

Toughening of Thermoset/Thermoplastic Composites Via Reaction-Induced Phase Separation: Epoxy/Phenoxy Blends

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ABSTRACT: Phase morphology and phase separation behavior of amine-cured bisphenol-A diglycidyl ether epoxy and phenoxy mixtures have been investigated by means of time-resolved small angle light scattering, optical microscopy, and scanning electron microscopy. The starting reactant mixtures composed of epoxy, phenoxy, and curing agents such as diaminodiphenyl sulfone (DDS) and methylene dianiline (MDA) were found to be completely miscible. Upon curing with DDS at 180°C, phase separation took place in various epoxy/phenoxy blends (compositions ranging from 10–40% phenoxy), whereas the MDA curing showed no indication of phase separation. The mechanical and physical properties of single-phase and two-phase networks were examined, in that the DDS-cured epoxy/phenoxy blends having a two-phase morphology showed improved ductility and toughness without significantly losing other mechanical and thermal properties such as modulus, tensile strength, glass transition and heat deflection temperatures. The energy absorbed to failure during the drop weight impact event was also found to improve relative to those of the single-phase MDA-cured blend as well as of the neat epoxy. Such property enhancement of the DDS-cured blends has been discussed in relation to the two-phase morphology obtained via scanning electron microscopy micrographs of fractured surfaces. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 1257–1268, 2000

Key words: thermoset/thermoplastic composites; epoxy/phenoxy blends; reaction-induced phase separation; morphology development; toughness enhancement

INTRODUCTION

Historically, epoxy resins have been used extensively as thermosetting matrix materials in the development of high-performance light-weight composites and toughened plastics.^{1–4} In this connection, epoxide technology has made remarkable progress with a wide range of applications that include areas as diverse as construction, electronics, adhesives, and coatings. A major limitation of neat epoxy resins, particularly those for high-temperature applications, is their inherent brittleness arising from the crosslinked structure. To circumvent

such shortcoming, toughening of brittle epoxy resins has been undertaken extensively by incorporating liquid rubber such as carboxyl terminated butadiene acrylonitrile copolymers.^{2–10} It was found that toughness could be enhanced at a low level (<10%) of rubber.^{2–4} At a higher rubber loading, the inclusion of rubber domains invariably resulted in significant reduction in the tensile strength and modulus of the composites. Various questions have been raised as to what kind of factors govern the emerging rubber domains, how much of the rubber remained dissolved in the matrix, and what effect the dissolved rubber might have on the ultimate toughness of the polymers.

A conventional task is to toughen epoxy resins without sacrificing their good properties such as modulus, tensile strength, and glass transition temperature (T_g). This gave birth to thermoplastic modified thermosetting polymers that incorpo-

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rate thermoplastic domains within a thermosetting matrix.²⁻⁴ Such a two-phase morphology can be achieved by mechanically dispersing thermoplastic particles into the matrix or through phase separation driven by a cure reaction.⁴ The mechanical properties of thermoplastic modified epoxy resins show strong dependence on crosslink density of the resin as well as on the morphology of phase separated domains and interfacial adhesion between these two phases.³⁻¹¹ Therefore, the subject requires thorough investigation of curing behavior, emergence of biphasic domain morphology, and mechanical performance of these blends.

In this study, a thermally stable, tough and ductile thermoplastic, namely, phenoxy has been used for modifying diglycidyl ether bisphenol-A (DGEBA) epoxy resin. The choice of this thermoplastic phenoxy is due to the similarity in chemical structure with DGEBA epoxy. The aim of the present study is to investigate relationships between domain structures and mechanical properties of the epoxy/phenoxy blends. It is well documented that toughening of brittle polymers occurs usually at the expense of strength and stiffness.^{2,4} Therefore, another goal of this work is to achieve a synergistic combination of enhanced toughness without appreciably sacrificing the strength and modulus. Of particular importance is that the phenoxy and modifiers such as diamino diphenyl sulfone (DDS) or methylene dianiline (MDA) can be dissolved in hot DGEBA epoxy and melt-blended without requiring any solvent. Upon curing with DDS, phase separation occurs in the phenoxy/epoxy blends, but MDA curing shows no indication of phase separation. The emergence of phase separated structure during the DDS curing was investigated using time-resolved light scattering, optical microscopy, and scanning electron microscopy (SEM). Temporal evolution of structural factor was analyzed in the context of a scaling law. Thermal and mechanical properties of the crosslinked networks have been characterized based on differential scanning calorimetry (DSC) and dynamic mechanical thermal analysis (DMTA). The mechanical properties of the DDS-cured epoxy/phenoxy composites are discussed in relation to the morphology of phase separated domains and also that of the MDA-cured single-phase blends.

