, Carlier V, Legras R, Mormann W (2003) *Macromol Symp* 198:323
- Torres A, De Ullibarri IL, Abad MJ, Barral L, Cano J, Garabal SG, Diez FJ, Lopez J, Ramirez C (2004) *J Appl Polym Sci* 92:461
- Teng KC, Chang FC (1996) *Polymer* 37:2385
- Guo Q, Huang J, Ge L, Feng Z (1992) *Eur Polym J* 28:405
- Iijima T, Tomoi M, Tochimoto T, Kakiuchi H (1991) *J Appl Polym Sci* 43:463
- Gianotti MI, Solsona MS, Galante MJ, Oyanguren PA (2003) *J Appl Polym Sci* 89:405
- Park SJ, Kim HC (2001) *J Polym Sci Part B Polym Phys* 39:121
- Iijima T, Mimura S, Fujimaki M, Taguchi T, Fukuda W, Tomoi M (1996) *J Appl Polym Sci* 61:163
- Pasquale GD, Motta O, Recca A, Garter JT, Mc Grail PT, Acierino D (1997) *Polymer* 38:4345
- Ratna D, Patri M, Chakraborty BC, Deb PC (1997) *J Appl Polym Sci* 65:901
- Zhong Z, Zheng S, Huang J, Cheng X, Guo Q (1998) *J WEI Polym* 39:1075
- Bennet GS, Farris RJ, Thompson SA (1991) *Polymer* 32:1633
- Francis B, Poel GV, Posada F, Groeninckx G, Rao VL, Ramaswamy R, Thomas S (2003) *Polymer* 44:3687
- Fox TG (1956) *Bull Am Phys Soc* 2:123
- Gordon M, Taylor J (1952) *J Appl Chem* 2:495
- Kelley FN, Bueche F (1961) *J Polym Sci* 50:549
- Belorgey G, Prud'homme RE (1982) *J Polym Sci Part B Polym Phys* 20:191
- Belorgey G, Aubin M, Prud'homme RE (1982) *Polymer* 23:1051
- Iijima T, Tochimoto T, Tomoi M (1991) *J Appl Polym Sci* 43:1685
- Martinez I, Martin MD, Eceiza A, Oyanguren P, Mondragon I (2000) *Polymer* 41:1027
- Min BG, Stachurski ZH, Hodgkin JH, Heath GR (1993) *Polymer* 34:3620
- Nielsen LE (1969) *Rev Makromol Chem* C3:77
- Bellenger V, Verdu J, Morel E (1987) *J Polym Sci B25*:1219
- Kramer EJ, Berger LL (1990) *Adv Polym Sci* 91/92:1
- Liello VD, Martuscelli E, Musto P, Ragosta G, Scarinzi G (1994) *J Polym Sci Part B Polym Phys* 32:409
- Chen MC, Hourston DJ, Sun WB (1992) *Eur Polym J* 28:1471
- Min HS, Kim SC (1999) *Polym Bull* 42:221
- Coats AW, Redfern JP (1964) *Nature* 201:68