

Epoxy-*tert*-butyl Poly(cyanoarylene ether) Blends: Phase Morphology, Fracture Toughness, and Mechanical Properties

Akanksha Saxena, Bejoy Francis, V. Lakshmana Rao, K. N. Ninan

Polymers and Special Chemicals Division, Propellants and Special Chemicals Group, Propellants, Chemicals and Materials Entity, Vikram Sarabhai Space Centre, Thiruvananthapuram, Kerala, India-695 022

Received 8 December 2004; accepted 15 March 2005

DOI 10.1002/app.22538

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: *Tert*-butyl hydroquinone-based poly(cyanoarylene ether) (PENT) was synthesized by the nucleophilic aromatic substitution reaction of 2,6-dichlorobenzonitrile with *tert*-butyl hydroquinone using *N*-methyl-2-pyrrolidone (NMP) as solvent in the presence of anhydrous potassium carbonate in a nitrogen atmosphere at 200°C. PENT-toughened diglycidyl ether of bisphenol A epoxy resin (DGEBA) was developed using 4,4'-diaminodiphenyl sulfone (DDS) as the curing agent. Scanning electron micrographs revealed that all blends had a two-phase morphology. The morphology changed from dispersed PENT to a cocontinuous structure with an increase in PENT content in the blends from 5 to 15 phr. The viscoelastic properties of the blends were investigated using dynamic mechanical thermal analysis. The storage modulus of the blends was less than that of the unmodified resin, whereas the loss modulus of the blends

was higher than that of the neat epoxy. The tensile strength of the blends improved slightly, whereas flexural strength remained the same as that of the unmodified resin. Fracture toughness was found to increase with an increase in PENT content in the blends. Toughening mechanisms like local plastic deformation of the matrix, crack path deflection, crack pinning, ductile tearing of thermoplastic, and particle bridging were evident from the scanning electron micrographs of failed specimens from the fracture toughness measurements. The thermal stability of the blends were comparable to that of the neat resin. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 3536–3544, 2006

Key words: PENT; thermosets; mechanical properties; morphology

INTRODUCTION

Epoxy resins are important thermosetting polymers, having many desirable properties such as high tensile strength and modulus, low creep and low shrinkage on cure, excellent chemical and corrosion resistance, and good thermal and electrical properties. Consequently these materials are used in a wide range of applications in areas as diverse as construction, electronics, structural adhesives, coatings, reinforced plastics, and, increasingly, aerospace, where they are employed as matrix materials in the development of high-performance, lightweight fiber-reinforced composites.^{1–4} Unfortunately, these highly crosslinked networks are inherently brittle and have poor resistance to crack propagation.⁵ A variety of toughening agents and flexibilizers have been used with thermally cured epoxy resins in order to prevent crack propagation and to make the epoxy network more flexible. Fillers are generally used in the plastic industry to lower cost while increasing final product rigidity. The

degree of toughness enhancement was found to depend on volume fraction as well as particle size and shape of the filler.^{6,7} Unfortunately, uniform mixing and good dispersion of these particles are rarely obtained because of the higher density of the inorganic filler particles compared to epoxy resins. The most successful method for improving the toughness of the epoxy matrix has been the addition of suitable elastomers as a second component. Brittle epoxy resins are generally toughened by the addition of liquid functional rubbers such as carboxyl-terminated polybutadiene (CTPB), copolymers of amino-terminated butadiene and acrylonitrile (ATBN),^{8,9} and carboxyl-terminated butadiene and acrylonitrile (CTBN) or other elastomeric modifiers such as silicones,^{10,11} acrylate elastomers,¹² poly(oxypropylene amines),¹³ and polysiloxane copolymers.¹⁴ Fracture toughness of rubber modified epoxy resin is strongly dependent on the crosslink density of the epoxy resin,^{15–17} the size of the rubber particles,¹⁸ and the cohesive strength of the particle. The addition of soft rubbery particles to an epoxy reduces its elastic modulus, yield strength, and thermal and creep resistance. In addition, rubber modification does not significantly improve fracture toughness in highly crosslinked systems. This is not

Correspondence to: V. L. Rao (rao_vl@rediffmail. com).

desirable as most advanced thermosetting resins used in aerospace applications are composed of highly crosslinked network polymers, which are often brittle.

Recently, several researchers reported that thermoplastics such as poly(ether sulfone)s,^{19,20} poly(ether imide),^{21,22} poly(ether ether ketone),²³ polyester,²⁴ acrylonitrile butadiene styrene copolymer,²⁵ and poly(phenylene oxide)²⁶ are effective modifiers of highly crosslinked epoxy resins. Often, the immiscibility of engineering thermoplastics containing epoxy resin is a major concern while blending. Even solution blending is difficult because of its excellent solvent resistance. An alternative for the improvement of the processability is to use functionalized polymers or polymers with bulky pendent groups as modifiers of epoxy resin. Phenolphthalein poly(ether ether ketone) (PEK-C) or functionally terminated PEEK with bulky pendent groups was used for the modification of epoxy resins.^{27–32} We recently reported the use of *tert*-butyl PEEK–epoxy blends with DDS as a curing agent.³³

Poly(cyanoarylene ether) (PEN) possesses attractive properties such as excellent heat, solvent, radiation, and flame resistance and good mechanical properties for use as a matrix resin in structural composites. In addition, the pendant nitrile group can give rise to dipole–dipole interaction forces, resulting in good adhesion to many substrates.^{34,35} However, PEN polymers are highly crystalline, resulting in low solubility in common organic solvents. This often restricts the use of these polymers in a wide range of applications. The introduction of substituents onto the aromatic ring was expected to suppress this crystallinity, thereby improving solubility. There have been no reports published on the use of poly(cyanoarylene ether) and its analogues as a toughening agent for epoxy resin. Hence, we report here the toughening of DGEBA-type epoxy resin with *tert*-butyl poly(cyanoarylene ether) and its thermophysical, fracture toughness, and mechanical properties. The resulting blends were found, as expected, to have superior toughness while retaining the thermomechanical properties of the neat epoxy resin. In addition, they possessed better adhesion to the substrate/reinforcing medium because of the dipole–dipole interaction of the nitrile group.