EXPERIMENTAL

Materials

The epoxy oligomer used in this study was a diglycidyl ether bisphenol-A (DGEBA), Epon 828,

(weight per epoxide = 185–192 g) supplied by Shell Chemical Company (Houston, TX). The materials used to toughen epoxy (hereafter called modifiers) were two grades of phenoxy resins, viz., PKHP-200 and PKHM-30, commercialized by Phenoxy Associates (Rockhill, SC). The high molecular weight thermoplastic phenoxy was derived from bisphenol-A and epichlorohydrin based on a one-step or a two-step synthesis route, i.e., starting with epichlorohydrin and bisphenol-A in 1:1 mol ratios or utilizing a purified diglycidyl ether bisphenol-A resin and a stoichiometric amount of bisphenol-A via solution polymerization. MDA and DDS were purchased from Aldrich Chemical Co (Milwaukee, WI). High-temperature aromatic curing agents such as MDA and DDS were used for crosslinking of epoxy in the mixtures. Dry 1,1,1,2-tetrafluoro ethane (TFE) was used as a mold release agent, which is effective in a temperature range from 46 to 260°C.

Blend Preparation

Epoxy oligomer was degassed in vacuum oven at 90°C for 1 h and melt-blended at 150°C with the modifiers in varying proportions using a Brabender type internal mixer (Plasti-Corder PL 2000). A stoichiometric amount (26 phr) of molten MDA was added to the clear epoxy/phenoxy mixture and further mixed for approximately 1 min. The mixture was then cast into a 152.4 × 152.4 × 3.2 mm aluminum cavity mold. The mold surface was first coated with Frekote sealer (B-15) to seal off the pores, surface scratches or imperfections and then further fine-sprayed with the dry TFE lubricant. The mold was precured at 90°C for 2 h and postcured at 170°C for another 2 h in a temperature-controlled oven. Upon completion of cure, the mold was cooled slowly to room temperature to prevent cracking caused by thermally induced stresses. The plaque was then cut into 12.7-mm bars using a band saw for flexural and heat deflection temperature (HDT) tests, and some were further routed into dog-bone shaped specimens using Vacu-Router (Shyodu Instrument Co.) for tensile testing.

Regarding preparation of DDS-cured blends, 28 phr of the molten hardener (0.85 times the stoichiometric amount, i.e., one epoxy group per 0.85 amine hydrogen from DDS)^{9,10} was added to the homogeneous mixture and the film was cast according to the procedure described above. The blend compositions loaded with DDS were precured at 120°C for 2 h and postcured at 200°C for

another 2 h in accordance with a scheme recommended by Shell Chemical Company.

For small angle light scattering (SALS) and optical microscopy studies, phenoxy was dissolved in a 5–10 wt % methylene chloride solution and mixed with epoxy oligomer and MDA. In the case of DDS curing, a mixed solvent of methylene chloride/methanol (90:10 volume ratio) was used for dissolving the modifier and the curing agent. The mixed solution was cast into films by spreading on glass slides at room temperature. The film thickness was approximately 10 μm . The residual solvent was removed by keeping the specimens in a vacuum oven at room temperature for 24 h.

Characterization Techniques

SALS

Temporal evolution of scattering profiles during isothermal curing of solution-cast phenoxy modified epoxy blends were monitored using a time resolved light scattering (TRLS) apparatus. The TRLS apparatus consists of a randomly polarized He-Ne laser light source (2 mW), a sample chamber, a 1-dimensional Reticon camera (1024 pixels) interlinked with a detector controller [Optical Multichannel Analyzer (OMA III), EG & G Princeton Applied Research] and associated electronics.

Optical Microscopy

Phase separation of the blends during curing was also investigated isothermally at a desired temperature using an optical microscope (Nikon Optipot 2-POL). The halogen bulb operated at 12 V and 100 W was used as a light source. The sample heating chamber (Mettler FP82 HT) equipped with a programmable temperature controller (Mettler Toledo FP90 Central Processor) was used to control experimental temperatures. The optical micrographs were obtained by using a 35 mm camera (FX-35DX, Nikon) connected to an automatic exposure time controller (UFX-DX, Nikon).

SEM

Morphological investigation was undertaken on the failed specimens of tensile tests by using SEM (model S-2150; Hitachi Co.). Each specimen was sputter coated with a thin layer of gold (100–200 Å). The ion sputtering device used was a high vacuum Polaron SEM Coating System. Quartz

PCI (version 3) image database system was used for data acquisition and processing of high-quality and high-resolution images from the electron microscope. Where etching was necessary, the fractured sample was immersed in methylene chloride and sonicated in a water bath for 1 h, then dried completely before sputter coating.

DSC

A DuPont DSC 910 module supported by the 9900 thermal analysis system was used to determine the extent of cure of modified epoxy networks. The heating rate was 10°C/min unless specified otherwise. Dry nitrogen gas was purged to provide an inert environment in the DSC cell during the experiment. The data collected in the first heating cycle were used in the analysis.

