

Toughening of an Epoxy Resin with Hydroxy-Terminated Poly(arylene ether nitrile) with Pendent Tertiary Butyl Groups

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ABSTRACT: Hydroxy-terminated poly(arylene ether nitrile) oligomers with pendent *tert*-butyl groups (PENTOH) were synthesized by the nucleophilic aromatic substitution reaction of 2,6-dichlorobenzonitrile with *tert*-butyl hydroquinone in *N*-methyl-2-pyrrolidone medium with anhydrous potassium carbonate as a catalyst at 200°C in a nitrogen atmosphere. The PENTOH oligomers were blended with diglycidyl ether of bisphenol A epoxy resin and cured with 4,4'-diaminodiphenyl sulfone. The curing reaction was monitored with infrared spectroscopy and differential scanning calorimetry. The morphology, fracture toughness, and thermomechanical properties of the blends were investigated. The scanning electron micrographs revealed a two-phase morphology with a particulate structure of the PENTOH phase dispersed in the epoxy matrix, except for the epoxy resin modified with PENTOH with a number-average molec-

ular weight of approximately 4000. The storage modulus of the blends was higher than that of the neat epoxy resin. The crosslink density calculated from the storage modulus in the rubbery plateau region decreased with an increase in PENTOH in the blends. The fracture toughness increased more than twofold with the addition of PENTOH oligomers. The tensile strength of the blends increased marginally, whereas the flexural strength decreased marginally. The dispersed PENTOH initiated several toughening mechanisms, which improved the fracture toughness of the blends. The thermal stability of the epoxy resin was not affected by the addition of PENTOH to the epoxy resin. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 1318–1331, 2007

Key words: mechanical properties; morphology; blends; toughness

INTRODUCTION

Epoxy resins are important thermosetting polymers because of their 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 for a wide range of applications that include areas as diverse as construction, electronics, structural adhesives, coatings, and reinforced plastics. They are also used as matrix materials in the development of high-performance, light-weight, fiber-reinforced composites, which are finding increasing use in the aerospace industry.^{1–4} Although epoxy resins are used for a wide range of applications, their inability to withstand impact is a major concern for several advanced applications because of their inherent brittle nature.⁵ There are several methods used to improve

the fracture toughness of epoxy resins. They include improving the flexibility of the system by the chemical modification of rigid epoxy to give a flexible backbone structure, increasing the epoxy monomer molecular weight, lowering the crosslink density of the cured resin, and incorporating a toughener into the resin. Among these, the addition of a dispersed toughener phase has been found to be the most effective method. Brittle epoxy resins are generally toughened by the addition of liquid functional rubbers such as carboxyl-terminated polybutadiene,^{6,7} copolymers of amino-terminated butadiene and acrylonitrile,^{8,9} and carboxyl-terminated butadiene and acrylonitrile or other elastomeric modifiers such as silicones,^{10,11} acrylate elastomers,¹² poly(oxypropylene amines),¹³ and polysiloxane copolymers.¹⁴ The fracture toughness of a rubber-modified epoxy resin is strongly dependent on the crosslink density of the epoxy resin,^{15–17} the size of the dispersed rubber particles¹⁸ 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 fails to produce significant improvements in the fracture toughness in highly crosslinked systems. This is not desirable as most of the advanced

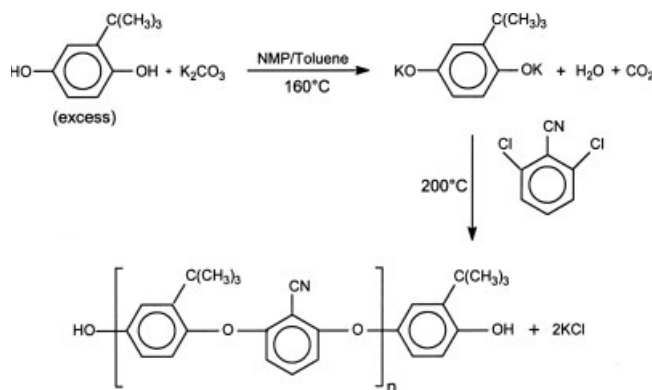
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thermosetting resins for aerospace applications consist of highly crosslinked network polymers, which are often brittle.

Of late, several researchers have reported 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 as effective modifiers for highly crosslinked epoxy resins. Often, the immiscibility of engineering thermoplastics with an epoxy resin is a major concern for blending. Even solution blending is difficult because of their excellent solvent resistance. To improve the processability, an alternative is to use functionalized polymers or polymers with bulky pendent groups as modifiers for the epoxy resin. Phenolphthalein poly(ether ether ketone) or functionally terminated poly(ether ether ketone) with bulky pendent groups have been used for modifying epoxy resins.²⁷⁻³² Recently, we reported methyl, *tert*-butyl, and di-*tert*-butyl poly(ether ether ketone)/epoxy blends and *tert*-butyl poly(cyanoarylene ether)/epoxy blends, using 4,4'-diaminodiphenylsulfone (DDS) as a curing agent.³³⁻³⁸

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 pendent nitrile group can give rise to dipole-dipole interaction forces resulting in good adhesion to many substrates.^{39,40} However, PEN polymers show highly crystalline properties, which result in low solubility toward common organic solvents. This often restricts the use of these polymers for a wide range of applications. The introduction of substituents onto the aromatic ring is expected to suppress the crystallinity, thereby improving the solubility. The use of PEN and its analogues as toughening agents for epoxy resins has not been reported in the open literature. In our earlier article,³⁸ we reported the phase morphology, fracture toughness, and mechanical properties of epoxy/*tert*-butyl poly(cyanoarylene ether) blends. We report here the toughening of an epoxy resin with hydroxy-terminated poly(arylene ether nitrile) with pendent tertiary butyl groups (PENTOH) to study the effect of the molecular weight of the functional oligomers on the phase morphology, fracture toughness, tensile and flexural properties, and thermal stability. The resultant blends are expected to have superior toughness with the retention of the thermomechanical properties of the neat epoxy resin. In addition, they possess better adhesion to the substrate/reinforcing medium because of the dipole-dipole interaction of the nitrile group and also because of the hydrogen-bonding/intermolecular or polar interactions of the functional hydroxyl group.



Scheme 1 Synthesis of PENTOH oligomers with pendent *tert*-butyl groups.

EXPERIMENTAL

Materials

High-purity 2,6-dichlorobenzonitrile (DCBN; Fluka, Steinheim, Germany) and *tert*-butyl hydroquinone (TBHQ; Fluka) were used as received. Anhydrous potassium carbonate (K_2CO_3 ; BDH) was dried at 400°C in a muffle furnace before use. *N*-Methyl-2-pyrrolidone (NMP, SISCO, Mumbai, India; SRL) was distilled under a vacuum over phosphorous pentoxide and stored over 4-Å molecular sieves. Toluene was distilled over sodium and stored over sodium wire. Diglycidyl ether of bisphenol A (DGEBA) epoxy resin (LY556, Ciba Geigy, UK) with an epoxide equivalent weight of 188.68 and high-purity DDS (Merck, Darmstad, Germany) were used as received.

Synthesis of the PENTOH oligomers

PENTOH oligomers were synthesized by the nucleophilic substitution reaction of DCBN with TBHQ by the use of anhydrous K_2CO_3 in an NMP medium with a 28% solid content at 200°C under a nitrogen atmosphere as per the general procedure described earlier.⁴¹ The molecular weight of the oligomers was controlled with the required amount of the monomers as per Carother's equation. The end-functional group was maintained with a calculated excess of the TBHQ monomer. The reactions involved in the synthesis are given in Scheme 1. A typical procedure for the synthesis of the PENTOH oligomer with a number-average molecular weight (M_n) of 4000 was as follows.