EXPERIMENTAL

Materials

2,6-Dichlorobenzonitrile (DCBN; Fluka) and *tert*-butyl hydroquinone (TBHQ; Fluka) were used as received. Anhydrous potassium carbonate (BDH) was dried in vacuum at 100°C before use. *N*-methyl-2-pyrrolidone (NMP; SRL) was distilled under vacuum over phosphorous pentoxide and stored over 4A molecular sieves. Toluene was distilled over sodium and stored

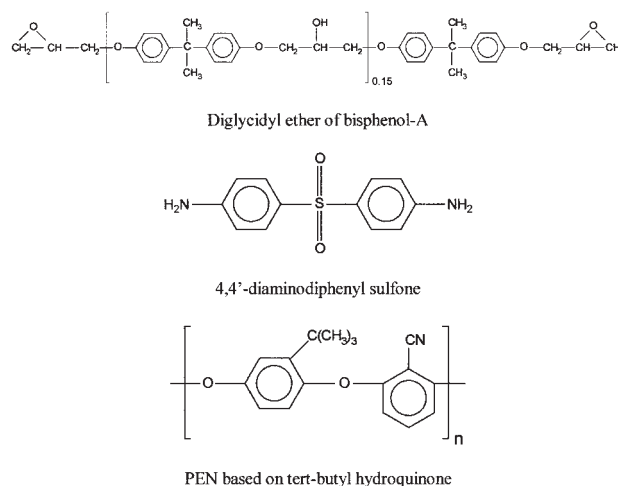


Figure 1 Chemical structures of epoxy resin, DDS, and PENT.

over sodium wire. Bisphenol A epoxy resin (LY 556, Ciba Geigy) with an epoxide equivalent weight of 188.68 and 4,4'-diaminodiphenyl sulfone (DDS; Aldrich) were used as received.

Synthesis of poly(cyanoarylene ether)

Poly(cyanoarylene ether) with pendent *tert*-butyl groups (PENT) was synthesized by the nucleophilic aromatic substitution reaction of 2,6-dichlorobenzonitrile with *tert*-butyl hydroquinone using slight excess of anhydrous potassium carbonate in NMP medium with 30% solid content at 200°C under a nitrogen atmosphere as per the procedure described previously.³⁶ The viscous reaction mixture was cooled to room temperature and precipitated in distilled water. The product was refluxed with water repeatedly and subjected to soxhlet extraction with methanol, filtered, and dried under vacuum at 100°C for 15 h.

Blend preparation

The epoxy–PENT blends were prepared by a solventless mixing technique. The chemical structures of the blend components are given in Figure 1. The calculated amounts of PENT were dissolved in epoxy resin at 140°C with constant stirring. After obtaining a homogeneous solution, a stoichiometric amount of the curing agent, 4,4'-diaminodiphenyl sulfone (DDS), was added to the mixture and allowed to dissolve completely by raising the temperature to 180°C. The resulting ternary solution was evacuated in a vacuum oven at 180°C and then poured into an open mold kept at 180°C. The curing was done in an air convection oven at 180°C for 3 h and postcured at 200°C for 2 h.

Characterization techniques

PENT characterization

The FTIR spectrum of PENT in KBr pellet was recorded using a Perkin Elmer Spectrum GX FTIR spectrometer. The ^{13}C -NMR spectrum was recorded at 75.4 MHz using a Bruker Avance-300 spectrometer with CDCl_3 as the solvent and TMS as an internal standard. The glass-transition temperature (T_g) was measured using a TA Instruments (DSC-2920) modulated differential scanning calorimeter operated in a standard DSC mode at a heating rate of $10^\circ\text{C}/\text{min}$ under a nitrogen atmosphere. Inherent viscosity was determined at 60°C for a 0.2% polymer solution in *p*-chlorophenol using an Ubbelohde suspended level viscometer. The molecular weight and molecular weight distribution of PENT were determined using gel permeation chromatography (GPC). A Waters Alliance separation module in conjunction with a Waters 410 differential refractive index detector was used. The machine was calibrated using a polystyrene standard. The GPC analysis was done using THF as a solvent at a flow rate of 1 mL/min.

Blend characterization

Mechanical properties

Specimens of the required size were cut from laminates using a diamond wheel cutter. Tensile properties were determined according to ASTM D638 using a Universal Testing Machine (Model TNE 5000) at a crosshead speed of 10 mm/min. The flexural strength was measured in three-point bend mode according to ASTM D790 at a crosshead speed of 10 mm/min. Flexural strength was calculated using eq. (1)

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

where P is the load at break, L is the span length, and b and d are the specimen's breadth and thickness, respectively.

The fracture toughness was measured according to ASTM STP410 using single-edge notch specimens $100 \times 35 \times 3$ mm in dimension. A 5-mm notch was made at the center of one edge. A precrack was made by pressing a fresh razor blade into the notch. The fracture toughness at crack initiation in terms of the critical stress intensity factor, K_{Ic} , 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, and d is

the thickness of the specimen. 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 Morphology of the blends was studied using scanning electron microscopy (SEM). Fracture surfaces from cryogenically fractured specimens and failed specimens from fracture toughness measurement were analyzed using a Hitachi SEM (model S-2400) at an accelerating voltage of 15 kV. The cryogenically fractured samples were etched with chloroform for 24 h in order to remove the thermoplastic phase. The specimens were dried in vacuum overnight to remove the solvent. All the specimens were sputter-coated with a thin layer of gold using a Hitachi gold ion sputter unit (E-101), so that the samples were electrically conductive.