DMTA

DMTA measurements were performed on the cured epoxy/phenoxy composites using a Polymer Laboratories DMTA at a frequency of 1 Hz in the single cantilever bending mode and at a heating rate of 4°C/min. The specimen size was 24 mm (length) \times 12 mm (width) \times 3.2 mm (thickness). The data were recorded and plotted in the form of storage modulus (E'), loss modulus (E''), and loss $\tan \delta$ as a function of temperature. Transition temperatures were taken from the peak maxima on the $\tan \delta$ versus temperature plots.

Physical Property Measurements

The tensile properties of the cured resins were determined at room temperature by means of an automated universal Instron testing tester (model 4465), interfaced with IX software. A strain gauge extensometer (model 2630) was used to measure uniaxial displacement. Tensile tests were conducted at a crosshead speed of 5.08 mm/min according to ASTM D638. Flexural test (3-point bending mode) was performed at a crosshead speed of 1.27 mm/min, per ASTM D790. Heat distortion temperature was measured under 1.82 MPa flexural load (HDTUL) using Custom Scientific Instruments, Inc., in accordance with ASTM D648. Shore D hardness testing was undertaken according to ASTM D2240.

Instrumented Falling Weight Impact (IFWI) Test

The instrumented impact tester (Dynatup, model 8250, General Research Corp.) was used to mea-

sure drop weight impact properties. The striking tup of this drop-weight system was instrumented with an output of the load transducer (tup) feeding to a transient signal recorder to produce data such as load-time and energy-time (derived from an integral curve) traces in a matter of milliseconds. These data were acquired on an IBM PC during the impact event by means of model 830-I data acquisition and analysis software. Epoxy samples were cut into 101.6×101.6 mm square plaques of 3.2–4.5-mm thickness. Impact testing was done at 0.83 m/s. The indenter was a cylindrical stainless steel shaft of 12.7-mm diameter with a 40-mm diameter support ring. The sampling time was 16 μ s. The testing was conducted at room temperature.

RESULTS AND DISCUSSION

Light Scattering

It is customary to cure most thermosetting blends in a single homogeneous phase. The solution cast films of the ternary mixture of epoxy, 0–40 wt % phenoxy (PKHP-200 as well as PKHM-30), and DDS were transparent under visual inspection and showed no texture under optical microscopic investigation at room temperature. The epoxy/phenoxy mixture containing DDS prior to curing showed no scattering of light suggesting the homogeneous character of the starting mixture. Upon curing at 180°C, the reactant mixture initially remained in the single phase for some time, but phase separation occurred with the progression of the reaction. Figure 1(a) shows time evolution of scattered intensity (I) versus scattering wavenumber (q) of the 70:30 blend composition during curing with DDS at 180°C. After a certain time lag (often called induction time), a scattering peak appears and shifts to a smaller scattering angle while the intensity increases. The scattering ring pattern is, although by no means a proof, suggestive of phase separation via spinodal decomposition (SD).^{5,12} The instability is induced by the decrease in conformational entropy associated with increasing molecular weight of epoxy during cure.^{5,7,13–17} One of the characteristics of SD is that the scattering peak (or the wavenumber maximum defined as $q_m = (4\pi/\lambda)\sin(\theta/2)$) remains stationary. This behavior was not seen in any of the SALS curves for the blend compositions studied herein, indicating either absence of the early stage of SD or too short a time interval during

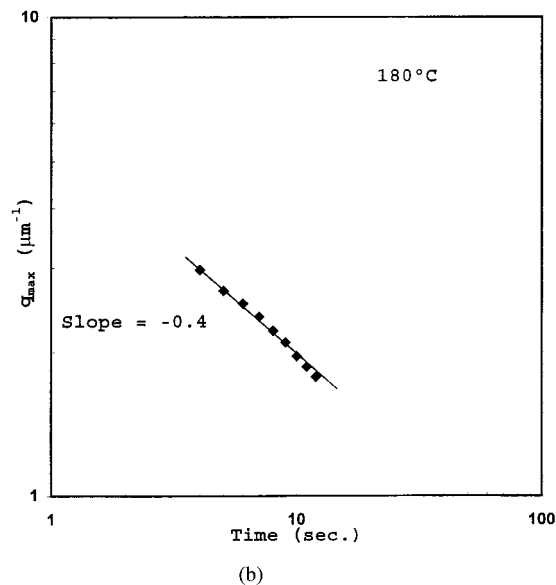
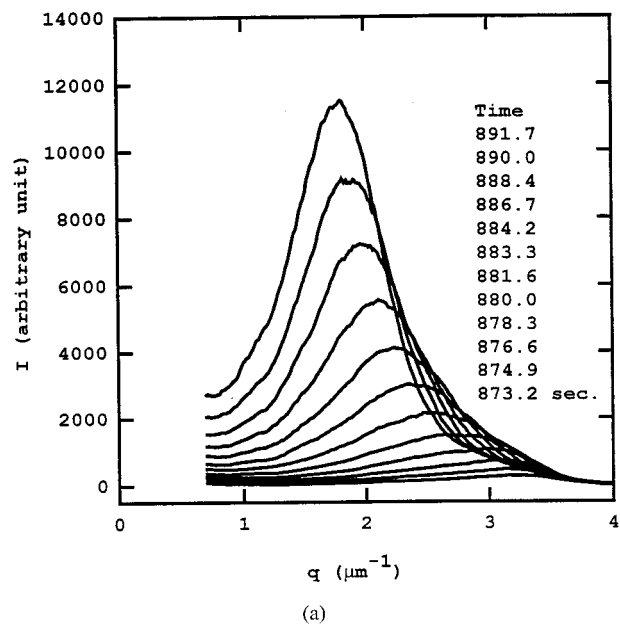