TBHQ (54.5 g, 0.33 mol), powdered anhydrous K_2CO_3 (54.38 g, 0.39 mol), NMP (250 mL), and toluene (150 mL) were charged into a four-necked flask equipped with a thermocouple, nitrogen inlet, mechanical stirrer, and Dean-Stark trap. The mixture was refluxed at 120–160°C with continuous stirring under a nitrogen atmosphere. Water was removed

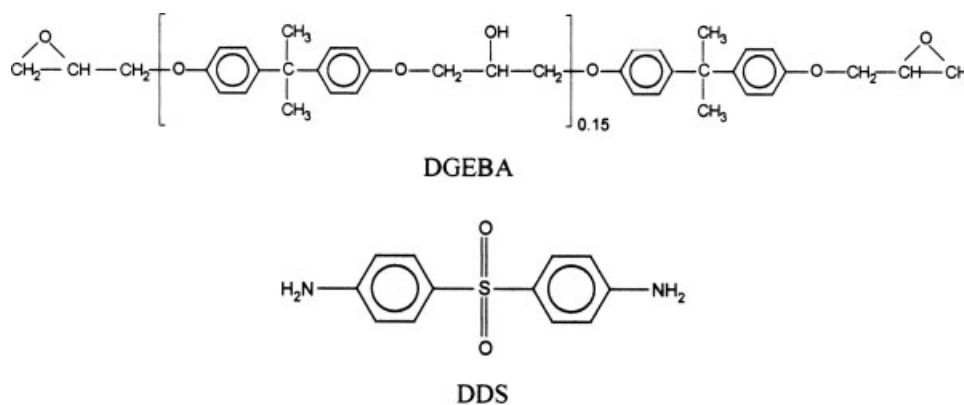


Figure 1 Chemical structures of the epoxy resin and DDS.

over a period of 3–4 h through azeotropic distillation with toluene. The reaction temperature was brought down to 100°C, and DCBN (49.39 g, 0.29 mol) and NMP (100 mL) were added to the flask. The reaction mixture was further heated to 200°C, kept there for 3 h, cooled to room temperature, and filtered through a fritted glass funnel. The filtrate was poured into a large excess of water, and the polymer precipitated. The precipitated polymer was collected by filtration, refluxed with water repeatedly, subjected to Soxhlet extraction with methanol, filtered, and dried under vacuum at 120°C for 15 h. The yield was 98%.

Blend preparation

The epoxy/PENTOH blends were prepared by a solvent-less mixing technique. The chemical structures of the epoxy resin and DDS are given in Figure 1. The required amount of PENTOH was dissolved in the epoxy resin at 140°C with constant stirring. Triphenylphosphine (TPP; 0.5 phr) was added to catalyze the reaction between the hydroxyl group of PENTOH and the epoxy ring. After a homogeneous solution was obtained, a stoichiometric amount of the curing agent DDS was added to the mixture and allowed to dissolve completely with the temperature raised 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 postcuring was conducted at 200°C for 2 h.

Characterization

PENTOH oligomers

The Fourier transform infrared (FTIR) spectra of the PENTOH oligomers in KBr pellets were recorded with a PerkinElmer (Fremont, CA) Spectrum GXA FTIR spectrometer. The glass-transition temperatures (T_g 's) were measured with a TA Instrument (New

Castle, DE) DSC-2920 modulated differential scanning calorimeter operated in the standard differential scanning calorimetry (DSC) mode at a heating rate of 10°C/min under a nitrogen atmosphere. The inherent viscosities were determined at 60°C for 0.2% polymeric solutions in *p*-chlorophenol with an Ubbelohde suspended-level viscometer. The hydroxyl value of the oligomers was determined with acid/base titration.

The molecular weights and molecular weight distributions of the oligomers were determined with gel permeation chromatography. A Waters Alliance (Milford, MA) separation module in conjunction with a Waters 410 differential refractive-index detector was used. Tetrahydrofuran was used as the solvent at a flow rate of 1 mL/min. M_n , the weight-average molecular weight (M_w), and the polydispersity index (PDI) were calculated with polystyrene standards.

Blends

Curing reaction and mechanical properties. The curing reaction of the epoxy/PENTOH blends with DDS as

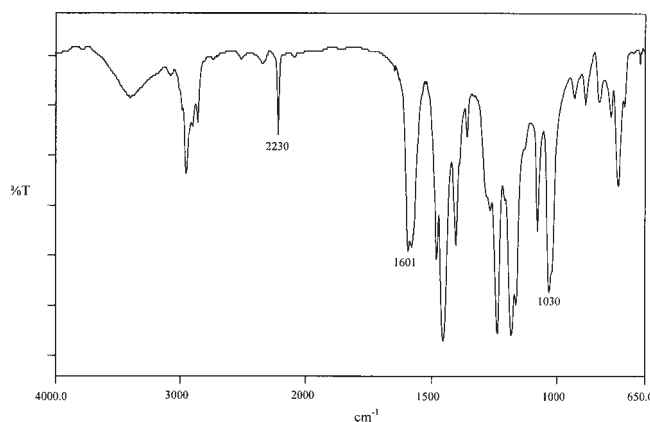


Figure 2 FTIR spectrum of PENTOH.

TABLE I
Properties of the PENTOH Oligomers^a

Oligomer	T_g (°C)	M_n	M_w	PDI	Inherent viscosity (dL/g)	Hydroxyl value (mg of KOH/g)
PENTOH12	197	11,000 (12,000)	20,500	1.84	0.33	10 (9.35)
PENTOH8	194	8,000 (8,000)	14,700	1.83	0.22	16 (14)
PENTOH4	191	3,900 (4,000)	5,700	1.44	0.10	30 (28)

^a Theoretical values are given in parentheses.

the curator was monitored with FTIR and DSC. Specimens for mechanical testing were machined to the required dimensions from cast laminates through cutting with a diamond wheel cutter. The tensile properties were determined per ASTM D 638 with a universal testing machine (Fuel Instruments and Engineers, Maharashtra, India) (model TNE 5000) at a crosshead speed of 10 mm/min. The flexural properties were measured in the three-point-bending mode according to ASTM D 790 at a crosshead speed of 10 mm/min with rectangular specimens of $100 \times 10 \times 3$ mm³. The flexural strength was calculated with eq. (1):

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

where P is the load, L is the span length, b is the breadth of the specimen, and d is the thickness of the specimen.

The fracture toughness was measured according to ASTM STP410 with single-edge-notched specimens of $100 \times 35 \times 3$ mm³. A notch of 5 mm was made at the center of one edge. A precrack was made by a fresh razor blade being tapped into the notch. The measurements were performed in the tension mode. The fracture toughness at crack initiation,

in terms of the critical stress intensity factor (K_{IC}), was calculated with 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 is calculated with the following equation:

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

Scanning electron microscopy (SEM). The morphology of the blends was studied with SEM. The fracture surfaces of cryogenically fractured specimens and failed specimens from fracture toughness measurements were analyzed with a Hitachi (Berkshire, UK) model S-2400 scanning electron microscope at an accelerating voltage of 15 kV. The cryogenically fractured surfaces were etched with chloroform for 24 h to remove thermoplastic phase. The specimens were dried in a vacuum overnight to remove the solvent.