Dynamic mechanical thermal analysis (DMTA)

Dynamic mechanical thermal analysis of the cured blends was performed using a TA DMA 2980 equipped with TA thermal analysis software for data analysis at a frequency of 10 Hz. Specimens with dimensions of $55 \times 10 \times 3$ mm were analyzed in three-point bend mode in a temperature range of 25°C – 275°C at a heating rate of $3^\circ\text{C}/\text{min}$. Storage modulus (E'), loss modulus (E''), and loss tangent ($\tan \delta$) were recorded as a function of temperature.

Thermogravimetric analysis (TGA)

Thermogravimetric analysis of the blends was performed using TA thermal analyzer (Model SDT 2960) in a nitrogen atmosphere going from room temperature to 900°C at a heating rate of $20^\circ\text{C}/\text{min}$.

RESULTS AND DISCUSSION

Poly(cyanoarylene ether) with a pendent *tert*-butyl group was synthesized by aromatic nucleophilic displacement of chlorine from an activated substrate DCBN by TBHQ. The FTIR spectrum of PENT was recorded in KBr pellets. The PENT showed characteristic bands at 2230 cm^{-1} because of symmetrical stretching of the nitrile groups. The peaks in the region, 1100 – 1250 cm^{-1} , resulted from ϕ -0 skeletal vibrations (oxygen attached on either side of the ring). The absence of a broad peak between 3000 and 3500 cm^{-1} indicated the absence of $-\text{OH}$ groups. The band at 1030 cm^{-1} resulted from the ether linkages ortho to $\text{C}\equiv\text{N}$. The peak at 1601 cm^{-1} was assigned to $\text{C}=\text{C}$

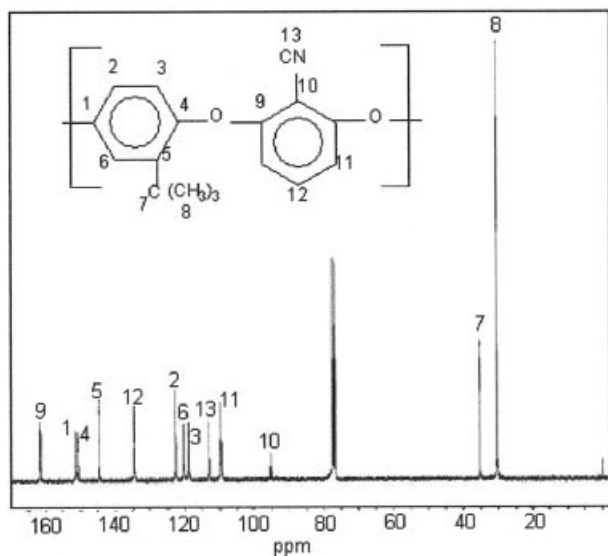


Figure 2 ^{13}C -NMR spectrum of PENT.

stretching of the benzene ring where oxygen was ortho to $\text{C}\equiv\text{N}$. The peaks in the $2962\text{--}2872\text{ cm}^{-1}$ region were a result of $\text{C}\text{--}\text{H}$ stretching vibration, whereas the band at 1364 cm^{-1} resulted from $\text{C}\text{--}\text{H}$ bending vibrations.

The ^{13}C -NMR spectrum of PENT was recorded using CDCl_3 as a solvent and TMS as an internal standard. A typical ^{13}C -NMR spectrum of PENT is shown in Figure 2. The ^{13}C -NMR spectrum showed 13 absorptions corresponding to 13 distinguishable carbon atoms, confirming the proposed structure. The chemical shift assignments of various carbons in the polymer were based on the additivity constants for substituted benzenes.³⁷ From GPC analysis the number-average molecular weight, weight-average molecular weight, and polydispersity index were found to be 20,500, 33,000, and 1.61, respectively. The inherent viscosity was 1.26 dL/g for a 0.2% polymer solution in *p*-chlorophenol at 60°C . The glass-transition temperature of PENT was 203°C according to DSC measurement.

Epoxy–PENT blends

Epoxy–PENT blends with 5-, 10-, and 15-phr PENT were prepared by melt-mixing. The binary blends were transparent and visually homogeneous. On curing, the blends became translucent, indicating heterogeneous morphology. The absence of a characteristic peak of epoxy at 915 cm^{-1} in the FTIR spectrum of the cured blends confirmed the completion of curing. This was further confirmed from DSC by the absence of an exothermic peak for the cured blends.

Dynamic mechanical thermal analysis

The viscoelastic properties of the unmodified and PENT-modified epoxy resin were investigated using a

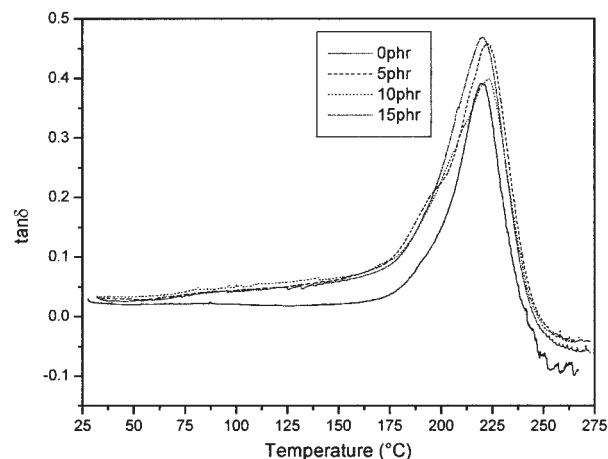


Figure 3 Tan δ versus temperature plot for PENT-modified epoxy resin.