Figure 1 (a) Time evolution of scattering profiles of 70:30 epoxy/PKHP-200 blend during phase separation at 180°C, driven by curing with 28 phr DDS, (b) $\log q_m$ versus $\log t$ plot.

which the early stage might have occurred. In the q_m versus time plot [Fig. 1(b)], the slope is approximately -0.4 , suggesting that the coarsening process has advanced appreciably beyond the intermediate stage of phase separation.

Optical Microscopic Investigation

The temporal evolution of domain structures was examined by optical microscopy during progres-

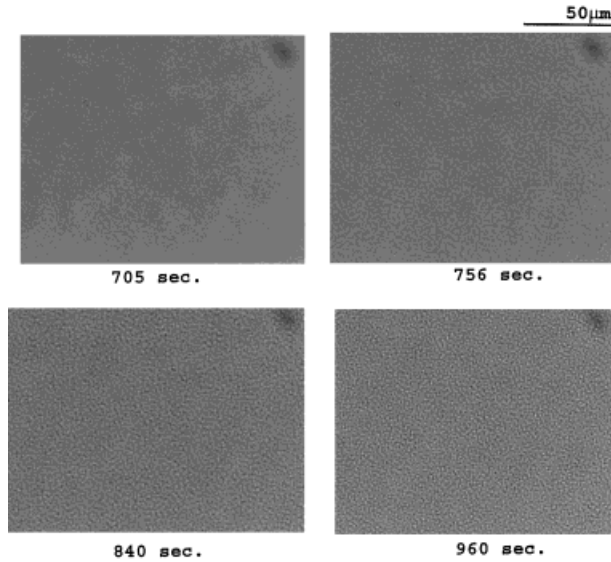


Figure 2 Optical microscopy pictures of spinodal decomposition of 90:10 epoxy/PKHP-200 blend, cured with 28 phr DDS at 180°C, emerging in time.

sive curing of the epoxy/PKHP-200 and epoxy/PKHM-30 blends with DDS at 180°C. Figure 2 depicts a typical coarsening of modulated structures in the 90:10 epoxy/PKHP-200 composition. A similar development of the periodic modulated structure was discerned in other epoxy/phenoxy compositions during reaction-induced phase separation (RIPS). The interconnected phase-separated structure may be similar to the spinodal texture; however, caution should be exercised in interpreting the mechanism because droplets can be seen as an interconnected structure when projected on the basal plane under the optical microscope.

A contrasting observation was made in the case of MDA curing. Before curing (i.e., at 25°C) the solution cast film from the ternary mixture of epoxy, 20 wt % PKHP-200, and 26 phr MDA was transparent and featureless. Upon curing isothermally at temperatures ranging from 125 to 200°C, the cured composites show no indication of phase separation at least under the visual inspection and/or optical microscopic investigation. It appears that the fast curing with MDA causes the epoxy matrix to vitrify rapidly such that the phenoxy molecules are entrapped in the epoxy network without undergoing phase decomposition.