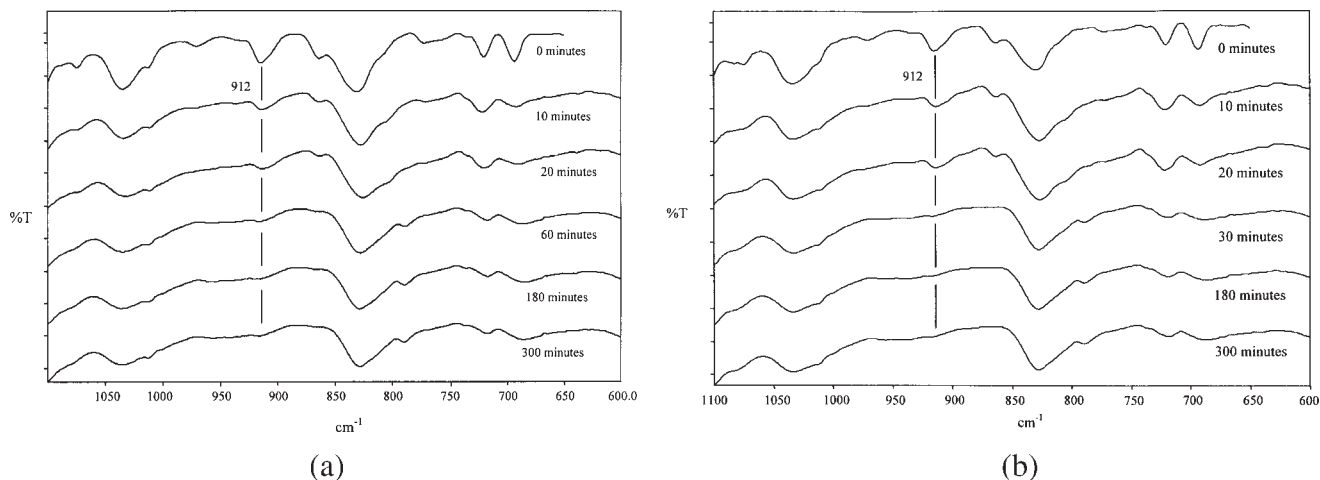


Figure 3 FTIR spectra showing the curing of (a) unmodified and (b) modified epoxy resins at different time intervals at 180°C for 3 h and at 200°C for 2 h.

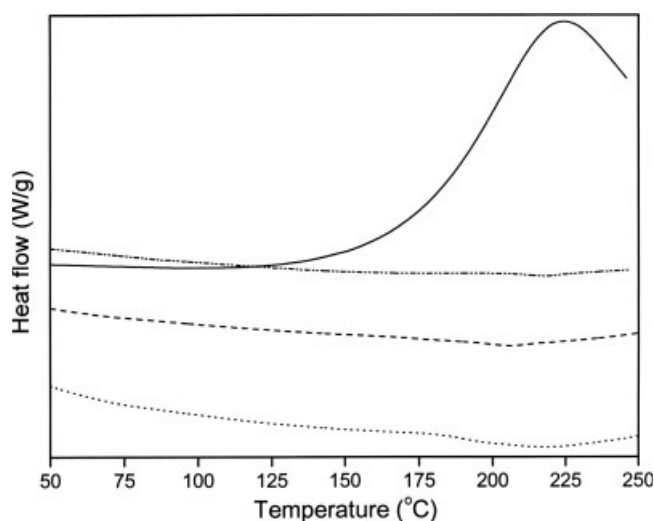
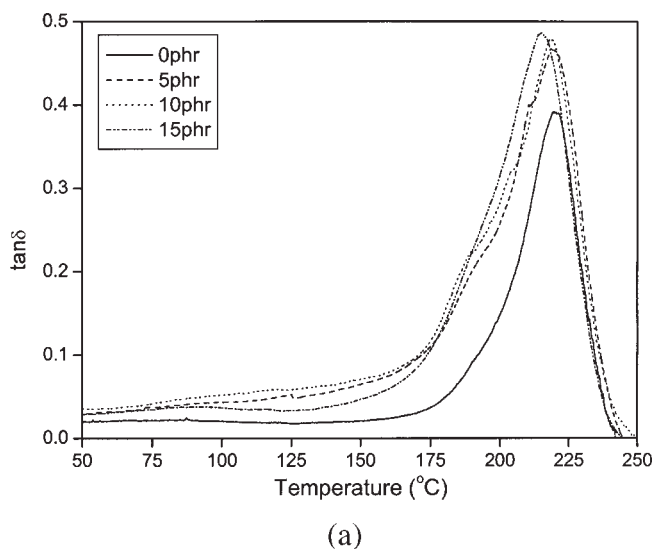


Figure 4 DSC traces of an unmodified epoxy resin showing the curing reaction at different time intervals: (—) 0 h, (---) 3 h at 180°C, (···) 3 h at 180°C and 1 h at 200°C, and (- · - ·) 3 h at 180°C and 2 h at 200°C.

All specimens were sputter-coated with a thin layer of gold with a gold-ion sputter unit (E-101) from Hitachi before the micrographs were taken.

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



Thermogravimetry. The thermogravimetric analysis of the blends was carried out with a TA Instrument model SDT-2960 thermal analyzer in a nitrogen atmosphere from room temperature to 900°C at a heating rate of 20°C/min.

RESULTS AND DISCUSSION

PENTOH oligomers

PENTOH oligomers were synthesized by the aromatic nucleophilic displacement of chlorine from an activated substrate, DCBN, by TBHQ as per Scheme 1. The FTIR spectrum of the PENTOH oligomer was recorded in KBr pellets. The FTIR spectrum of the PENTOH oligomer shown in Figure 2 reveals characteristic bands at 2230 cm^{-1} due to symmetrical stretching of nitrile groups. The peaks in the region between 1100 and 1250 cm^{-1} are due to ϕ -O skeletal vibrations (oxygen attached on either side of the ring). The broad peak between 3000 and 3500 cm^{-1} confirms the presence of hydroxyl groups in the oligomers. The band at 1030 cm^{-1} is due to the ether linkages ortho to $\text{C}\equiv\text{N}$. The peak at 1601 cm^{-1} has been assigned to $\text{C}=\text{C}$ stretching of the benzene ring in which oxygen is ortho to $\text{C}\equiv\text{N}$. The peaks in the region between 2962 and 2872 cm^{-1} are due to the $\text{C}-\text{H}$ stretching vibration, whereas the peak at 1364 cm^{-1} is due to the $\text{C}-\text{H}$ bending vibrations of the $-\text{CH}_3$ groups in the *tert*-butyl group.

The molecular weights, inherent viscosities, hydroxyl values, and T_g values of the oligomers are given in Table I. The experimental M_n values are in close agreement with the theoretical M_n values, and this is further confirmed by their hydroxyl values.