dynamic mechanical thermal analyzer. The tan δ curves for the PENT-modified epoxy resin are shown in Figure 3. The dynamic mechanical spectrum of the blends showed only a single T_g . Though two T_g 's, corresponding to epoxy-rich and thermoplastic-rich phases were expected, only one T_g was observed because of the close proximity of the T_g 's of the PENT- and the T_g of the DDS-cured epoxy resin. The peak position of the tan δ curve remained unchanged for the PENT-modified epoxy resin system, indicating that the T_g of the blends remained the same as that of unmodified epoxy resin regardless of the concentration of PENT in the blends. The tan δ peak height, peak area, and peak width at half height are summarized in Table I. All the parameters of the blends were found to be higher than those of the unmodified resin. The increases in peak width and peak area indicated better miscibility and damping properties of the blends. The storage modulus (E') values, recorded as a function of temperature for modified and unmodified epoxy resin, are given in Figure 4. The storage modulus of modified epoxy resin was found to be higher than that of neat resin below T_g . With increased temperature, the storage modulus decreased, and a sharp decrease was observed near T_g . The storage modulus of the blends was slightly less than that of the neat

TABLE I
Peak Height, Peak Width at Half Height, and Peak Area from Dynamic Mechanical Analysis of DGEBA–PENT Blends

PENT content	Peak height	Peak width at half height	Peak area
0	0.3716	24.4	13.92
5	0.4071	29.2	21.16
10	0.3390	33.1	16.41
15	0.4209	29.9	19.41

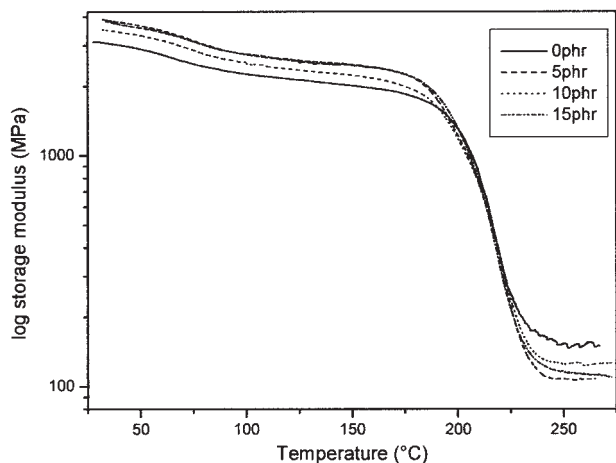


Figure 4 Storage modulus versus temperature plot of epoxy resin modified with PENT.

epoxy resin in the rubbery plateau region, that is, after T_g . The storage modulus in the plateau region is a measure of the crosslink density of the material. The higher the storage modulus, the higher is the crosslink density. In PENT-modified epoxy resin, the storage modulus of the blends was less than that in the unmodified resin, indicating lower crosslink density of the blends. The loss modulus recorded as a function of temperature for the modified and unmodified resins is shown in Figure 5. The loss modulus of the blends was higher than that of the neat epoxy resin system, indicating better damping properties.

The molecular weight between crosslinks of the blends could be calculated from the storage modulus values in the rubbery plateau region. In principle, the crosslink density of a cured epoxy network could be calculated from the theory of rubber elasticity. The shear modulus, G , of a crosslinked rubber is given by³⁸

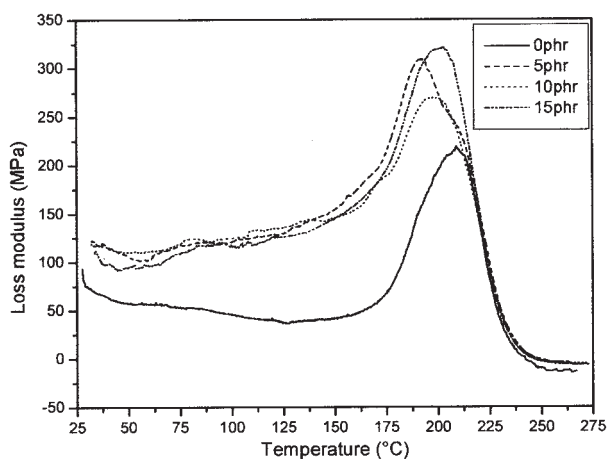


Figure 5 Plot of loss modulus against temperature for epoxy resin modified with PENT.

TABLE II
 E' and M_c Values for DGEBA-PENT Blends

PENT content (phr)	E' at $T_g + 40^\circ\text{C}$ (MPa)	M_c (g/mol)
0	151	0.105
5	107	0.149
10	124	0.129
15	113	0.142

$$G = \frac{\bar{r}_1^2}{\bar{r}_f^2} \frac{dRT}{M_c} \left(1 - \frac{2M_c}{\bar{M}_n} \right) \quad (4)$$

where d is the density, R is the universal gas constant, T is the absolute temperature, M_c is the molecular weight between crosslinks, \bar{M}_n is the chain backbone molecular weight, and \bar{r}_1^2/\bar{r}_f^2 is the ratio of the mean square end-to-end distance of the polymer chain in the sample to the same quantity in a randomly coiled chain. In this case, this ratio was assumed to be unity. The factor $1 - 2M_c/\bar{M}_n$ is a correction factor for chain ends and becomes negligible when \bar{M}_n is very large relative to M_c , as it is for highly crosslinked systems like epoxy. Hence, eq. (4) becomes

$$G = \frac{dRT}{M_c} \quad (5)$$

where G must be measured in the rubbery plateau region above T_g , shear modulus G can be taken as $E'/3$,³⁹ and E' was measured at $T_g + 40^\circ\text{C}$. The storage modulus in the rubbery plateau region and the M_c values are shown in Table II. The M_c values were found to increase with an increase in PENT content. This indicates that the addition of PENT reduced the crosslink density of the cured resin, making the system more flexible.