SEM

The fractured surfaces of various epoxy/PKHP-200 and epoxy/PKHM-30 blend compositions

were examined using SEM. To obtain a better contrast, some of these surfaces were etched with methylene chloride to remove the phenoxy component. The observed SEM pictures at all concentrations present clear evidence that the phenoxy (both PKHP-200 and PKHM-30) rich phase segregated from the epoxy matrix during curing with DDS (Fig. 3). The observed spherical cavities are due to the removal of the phenoxy inclusions during solvent etching. The droplet morphology is seemingly different from the interconnected domains observed in optical microscopic investigation. This may be a consequence of the fact that the interconnected SD domains tend to transform into droplets driven by surface tension.¹⁴ In some instances, a well-aligned lamellar-like structure develops in the reaction induced phase separation,¹² which eventually breaks down to form arrays of droplets due to the instability of the lamellar domain.¹⁸

As noted earlier, all compositions of MDA-cured epoxy/phenoxy blends were optically clear and scattered no light. The SEM micrograph for the MDA-cured 80:20 epoxy/PKHP-200 blend was featureless (Fig. 3). The DMTA curve for the aforesaid blend, as will be discussed below, exhibited a single T_g . Taking all these pieces of evidence together, namely, optical clarity, featureless SEM micrograph, and a single T_g , implies that the MDA-cured epoxy/phenoxy blend compositions are probably in the homogeneous state. As pointed out earlier, there is presumably no sufficient time for phase separation to occur due to the rapid vitrification of the epoxy by MDA curing.

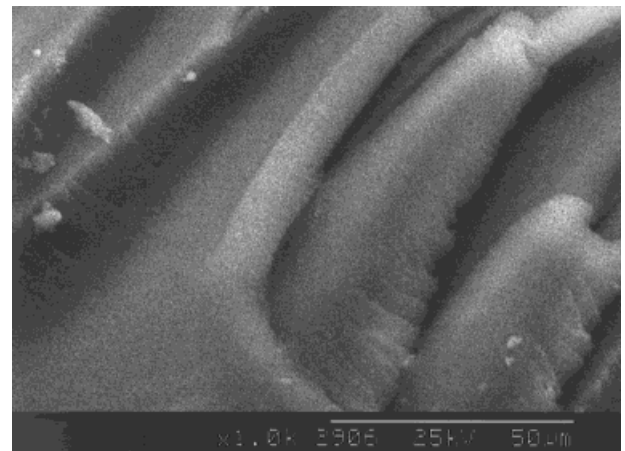


Figure 3 SEM micrograph of etched fracture surface of MDA-cured 80:20 epoxy/PKHP-200 blend, showing miscible (single-phase character).