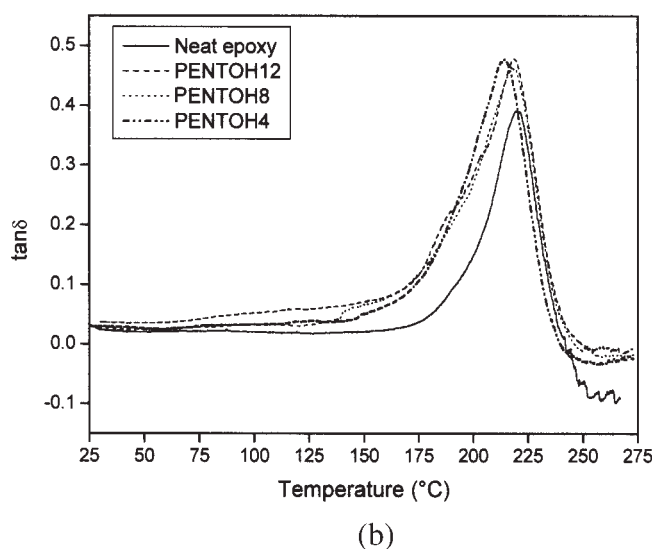


Figure 5 $\tan \delta$ versus the temperature for (a) the PENTOH12-modified epoxy resin and (b) epoxy resins modified with PENTOH oligomers of different molecular weights (10 phr).

TABLE II
Peak Heights, Peak Widths, Peak Areas, M_c Values, and ν_e Values of Epoxy/PENTOH Blends

	PENTOH (phr)	Peak height	Peak width at half-height (°C)	Peak area	M_c (g/mol)	ν_e ($\times 10^{27}$ chains/m ³)
Epoxy resin	0	0.37	24.4	13.92	106	6.82
Epoxy/PENTOH12	5	0.49	31.7	18.30	132	5.47
	10	0.46	39.0	17.52	153	4.72
	15	0.49	35.5	19.21	156	4.63
Epoxy/PENTOH8	10	0.47	35.8	19.59	142	5.09
Epoxy/PENTOH4	10	0.49	33.1	18.36	138	5.24

The inherent viscosities and T_g values of the oligomers increase with an increase in the molecular weight as they are dependent on the molecular weight.

Epoxy/PENTOH blends

All the oligomers used were soluble in the epoxy resin without the use of solvents. Blends with 5, 10, or 15 phr oligomer were prepared. The binary blends were transparent and visually homogeneous. On curing, the blends became translucent, and this indicated a heterogeneous morphology. The samples were cured at specified temperatures with respect to time and analyzed with FTIR and DSC. The FTIR spectra of both unmodified and modified epoxy resins show the disappearance of the epoxy peak at 912 cm⁻¹ after 3 h of curing at 180°C [Fig. 3(a,b)] and reveal the absence of unreacted epoxy groups. The DSC trace of the unmodified epoxy resin (Fig. 4) shows no exotherm for the 3-h-cured sample at 180°C, indicating the completion of the curing reac-

tion. A similar trend was observed for the PENTOH-modified epoxy resin systems.

Dynamic mechanical thermal analysis

The viscoelastic properties of the unmodified and PENTOH-modified epoxy resins were investigated with a dynamic mechanical thermal analyzer. The plot of $\tan \delta$ versus the temperature for the PENTOH12-modified epoxy resin is given in Figure 5(a). The T_g of the epoxy phase was observed near 230°C in the dynamic mechanical spectrum. No distinct peak due to the PENTOH12-rich phase was observed in the $\tan \delta$ curves of the blends because of the proximity of the T_g of PENTOH12 and that of the DDS-cured epoxy resin. However, a shoulder was observed near 190°C in the dynamic mechanical spectrum, which may due to the phase-separated PENTOH. A comparison of the variation of $\tan \delta$ with the temperature for epoxy resins modified by PENTOHs (10 phr) of different molecular weights is shown in Figure 5(b), and the overall behavior is

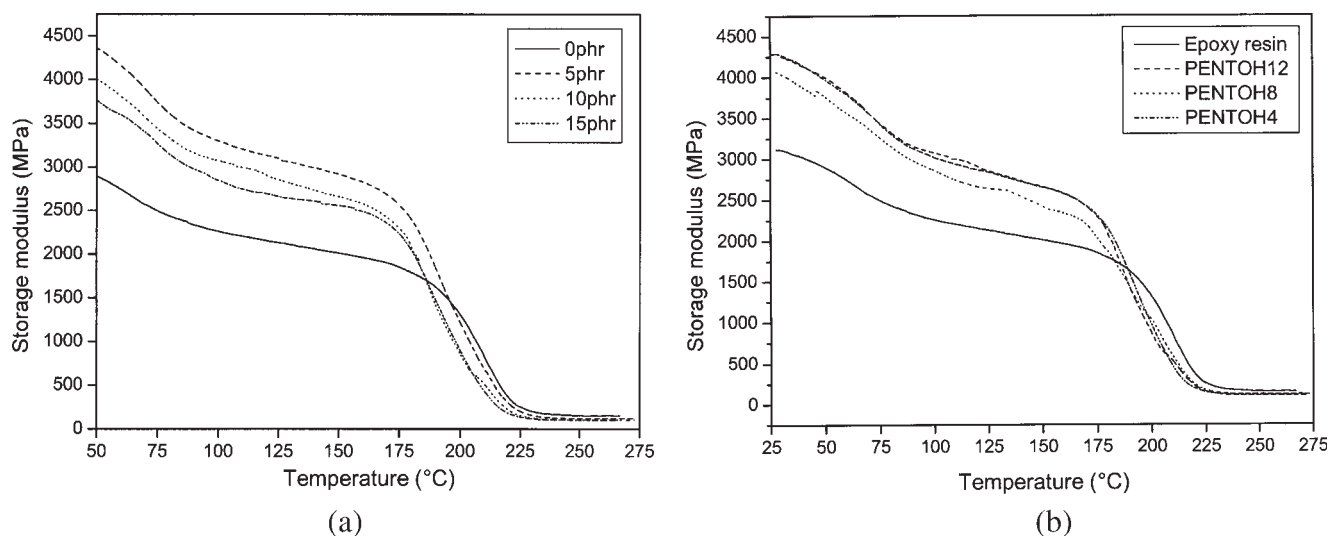
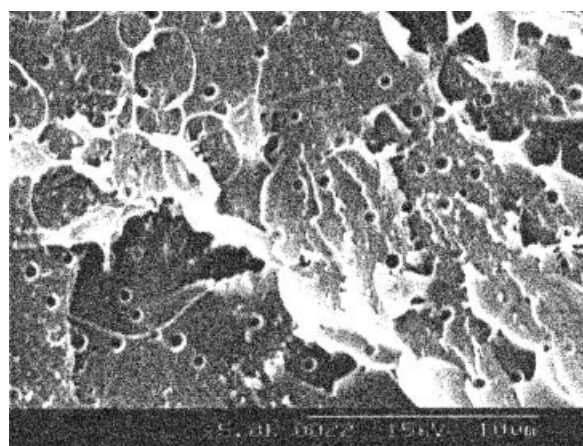
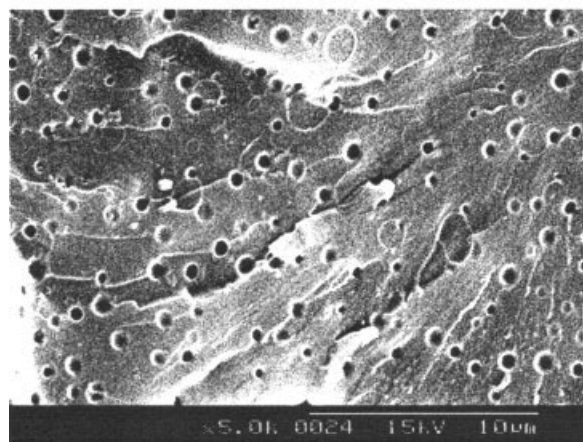


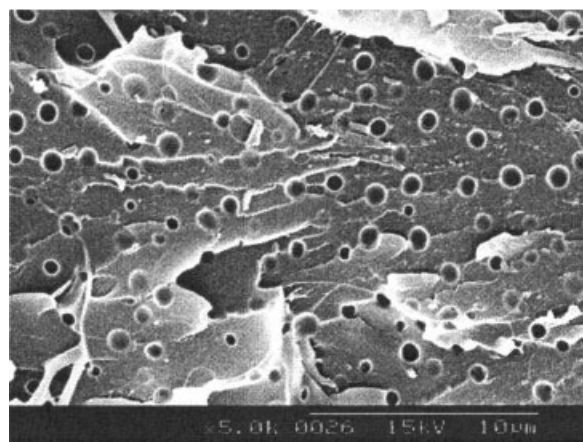
Figure 6 E' versus the temperature for (a) the PENTOH12-modified epoxy resin and (b) epoxy resins modified with oligomers of different molecular weights (10 phr).