Morphological studies

The morphology of the blends was examined using a scanning electron microscope. To get a clear picture, the fracture surfaces were etched with chloroform. The scanning electron micrographs of the 5-, 10-, and 15-phr blends are shown in Figure 6(a-c). The spher-

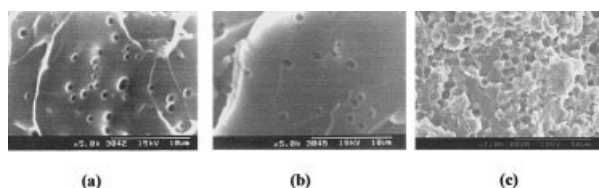


Figure 6 Scanning electron micrographs of epoxy-PENT blends: (a) 5 phr, (b) 10 phr, (c) 15 phr.

TABLE III
Domain Diameter and Polydispersity Index
of DGEBA-PENT Blends

PENT content (phr)	\bar{D}_n (μm)	\bar{D}_w (μm)	PDI
5	0.68	0.71	1.05
10	0.94	0.96	1.03

ical cavities occurred because the solvent removed the PENT-rich phase from the surface. Epoxy-PENT blends with 5- and 10-phr PENT showed a droplet-matrix morphology in which the PENT-rich phase was dispersed in the epoxy-rich matrix. Epoxy-PENT blends with 15-phr PENT [Fig. 6(c)] showed a cocontinuous morphology, and the micrograph was taken without etching. The micrographs of the 5- and 10-phr blends showed white circular diffuse zones between the epoxy matrix and the empty holes. These diffuse zones were probably transition zones of incomplete phase separation where both PENT and epoxy were present. A similar observation in epoxy-phenoxy blends was reported by Teng et al.⁴⁰ Table III shows the number-average diameter, weight-average diameter, and polydispersity index of the 5- and 10-phr blends, which were calculated using eqs. (6)–(8):

$$\text{Number average diameter, } \bar{D}_n = \frac{\sum n_i d_i}{\sum n_i} \quad (6)$$

$$\text{Weight average diameter, } \bar{D}_w = \frac{\sum n_i d_i^2}{\sum n_i d_i} \quad (7)$$

$$\text{Polydispersity index, PDI} = \frac{\bar{D}_w}{\bar{D}_n} \quad (8)$$

where n_i is the number of domains having diameter d_i .

The domain diameters increased with an increase in PENT content of the blends. Figure 7 shows the domain size distribution for the blends. From Figure 7 it is clear that a 5-phr blend exhibited a broader size distribution than did a 10-phr blend. In the 5-phr blend the domain size was in the range of 0.37–1.1 μm . With a 10-phr blend, more than 90% of the domains were between 0.7 and 1.1 μm in size. The increase in domain size resulted from the coalescence of the domains after phase separation. From SEM studies it was clear that the initial homogeneous blends became phase-separated upon curing. A heterogeneous morphology developed because of reaction-induced phase separation. The initial miscibility of the epoxy-thermoplastic blends was attributed to the low molecular weight of the epoxy prepolymer. On curing, the molecular weight of the resin increased, and the contri-

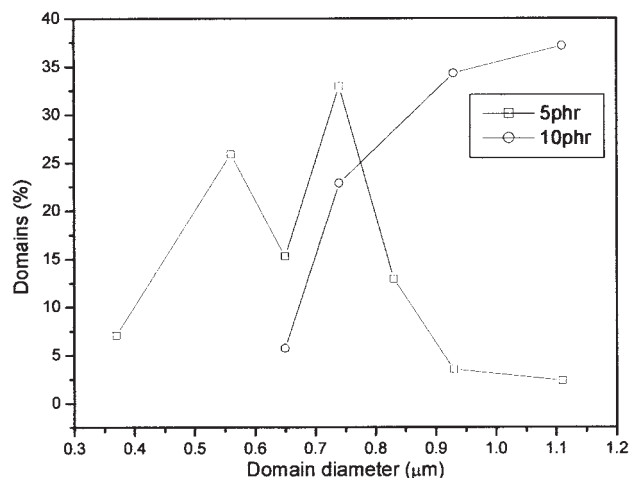


Figure 7 Domain size distribution of DGEBA-PENT blends.

bution of entropy to free energy of mixing lessened, resulting in two-phase morphology.

Tensile and flexural properties

The mechanical properties of DDS-cured PENT-epoxy blends are given in Table IV. The data revealed increased tensile strength for PENT-epoxy blends, whereas flexural strength and flexural modulus remained the same as those of the unmodified resin. The tensile and flexural properties were found to be maximum for 15-phr PENT-modified blends, which was a result of the cocontinuous morphology of the blend. Similar observations were made by Yamanaka et al.⁴¹ and Sidhamalli et al.⁴² for DDS-cured epoxy-polyether sulfone (PES) and epoxy-phenoxy blends, respectively, with a cocontinuous morphology. The tensile stress-strain and flexural stress-strain curves are given in Figures 8 and 9, respectively, which show that the tensile strain of the blends was slightly higher than that of the unmodified resin, whereas the flexural strain remained the same as that of the neat resin. The increase in tensile strain was a result of the decreased crosslink density of the blend, which was evident from the dynamic mechanical analysis. But this effect was not observed in the flexural properties of the blends.