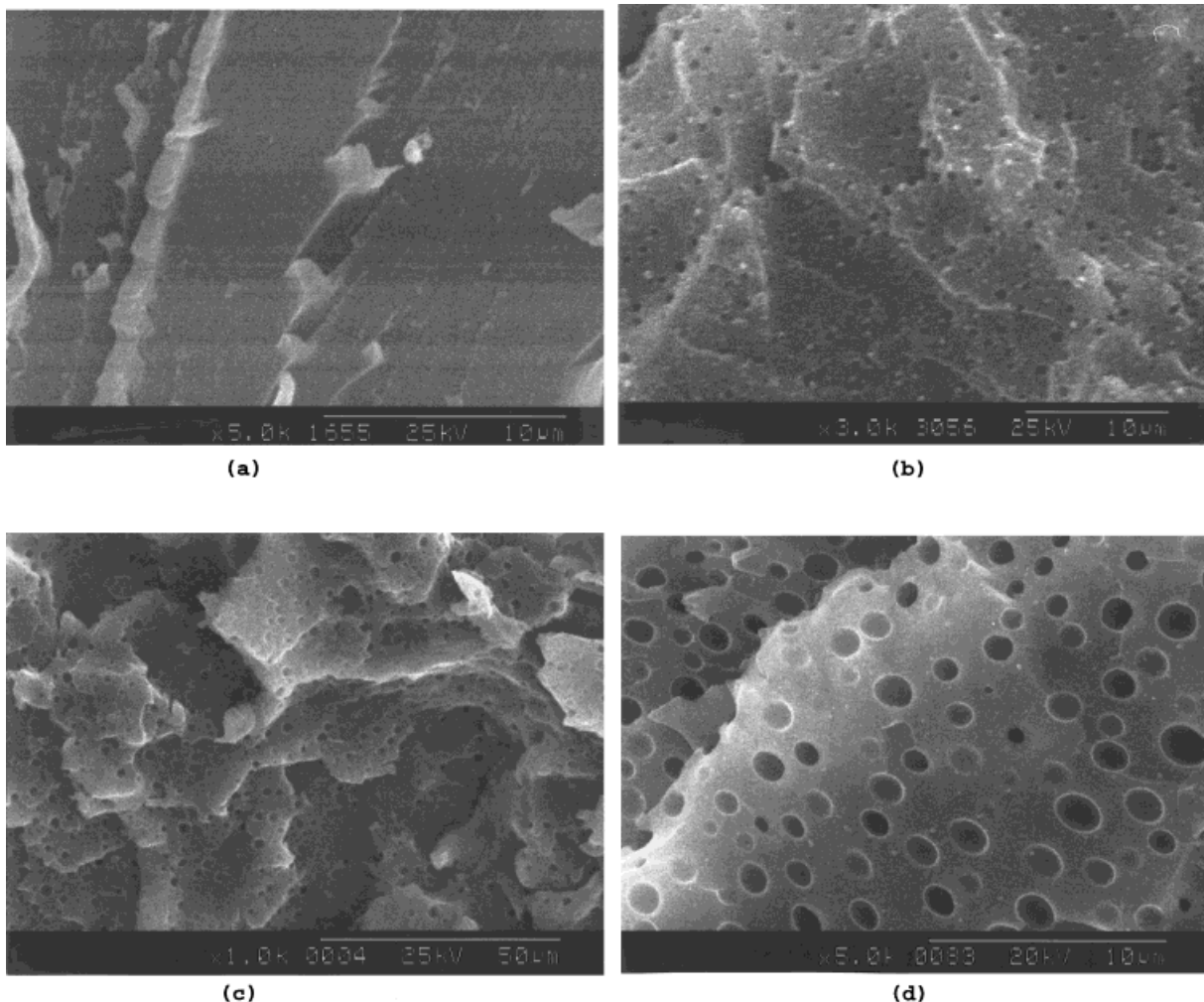


Figure 4 SEM micrographs of fracture surfaces of DDS-cured epoxy/phenoxy blend compositions: (a) neat epoxy exhibiting homogeneity; (b) 10% PKHP-200; (c) 10% PKHM-30; (d) 20% PKHM-30, all displaying particulate morphology.

Since the phenoxy molecules are entrapped and mixed intimately in the MDA-cured epoxy matrix, it was not possible to remove phenoxy chains from the cured network during etching with methylene chloride.

Figure 4(a) shows the fractured surface of the DDS-cured neat epoxy sample, revealing homogeneity as expected. At lower phenoxy contents [10% PKHP-200, Figure 4(b), and up to 20% PKHM-30, Figures 4(c,d)] the thermoplastic component segregates into spherical domains with diameters of approximately $1\mu\text{m}$ or less in the case of 10% PKHP-200 as well as PKHM-30 modified epoxy blends. The size increases up to approximately $2\mu\text{m}$ in the case of 20% PKHM-30 epoxy modification, uniformly distributed within the matrix. The etching removed the phenoxy in-

clusions, leaving smooth cavities (spherical pits) where the domains were located. This result indicates that the phenoxy is not directly involved in the crosslinking reaction and hence it retains its ductility that deforms plastically under loading.

In the 20% PKHP-200/epoxy composition cured with DDS, a unique co-continuous morphology was observed showing the connected-globule structure. The micrographs of both the unetched and etched surfaces of the epoxy/PKHP-200 blends are depicted in Figures 5(a) and 5(b), respectively, for comparison. This composition withstood the etching process and resulted in the interconnected arrays of spherical epoxy-rich domains ($1\text{--}9\mu\text{m}$ in diameter) in the phenoxy (PKHP-200)-rich matrix. In our recent simulation

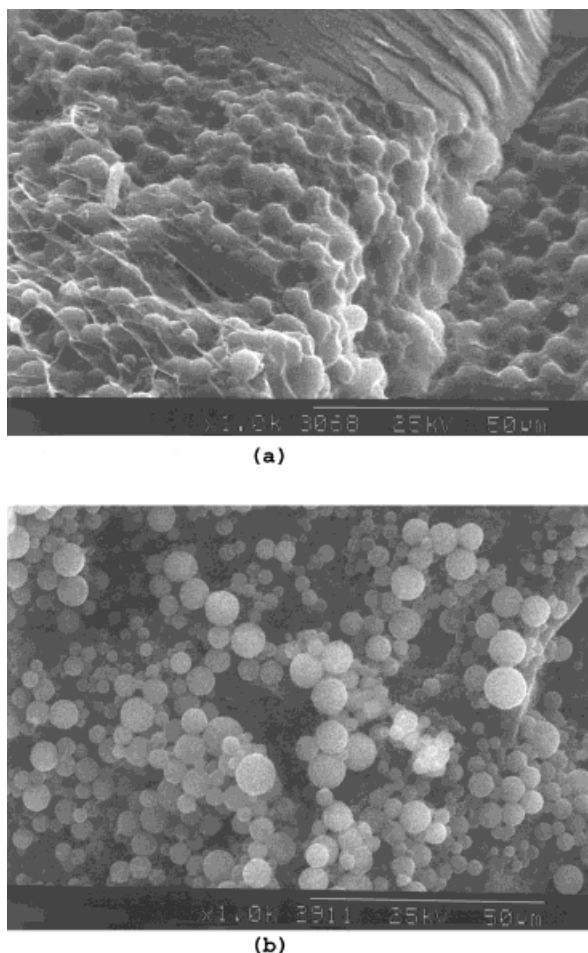


Figure 5 SEM micrographs of fracture surfaces of DDS-cured 80:20 epoxy/PKHP-200 blend, showing interconnected globular (spinodal) structure: (a) unetched; (b) etched.