(a)



(b)

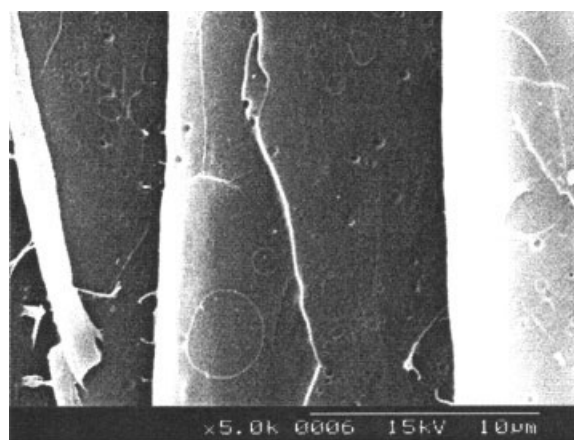


(c)

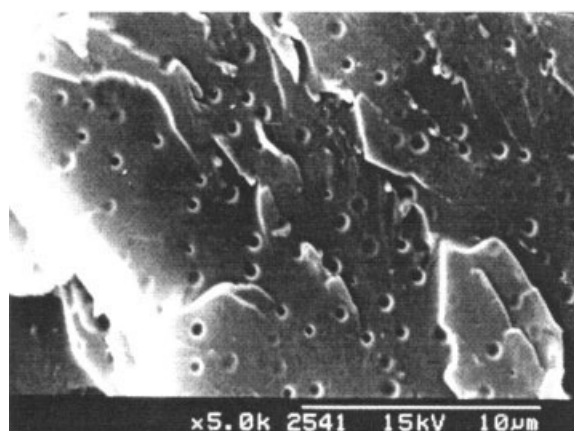
Figure 7 SEM images of the PENTOH12-modified epoxy resin: (a) 5, (b) 10, and (c) 15 phr.

similar to that of the PENTOH12-modified epoxy resin. The T_g of the cured epoxy resin decreases with the addition of PENTOH12, and the decrease becomes prominent with an increase in the PENTOH12 content in the blends. As the oligomer concentration increases, the $\tan \delta$ curve becomes

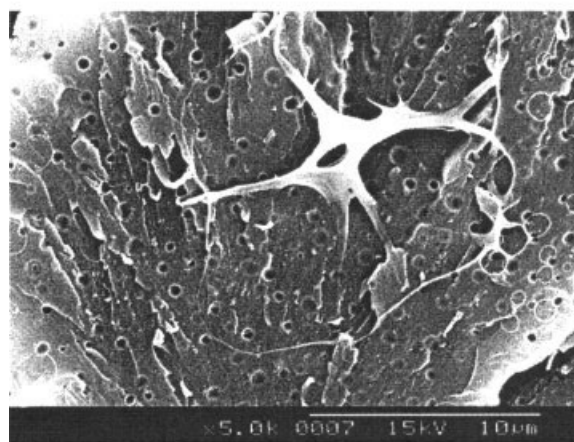
broader and shifts toward a lower temperature. The decrease in T_g increases with the decrease in the molecular weight of the PENTOH. The $\tan \delta$ peak height, peak area, and peak width at the half-height are given in Table II. These parameters are higher



(a)



(b)



(c)

Figure 8 SEM images of the PENTOH8-modified epoxy resin: (a) 5, (b) 10, and (c) 15 phr.

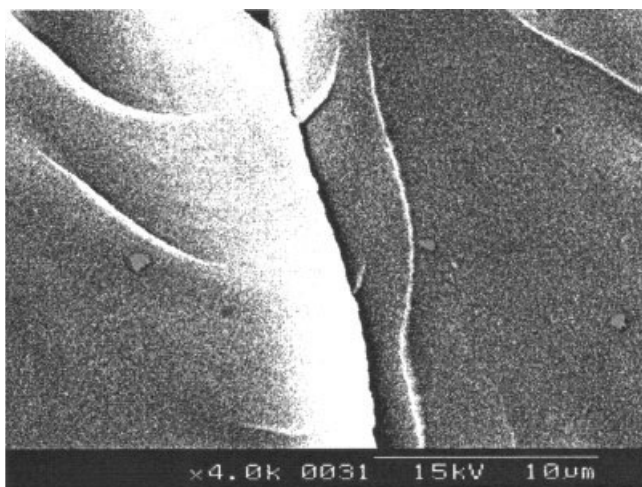


Figure 9 SEM image of the PENTOH4-modified epoxy resin (10 phr).

for the blends than for the unmodified resin. The increase in peak the width and area for all the blends indicates better interactions between the blend components. Similar observations were made by us earlier for a tert-butyl poly(cyano arylene ether) (PENT)-modified epoxy system.³⁸ This is due to the better interaction between the epoxy resin and PENTOH. TPP was used to catalyze the reaction between the hydroxyl group of PENTOH and epoxy. As a result, some of the hydroxyl groups reacted with epoxy and became part of the crosslinked network.

The E' values of the blends [Fig. 6(a,b)] were higher than that of the neat resin below T_g , became lower than that of the neat resin near the glass-transition region, and continued to be the same in the rubbery plateau region. The lower value of E' in the plateau region is an indication of the decrease in the crosslink density.

The crosslink density of the blends can be calculated from the E' 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 by⁴²

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

where d is the density, R is the universal gas constant, T is the absolute temperature, M_c is the molecular weight between crosslinks, 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, the ratio was assumed to be unity. The factor $1 - 2M_c/M_n$ is a correction factor for chain ends and becomes negli-

ble when M_n is very large with respect to M_c as it is in the case of highly crosslinked systems such as epoxy. Hence, eq. (4) becomes

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

G must be measured in the rubbery plateau region above T_g . G can be taken as $E'/3$,⁴³ and E' was measured at $T_g + 40^\circ\text{C}$. The effective crosslink density (ν_e) was calculated from M_c with the following equation:

$$\nu_e = \frac{\rho N_A}{M_c} \quad (6)$$

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

The M_c and ν_e values are tabulated in Table II. The M_c values were found to increase with an increase in the oligomer content and with an increase in the molecular weight of PENTOH. This indicates that the addition of PENTOH reduced the crosslink density of the cured resin. The reduction in the crosslink density is evident from Table II. The reduction in the crosslink density decreased the T_g of the blends. This is due to the incorporation of some of the modifier chains into the crosslinked structure as a result of the interaction between PENTOH and epoxy.