TABLE IV
Tensile and Flexural Properties of DGEBA-PENT Blends

PENT content (phr)	Tensile strength (MPa)	Young's modulus (GPa)	Flexural strength (MPa)	Flexural modulus (GPa)
0	60	1.01	121	3.0
5	68	1.02	118	2.7
10	70	1.06	123	2.9
15	71	0.92	127	2.9

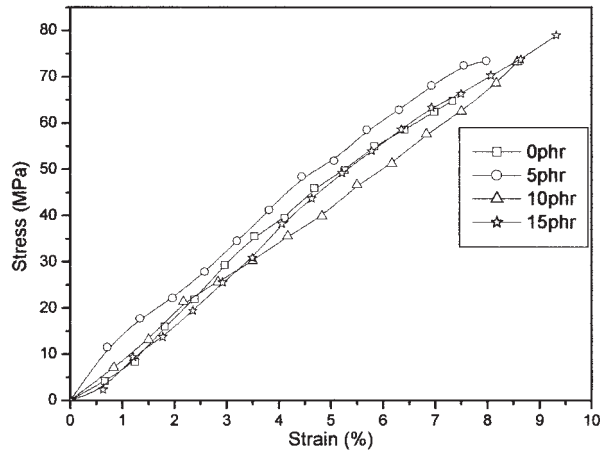


Figure 8 Tensile stress-strain curves for DGEBA-PENT blends.

Fracture toughness

The fracture toughness, expressed as the critical stress intensity factor (K_{Ic}), of modified resin increased with an increase in PENT concentration. The variation of fracture toughness with composition is shown in Figure 10. The K_{Ic} value of 15-phr PENT-modified epoxy blends increased by 83% in addition to the marginal increase in the mechanical properties. The increase in fracture toughness occurred for many reasons. One important requirement for obtaining enhanced fracture toughness in a thermoset/thermoplastic blend is a two-phase morphology. The dispersed thermoplastic phase will initiate different processes that will increase the fracture toughness. The scanning electron micrographs in Figure 6 show the two-phase morphology of the blends. To further investigate the toughening mechanisms, scanning electron micrographs were taken of the fracture surface of failed specimens,

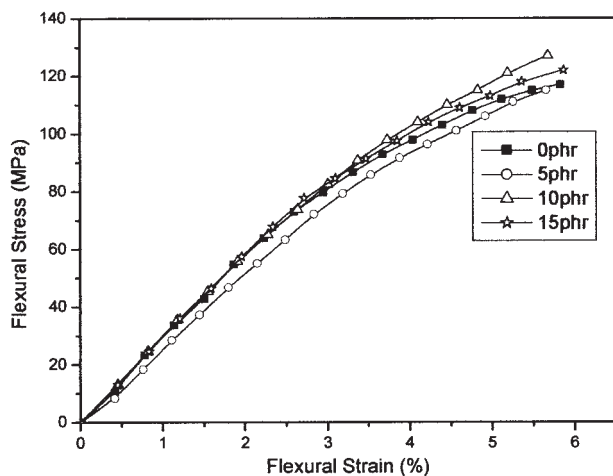


Figure 9 Flexural stress-strain curves for DGEBA-PENT blends.

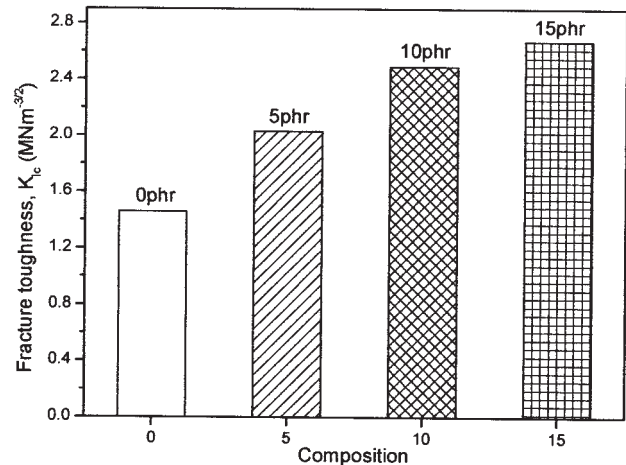


Figure 10 Fracture toughness of DGEBA-PENT blends.

which are shown in Figure 11. The fracture surfaces of the modified epoxy resin were rough and ridgy, and river marks were observed on the surface. The fracture surface of the unmodified epoxy resin showed characteristic features of brittle fracture. The surface was smooth, with free and regular crack propagation. In DGEBA-PENT blends, the PENT phase will act as a stress concentrator on applying external load, leading to plastic deformation of the matrix surrounding the particle. The river marks on the fracture surfaces also indicated plastic deformation of the matrix.⁴³⁻⁴⁶ The frequency of the domains increased with an increase in PENT in the blends, resulting in the interaction of the stress fields created by each domain. This would also increase the fracture toughness of the blend. The roughness of the fracture surface indicated the ductile nature of the crack. The ductility resulted from the reduced crosslink density of the blends. The decrease in crosslink density was evident from the increase in M_c values, given in Table II. The roughness of the fracture surface also indicated that the crack deviated from its original plane, resulting in an increased surface area of the crack, which increased the toughness. From the micrographs (Fig. 11), it can be seen that the dispersed thermoplastic particles were not fully pulled out from the fracture surface. This means there was good interfacial adhesion between the matrix and the dispersed domains. The dispersed thermoplastic particles were found to be torn off as the crack prop-

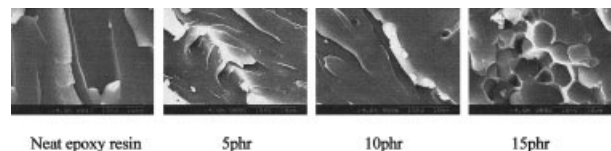


Figure 11 Scanning electron micrographs of failed surfaces of DGEBA-PENT blends.