of polymerization induced phase separation, the co-continuous SD structure evolves to a lamellar-like morphology.¹⁸ Later these lamellar stripe domains become unstable and eventually break down to give oriented droplet arrays.¹⁸

At a higher phenoxy content (30 or 40% PKHP-200 or PKHM-30) a phase-inverted morphology was observed (Figure 6), indicating that the phenoxy component forms the continuous phase. The epoxy resin is segregated into spherical domains, which are uniformly coated with a thermoplastic skin. Samples with the higher phenoxy content (30 or 40% PKHP-200 or PKHM-30) did not survive the etching treatment. This is because the phase-inverted regions have spherical epoxy domains wrapped in the layer of thermoplastics and the thermoplastic continuum is apparently dissolved away during the etching process, resulting

in disintegration of the sample. Visual comparison of the fractured surfaces also reveals stress whitening, an indication of plastic deformation, for the phenoxy (both PKHP-200 and PKHM-30) modified epoxy blends, but it is absent in the neat resin specimens. At low phenoxy concentrations where the thermoplastic formed the discrete particulate phase, the fractured surface was visually found to be smooth. In contrast, rougher fractured surfaces were seen for compositions with co-continuous phase blend morphologies, suggestive of the ductile failure.

Mechanical and Physical Properties

Mechanical and physical properties of DDS-cured epoxy/0–40% PKHP-200 and epoxy/0–40% PKHM-40 blend compositions are presented in Tables I–III. It is seen that at the 20 wt % modification with PKHP-200, a maximum enhancement in tensile toughness was obtained without any significant reduction in elastic modulus, glass transition, or heat deflection temperature. Similarly, an optimum improvement in physical properties was achieved at the 20% PKHM-30 modified epoxy resin. The blend containing 40% PKHM-30 showed a large increase in tensile elongation and toughness as compared with the neat epoxy, but it was accompanied by drastic reduction in heat deflection temperature. This is not surprising in view of the fact that the ductile matrix (as characterized by low T_g of approximately 40°C for PKHM-30) is expected to show larger strain softening.

The tensile elongation and tensile strength also exhibited a maximum at the 20% PKHP-200 modified epoxy blend and these values were greater than those of the neat epoxy. It has been shown by light scattering, optical microscopy, and SEM that the 20% PKHP-200 modified epoxy blend displays interconnected globular structure. Yamanaka and Inoue¹⁴ reported that the DDS-cured epoxy/poly(ether sulfone) (PES) blend with a morphology of interconnected epoxy globules (spheroids) distributed uniformly throughout the thermoplastic resin (PES) matrix exhibited higher adhesive strength both in peel as well as shear modes. Physical properties of DDS- and MDA-cured 20% PKHP-200 modified epoxy blends are included in Table II for the purpose of comparison between the homogeneous (MDA-cured) and heterogeneous (DDS-cured) blends. To obtain a synergistic combination of properties in a