Morphological analysis

The phase morphology of the blends was investigated with SEM. To get a clear picture, the fracture surfaces of the blends were etched with chloroform. The SEM micrographs of the fracture surfaces of the blends are given in Figures 7–9. The SEM micrographs reveal a sea-island morphology, except for the PENTOH4-modified epoxy resin (Fig. 9). The epoxy/PENTOH12 and epoxy/PENTOH8 blends at all compositions showed a particulate morphology in which the PENTOH-rich phase was dispersed in a continuous epoxy matrix. The observed spherical cavities are due to the removal of the oligomer inclusion during solvent etching. The etched holes show white, circular diffuse zones between the epoxy ma-

TABLE III
Parameters Obtained from SEM Micrographs of Epoxy/PENTOH Blends

	PENTOH (phr)	D_n (μm)	D_w (μm)	PDI
Epoxy/PENTOH12	5	0.38	0.41	1.06
	10	0.41	0.45	1.11
	15	0.51	0.56	1.11
Epoxy/PENTOH8	5	0.34	0.35	1.02
	10	0.42	0.44	1.05
	15	0.34	0.38	1.10

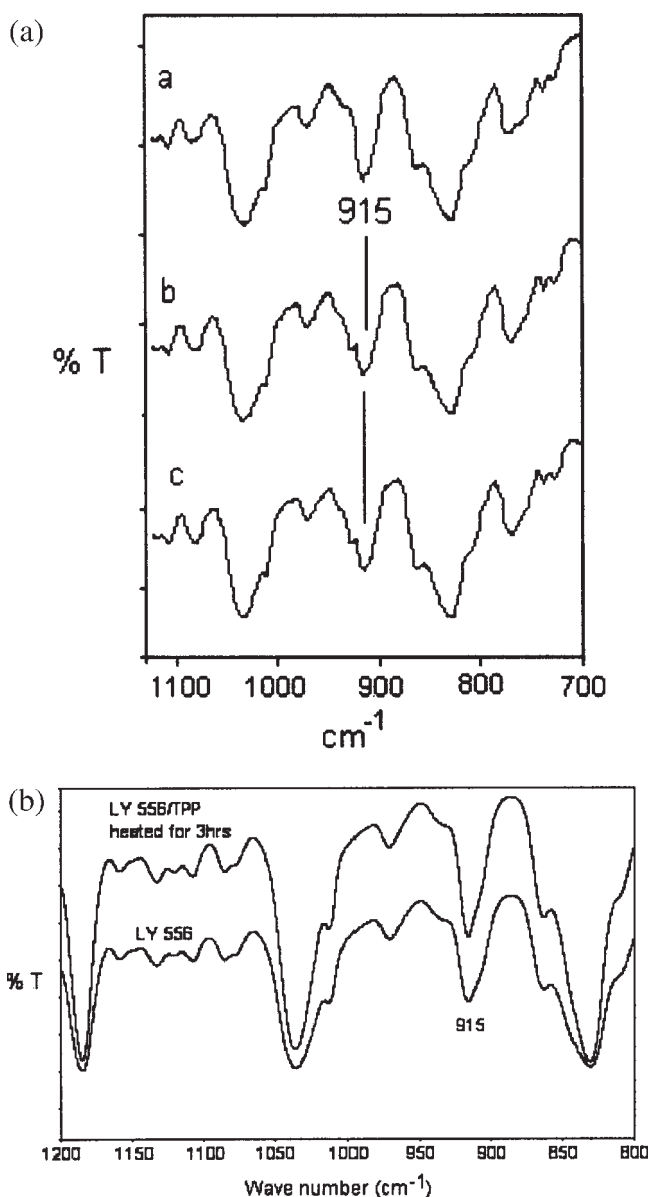


Figure 10 (a) FTIR spectra of (a) the neat epoxy resin and (b,c) the binary epoxy resin/15 phr PENTOH12 blend heated with TPP for 1 or 3 h, respectively, and (b) FTIR spectra of the neat epoxy resin and the epoxy resin heated with TPP for 3 h.

trix and the empty holes. These diffuse zones are transition zones of incomplete phase separation in which both PENTOH and epoxy are present. The presence of the diffuse zones was reported by Teng and Chang⁴⁴ in epoxy/phenoxy blends and by us in epoxy/PENT blends.³⁸ The domain diameters and PDIs were calculated with eqs. (7)–(9). An image analysis technique was used to measure the domain diameter, and it was an average of at least 200 domains:

$$D_n = \frac{\sum n_i d_i}{\sum n_i} \quad (7)$$

$$D_w = \frac{\sum n_i d_i^2}{\sum n_i d_i} \quad (8)$$

$$PDI = \frac{D_w}{D_n} \quad (9)$$

where D_n is the number-average diameter, D_w is the weight-average diameter, and n_i is the number of domains having diameter d_i .

Table III reveals that the domain size increased with the PENTOH12 content in the blend. In PENTOH8-modified systems, the domain size increased up to 10 phr, and a slight decrease was observed at 15 phr PENTOH8. This may be due to the reaction between the PENTOH and epoxy resin. Because of the lower molecular weight of PENTOH8, a greater amount of PENTOH8 remained bonded with the epoxy resin, and this resulted in a decrease in the domain size. The PENTOH4-modified epoxy resin showed a homogeneous phase morphology (Fig. 9). No particulate morphology was observed, but the fracture surface was rough. A similar observation was made by Teng and Chang⁴⁴ for epoxy/phenoxy blends. A similar morphological feature was also observed in a poly(ethylene phthalate) (PEP)-modified DGEBA resin cured with hexahydrophthalic anhydride. Lower molecular weight PEP showed no phase

TABLE IV
Mechanical Properties of PENTOH-Modified Epoxy Resins

	PENTOH (phr)	Tensile strength (MPa)	Young's modulus (GPa)	Flexural strength (MPa)	Flexural modulus (GPa)
Epoxy resin	0	60 ± 3	1.6 ± 0.03	121 ± 5	3.0 ± 0.04
Epoxy/PENTOH12	5	65 ± 4	1.9 ± 0.02	114 ± 6	2.8 ± 0.05
	10	68 ± 2	1.5 ± 0.05	108 ± 3	2.9 ± 0.02
	15	69 ± 5	1.6 ± 0.04	106 ± 7	2.9 ± 0.03
Epoxy/PENTOH8	5	66 ± 3	1.5 ± 0.02	95 ± 5	2.9 ± 0.04
	10	66 ± 4	1.6 ± 0.05	95 ± 5	2.8 ± 0.06
	15	66 ± 5	1.2 ± 0.04	94 ± 4	2.9 ± 0.05
Epoxy/PENTOH4	5	68 ± 5	1.5 ± 0.04	121 ± 3	2.7 ± 0.04
	10	66 ± 4	1.8 ± 0.02	105 ± 6	2.2 ± 0.03
	15	70 ± 2	1.4 ± 0.03	111 ± 3	2.6 ± 0.02

TABLE V
Fracture Toughness of PENTOH-Modified Blends

	PENTOH (phr)	K_{IC} (MN/m ^{-3/2})
Epoxy resin	0	1.46 ± 0.02
Epoxy/PENTOH12	5	2.49 ± 0.01
	10	2.43 ± 0.03
	15	2.57 ± 0.02
Epoxy/PENTOH8	5	2.08 ± 0.02
	10	3.08 ± 0.03
	15	2.56 ± 0.04
Epoxy/PENTOH4	5	2.56 ± 0.03
	10	3.42 ± 0.04
	15	2.76 ± 0.05

separation, and this indicated good compatibility with epoxy.⁴⁵ Similarly, the PENTOH4-modified epoxy resin also showed no phase separation. This is due to two factors: the chemical reaction between the hydroxyl groups and epoxy and the gelation of the blend before phase separation. We used TPP to catalyze the reaction between the PENTOH and epoxy resin. The chemical reaction was investigated with FTIR spectroscopy. FTIR spectra of the neat epoxy resin and 15 phr blends heated with TPP without a hardener for various times are shown in Figure 10(a). The intensity of the epoxy peak in the blends was less than that of the neat epoxy resin. This means that some of the hydroxyl groups reacted with the epoxy resin. Because TPP could catalyze the polyetherification of the epoxy resin, the FTIR spectra of the epoxy resin heated with TPP were also taken [Fig. 10(b)]. In this case also, we observed a slight decrease in the intensity of the epoxy peak. However, the decrease in the intensity of the epoxy peak was less than that of the blends. Hence, it was concluded that PENTOH reacted with the epoxy resin. Because of the low molecular weight of PENTOH4, the number of hydroxyl groups in this oligomer was more than that in the higher molecular weight PENTOH, resulting in a better interaction with the epoxy.