agated. The ductile tearing of the thermoplastic improved the toughness of the modified resin. Also the PENT-rich phase could bridge the crack to some extent. Tail marks could be seen behind the particles in the scanning electron micrographs. This is characteristic of a crack-pinning mechanism.⁴⁷ All these mechanisms together produced the overall improvement in toughness. Other factors that influenced fracture toughness were interparticle distance and interfacial area per unit volume, which were calculated using the following equations

$$\text{Interparticle distance} = d_{TP} \left[\left(\frac{\pi}{6\phi_{TP}} \right)^{1/3} - 1 \right] \quad (9)$$

$$\text{Interfacial area per unit volume} = \frac{3\phi_{TP}}{r} \quad (10)$$

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 data on interparticle distance and interfacial area per unit volume are summarized in Table V.

Both these factors were favorable for increasing fracture toughness with an increase in PENT content. Thus, these parameters favored the increase in toughness of the 10-phr blend over the 5-phr blend. In the 15-phr PENT blend cocontinuous morphology was observed. Cocontinuous morphology facilitates more uniform stress distribution under load and avoids premature failure.⁴² In this case the crack has to advance through a more ductile thermoplastic-rich phase, thereby increasing fracture toughness. Hence, maximum toughness was observed in the 15-phr blend.

Thermogravimetric analysis

Thermogravimetric analysis provided insight into the thermal stability of the blends. Parameters like initial decomposition temperature (IDT), temperature at maximum rate of weight loss (T_{max}), and activation energy for decomposition (E) were important in expressing the thermal stability of the material and could be used for assessing its lifetime. These parameters are summarized in Table VI. Both the IDT and

TABLE V
Interparticle Distance and Interfacial Area/Unit Volume of DGEBA-PENT Blends

PENT content (phr)	Interparticle distance (μm)	Interfacial area/unit volume (μm^{-1})
5	0.87	0.3891
10	0.79	0.5394

TABLE VI
Thermogravimetric Analysis of DGEBA-PENT Blends

PENT content (phr)	IDT ($^{\circ}\text{C}$)	T_{max} ($^{\circ}\text{C}$)	Activation energy (kJ/mol)
0	410	430	280
5	400	424	284
10	400	426	279
15	400	425	262

T_{max} of the blends remained close to those of the unmodified resins.

The activation energy for decomposition was determined using the Horowitz and Metzger equation⁴⁸

$$\ln[\ln(1 - \alpha)^{-1}] = E\theta/RT_{max}^2 \quad (11)$$

where α is the decomposed fraction, E is the activation energy for decomposition, T_{max} is the temperature at maximum rate of weight loss, R is the universal gas constant, and θ is given by $T - T_{max}$. From the slope of the plot of $\ln[\ln(1 - \alpha)^{-1}]$ against θ , the value of activation energy was calculated. The activation energy of the blends was close to that of the unmodified resin, indicating no deterioration in the thermal stability of the blends.

CONCLUSIONS

The important conclusions that can be drawn from the present study are:

1. *Tert*-butyl hydroquinone-based poly(cyanoarylene ether) was synthesized from 2,6-dichlorobenzonitrile and *tert*-butyl hydroquinone and used as a toughening agent for DGEBA epoxy resin. The binary blends of epoxy resin and PENT were visually homogeneous.
2. Reaction-induced phase separation occurred in the blends on curing with DDS. Droplet matrix morphology was observed in the 5- and 10-phr blends, and cocontinuous morphology was seen in the 15-phr blend.
3. The domain size and domain size distribution were dependent on the composition of the blends. An increase in domain size with composition was a result of the coalescence of the domains after phase separation.
4. The $\tan \delta$ versus temperature plot showed a single peak because of the close proximity of the T_g values of PENT- and DDS-cured epoxy resins. The increase in peak width and peak area indicated the blend had better miscibility and damping properties.

5. The storage modulus of the blends was lower in the rubbery plateau region compared to the unmodified resin, indicating lower crosslink density of the blends.
6. The loss modulus of the blends was higher than that of neat resin, indicating better damping properties of the blends.
7. The mechanical properties of the blends were comparable to those of the unmodified epoxy resin.
8. Fracture toughness of the blends was higher than that of neat resin, and the extent of improvement depended on the composition of the blends. Maximum enhancement in toughness was shown by the 15-phr blend, in which co-continuous morphology was observed.
9. Various toughening mechanisms such as local plastic deformation, crack path deflection, ductile tearing of thermoplastic, particle bridging, and crack pinning took part in improving the toughness of the PENT-epoxy blends.
10. The overall thermal stability was not affected by the addition of PENT to epoxy resin.

The authors thank the authorities of Vikram Sarabhai Space Centre for giving permission to publish this article. One of the authors (A.S.) thanks the Indian Space Research Organization for awarding a research fellowship. Thanks are also due colleagues of the Analytical and Spectroscopy Division of VSSC and the Sree Chitra Thirunal Institute for providing analytical support.

REFERENCES

1. Potter, W. G. *Epoxide Resins*; Springer: New York, 1970.
2. May, C. A.; Tanaka, G. Y. *Epoxy Resin Chemistry and Technology*; Marcel Dekker: New York, 1973.
3. Bauer, R. S.; *Epoxy Resin Chemistry*; *Advances in Chemistry* 114; American Chemical Society: Washington DC, 1979.
4. Lee, H.; Neville, K. *Handbook of Epoxy Resins*; McGraw Hill: New York; 1967.
5. Kim, B.S.; Chiba, T.; Takashi, I. *Polymer* 1995, 36, 43.
6. Moloney, A. C.; Kusch, H. H.; Stieger, H. R. *J Mater Sci* 1983, 18, 208.
7. Moloney, A. C.; Kusch, H. H.; Stieger, H. R. *J Mater Sci* 1984, 19, 1125.
8. Sasidaran, A. P.; Latha, P. B.; Ramaswamy, R. *J Appl Polym Sci* 1990, 41, 15.
9. Yee, A. F.; Pearson, R. A. *J Mater Sci* 1986, 21, 2462.
10. Bussi, P.; Ishida, H. *J Appl Polym Sci* 1994, 32, 647.
11. Zheng, S.; Wang, H.; Dai, Q.; Luo, X.; Ma, D.; Wang, K. *Makromol Chem* 1995, 196, 269.
12. Bauer, R. S. *Epoxy Resin Chemistry*, ACS Symposium Series 21; American Chemical Society: Washington DC, 1984.
13. Buner, I. R.; Rushford, J. L.; Rose W. S.; Hunston, D. L.; Riew, C. K. *J Adhesion* 1982, 13, 242.
14. Riew, C. K.; Gillham J. K. *Rubber Modified Thermoset Resins*, *Advances in Chemistry Series* 208; American Chemical Society: Washington DC, 1984.
15. Pearson, R. A.; Yee, A. F. *J Mater Sci* 1989, 24, 2571.
16. Levita, G. *Polym Prep* 1988, 29, 179.
17. Bradley, W. L. *Polym Prep* 1988, 29, 179.
18. Pearson, R. A.; Yee, A. F. *J Mater Sci* 1991, 26, 3828.
19. Blanco, I.; Cicala, G.; Faro, C. L.; Recca, A. *J Appl Polym Sci* 2003, 89, 268.
20. Giannotti, M. I.; Galante, M. J.; Oyanguren, P. A.; Vallo, C. I. *Polym Test* 2003, 22, 429.
21. Bonnet, A.; Lestriez, B.; Pascault, J. P.; Sautereau, H. *J Polym Sci B Polym Phys* 2001, 39, 363.
22. Kim, S. H.; Lee, D. W.; Chung, K. H.; Park, J. K.; Juang, J. I.; Jeong, S. H. *J Appl Polym Sci* 2002, 86, 812.
23. Iijima, T.; Tochimoto, T.; Tomoi, M. *J Appl Polym Sci* 1991, 43, 1685.
24. Cao, Y.; Shao, Y.; Sun, J.; Lin, S. *J Appl Polym Sci* 2003, 90, 3384.
25. Torres, A.; de Ullibarri, I. L.; Abad, M. J.; Barral, L.; Cano, J.; Garabal, S. G.; Diez, F. J.; Lopez, J.; Ramirez, C. *J Appl Polym Sci* 2004, 92, 461.
26. Wu, J.; Lin, T. K.; Shyu, S. S. *J Appl Polym Sci* 2000, 75, 26.
27. Song, X.; Zheng, S.; Huang, J.; Jhu, P.; Guo, Q. *J Appl Polym Sci* 2001, 79, 598.
28. Zhong, Z.; Zheng, S.; Huang, J.; Cheng, X.; Guo, Q.; Wei, J. *Polymer* 1998, 39, 1075.
29. Guo, Q.; Huang, J.; Li, B.; Chen, T.; Zhang, H.; Feng, Z. *Polymer* 1991, 32, 58.
30. Guo, Q.; Huang, J.; Ge, L.; Feng, Z. *Eur Polym J* 1992, 28, 405.
31. Cecere, J.; McGrath, J. E. *Polym Prep* 1986, 27, 299.
32. Bennet, G. S.; Faris, R. J.; Thompson, S. A. *Polymer* 1991, 32, 1633.
33. Francis B.; Vanden Poel, G.; Posada, F.; Groeninckx, G.; Rao, V. L.; Ramaswamy, R.; Thomas, S. *Polymer* 2003, 44, 3687.
34. Verbort, J.; Marvel, C. S. *J Polym Sci Polym Chem* 1973, 11, 261.
35. Sivaramakrishnan, K. V.; Marvel, C. S. *J Polym Sci Polym Chem* 1974, 12, 651.
36. Saxena, A.; Rao, V. L.; Ninan, K. N. *Eur Polym J* 2003, 39, 57.
37. Pretsch, E.; Buhlmann, P.; Affolter, C. *Structure Determination of Organic Compounds*, 3rd ed.; Springer Verlag: New York, 2000.
38. Tobolsky, A. V.; Carlson, D. W.; Indictor, N. *J Polym Sci* 1961, 54, 175.
39. Tobolsky, A. V. *J Polym Sci C* 1965, 9, 174.
40. Teng, K. C.; Chang, F. C.; *Polymer* 1996, 37, 2385.
41. Yamanaka, K.; Inoue, T. *Polymer* 1989, 30, 662.
42. Siddhamalli, S. K.; Kyu, T. *J Appl Polym Sci* 2000, 77, 1257.
43. Alig, I.; Rüllmann, M.; Holst, M.; Xu, J. *Macromol Symp* 2003, 198, 245.
44. Oyanguren, P. A.; Galante, M.; Andromaque, K.; Frontini, P. M.; Williams, R. J. *J. Polymer* 1999, 40, 5249.
45. Yoon, T.; Kim, B. S.; Lee D. S. *J Appl Polym Sci* 1997, 66, 2233.
46. Williams, R. J. J.; Rozenberg, B. A.; Pascault, J. P. *Adv Polym Sci* 1996, 128, 95.
47. Pearson, R. A.; Yee, A. F. *Polymer* 1993, 34, 3658.
48. Horowitz, H. H.; Metzger, G. *Anal Chem* 1963, 35, 1464.