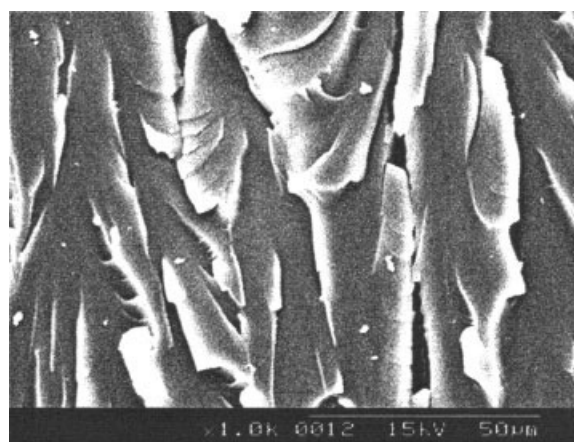
Tensile and flexural properties

The mechanical properties of the blends are given in Table IV. The data reveal that there was a marginal increase in the tensile strength and the modulus remained close to that of the neat epoxy resin. The flexural strength and flexural modulus showed a marginal decrease, regardless of the molecular weight and composition of the modifier.

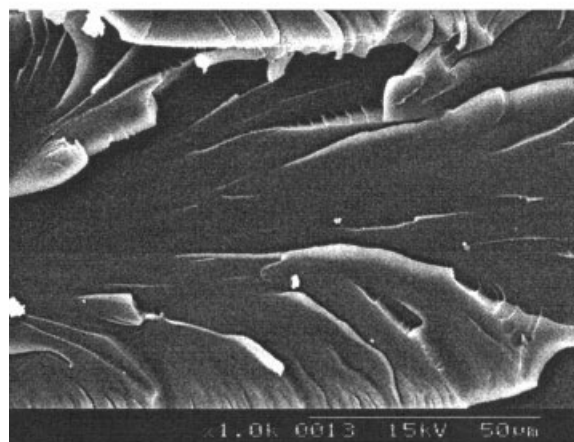
Fracture toughness

The fracture toughness, expressed as K_{IC} , is given in Table V. Regardless of the molecular weight, the addition of PENTOH increased the fracture toughness of the epoxy resin. The maximum improvement

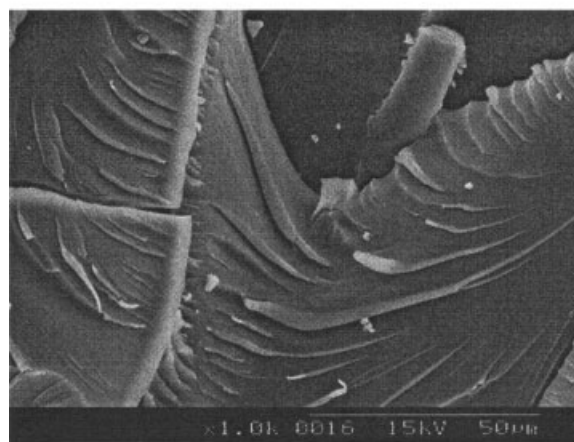
in the fracture toughness (134%) was obtained by the addition of 10 phr PENTOH4. In an earlier article,³⁸ we reported the toughening of an epoxy resin with PENT and obtained more than an 80%



(a)

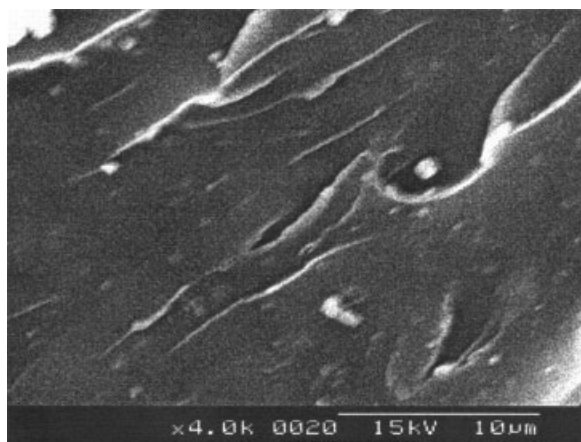


(b)

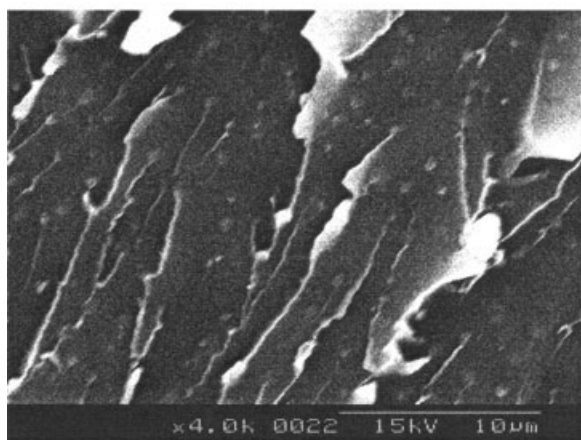


(c)

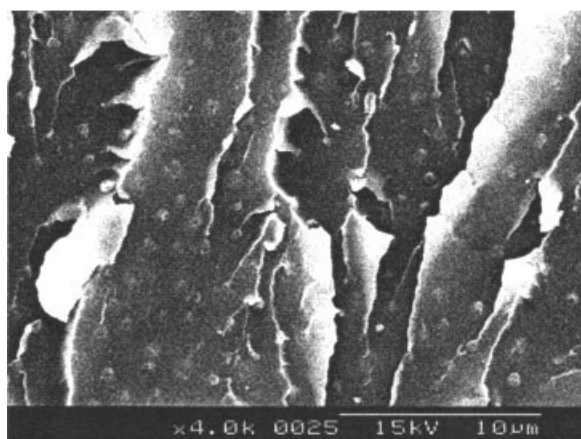
Figure 11 SEM micrographs of fractured surfaces of the PENTOH4-modified epoxy resin: (a) 5, (b) 10, and (c) 15 phr.



(a)



(b)



(c)

Figure 12 SEM micrographs of fractured surfaces of the PENTOH12-modified epoxy resin: (a) 5, (b) 10, and (c) 15 phr.

increase in the fracture toughness. The increase in the fracture toughness for the epoxy/PENT blends was lower than that for the PENTOH-modified epoxy resin. The difference was attributed to the reaction between the epoxy resin and PENTOH.

In contrast to the usual behavior, the homogeneous blend system gave the maximum improvement in the toughness. The homogeneity of the blends was due to the interaction between the epoxy and hydroxyl group. Similar observations have been reported for epoxy/polyester blends.⁴⁵ The increase in the fracture toughness was due to the increase in the ductility of the blend as a result of the decrease in the crosslink density. The decrease in the crosslink density was evident from the decrease in T_g and lower E' in the plateau region of the dynamic mechanical spectrum. To investigate the toughening mechanisms, the SEM micrographs of the fracture surfaces of the failed specimens were taken. The micrographs of PENTOH4-toughened epoxy resin are given in Figure 11. The fracture surface of the blends was rougher than that of the neat resin, and river marks could be seen on the fracture surfaces. The roughness of the fracture surface indicates the ductile nature of the crack due to the decrease in the crosslink density of the blends. The roughness also indicates that the crack deviated from its original plane, resulting in an increase in the surface area of the crack. Therefore, more energy was needed to propagate the crack. The SEM micrographs of PENTOH12- and PENTOH8-modified epoxy resins are shown in Figures 12 and 13, respectively. The fracture surfaces were rough, indicating that the crack deviated from the original plane, increasing the surface area of the crack. Also, river marks could be seen on the fracture surface indicating plastic deformation of the matrix.⁴⁶ The dispersed domains acted as obstacles and prevented the crack propagation to some extent. Moreover, the domains acted as stress concentrators, leading to plastic deformation of the matrix surrounding the domains.^{47,48} In addition, as the frequency of the domains increased, stress fields caused by each domain interacted, resulting in

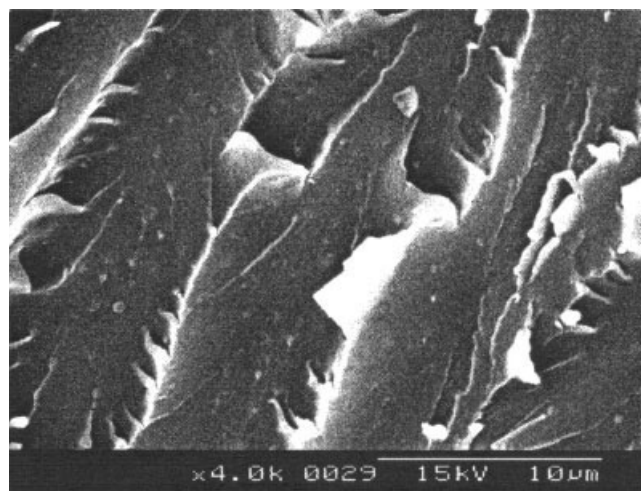


Figure 13 SEM micrograph of the fractured surface of the PENTOH8-modified epoxy resin (10 phr).

TABLE VI
Interparticle Distance and Interfacial Area per Unit of Volume for Epoxy/PENTOH12 and Epoxy/PENTOH8 Blends

	PENTOH (phr)	Interparticle distance (μm)	Interfacial area per unit of volume (μm^{-1})
Epoxy/PENTOH12	5	0.49	0.70
	10	0.34	1.24
	15	0.32	1.43
Epoxy/PENTOH8	5	0.44	0.78
	10	0.35	1.21
	15	0.21	2.15

increased fracture toughness. It can also be seen from the micrograph that the domains were not completely pulled out from the fracture surface. The ductile tearing of the domains also contributed to the overall increase in the fracture toughness of the blends and indicated good interactions between the domains and matrix. Furthermore, tail marks could be seen near the domains, indicating a crack pinning mechanism.

The fracture toughness of the PENTOH12 and PENTOH8 blends varied according to the blend ratio. In the PENTOH12-toughened system, the addition of 15 phr gave the maximum toughness improvement, whereas the addition of 10 phr gave the maximum toughness in the PENTOH8-modified epoxy resin. The interfacial area per unit volume, interparticle distance, domain size, domain size distribution, and so forth could influence the fracture toughness in thermoset/thermoplastic blends. The interparticle distance and interfacial area per unit of volume were calculated with 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. The values are summarized in

Table VI. The interparticle distance decreased with an increase in the oligomer content in the blends. The interfacial area per unit of volume also increased with an increase in the oligomer content in the blends. Both factors favored a increase in the fracture toughness. Therefore, it can be inferred from this discussion that the local plastic deformation of the matrix and other mechanisms such as crack path deflection, crack pinning, and ductile tearing of the thermoplastic were responsible for the increase in the fracture toughness of the PENTOH12- and PENTOH8-modified epoxy resins, and the increase in the fracture toughness of the PENTOH4-modified epoxy resin was mainly due to the ductile nature of the crack.

Thermogravimetric analysis

Thermogravimetric analysis gives us insight into the thermal stability of blends. Parameters such as the initial decomposition temperature (IDT), the temperature at the maximum rate of weight loss (T_{max}), and the activation energy for decomposition (E) are important in expressing the thermal stability of a material and can be used to assess a material's lifetime.⁴⁹ E was determined with the Horowitz–Metzger equation:⁵⁰

$$\ln \left[\ln(1 - \alpha)^{-1} \right] = E\theta/RT_{\text{max}}^2 \quad (12)$$

where α is the decomposed fraction and θ is given by $T - T_{\text{max}}$. From the slope of the plot of $\ln[\ln(1 - \alpha)^{-1}]$ against θ , the value of the activation

TABLE VII
Thermal Analysis of PENTOH-Modified Epoxy Resin

	PENTOH (phr)	IDT ($^{\circ}\text{C}$)	T_{max} ($^{\circ}\text{C}$)	Activation energy (kJ/mol)
Epoxy resin	0	420	430	280
Epoxy/PENTOH12	5	400	430	281
	10	400	431	290
	15	410	431	293
	10	400	424	301
Epoxy/PENTOH4	10	400	431	300

energy was calculated. The various parameters obtained from thermogravimetric analysis measurements are summarized in Table VII. It is evident that all blends were stable up to 400°C. However, no appreciable change was observed in the overall thermal stability and activation energy of the blends in comparison with the unmodified resin, regardless of the molecular weight of the toughener and composition of the blend.

CONCLUSIONS

The important conclusions that can be drawn from this study are as follows:

- Hydroxy-terminated PEN oligomers with tertiary butyl groups were synthesized and used as toughening agents for a DGEBA-type epoxy resin.
- Reaction-induced phase separation occurred in PENTOH12- and PENTOH8-modified epoxy resins, resulting in a droplet matrix morphology, and no phase separation was seen in the PENTOH4-modified epoxy resin.
- The plot of $\tan \delta$ versus the temperature showed a single peak because of the close proximity of the T_g values of the PENTOH and DDS-cured epoxy resins. The increase in the peak width and peak area indicated interactions between the epoxy resin and PENTOH.
- The $\tan \delta$ curve for the blends shifted to the lower temperature side with a decrease in the molecular weight of the hydroxy-terminated PENT oligomer and with an increase in the oligomer concentration.
- E' of the blends was lower than that of the neat resin in the rubbery plateau region, indicating the decrease in the crosslink density of the blends.
- The tensile and flexural properties of the blends were comparable to those of the unmodified epoxy resin.
- The fracture toughness of the blends was higher than that of the neat resin, and the extent of improvement was dependent on the composition of the blends. The maximum enhancement of the toughness was shown by the 10 phr PENTOH4 blend, for which a homogeneous morphology was observed.
- Various toughening mechanisms such as local plastic deformation, crack path deflection, ductile tearing of the thermoplastic, particle bridging, and crack pinning took part in improving the toughness of the epoxy/PENTOH blends.
- The thermal stability of the blends was comparable to that of a DDS-cured epoxy resin system.

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