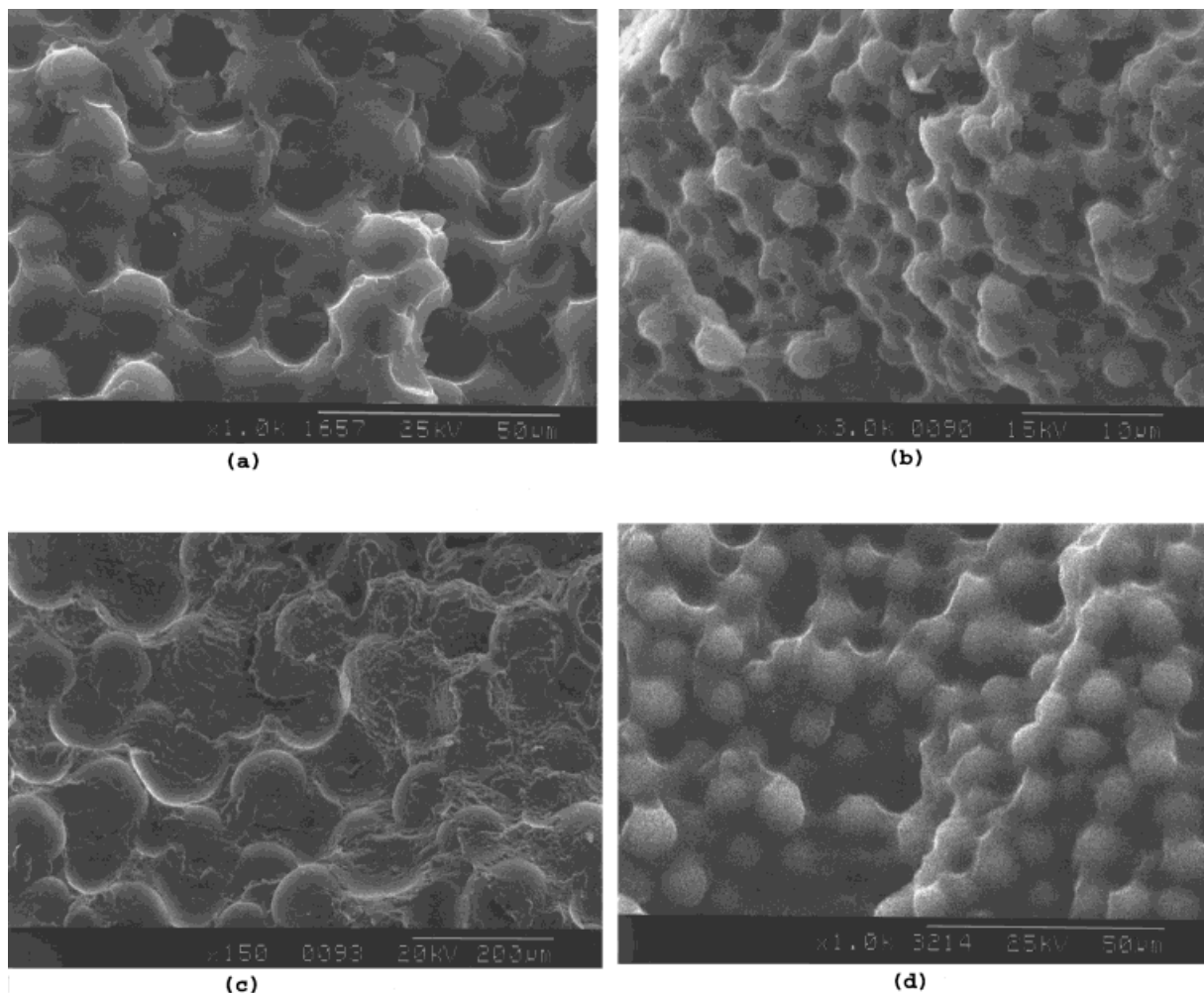


Figure 6 SEM micrographs of fracture surfaces of DDS-cured epoxy/phenoxy blend compositions showing phase-inverted morphology: (a) 30% PKHP-200; (b) 40% PKHP-200; (c) 30% PKHM-30; (d) 40% PKHM-30.

polymer alloy, the blend should be in two-phase (heterogeneous). As evident in Table II, the two-phase DDS-cured 20% PKHP-200 modified epoxy

blend exhibits better mechanical and thermal properties than the single phase (miscible) MDA-cured 20% PKHP-200 modified epoxy blend com-

Table I Physical Properties of DDS-Cured, PKHP-200 Modified Epoxy

Property	Control	Phenoxy (%)			
		10	20	30	40
Flexural strength (MPa)	132 ± 10	128 ± 14	123 ± 5	108 ± 4	78 ± 10
Elastic modulus (GPa)	3 ± 0.1	3 ± 0.1	2.9 ± 0.1	2.8 ± 0.1	2.5
Tensile strength (MPa)	33 ± 3	41 ± 3	74 ± 10	62 ± 5	47
Tensile elongation (%)	1.9 ± 0.6	2.8 ± 0.4	6.7 ± 1.3	5.6 ± 0.7	3.4 ± 0.3
Tensile toughness (MPa)	0.7	0.9 ± 0.2	3.2 ± 0.9	2.3 ± 0.3	1.1 ± 0.1
HDTUL, 1.82 MPa (°C)	173	187	170	120	95
Shore hardness	D/84/10	D/84/10	D/80/10	D/78/10	D/78/10

Table II Comparison of Physical Properties of MDA- and DDS-Cured, 20 wt % PKHP-200 Modified Epoxy Blends

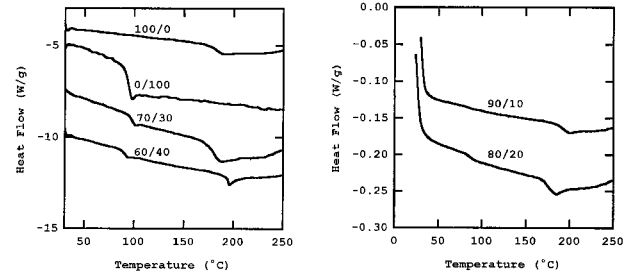
Property	MDA-Cured	DDS-Cured
Flexural strength (MPa)	120 ± 3	123 ± 5
Flexural modulus (GPa)	2.5 ± 0.1	2.9 ± 0.1
Tensile strength (MPa)	50 ± 5	74 ± 10
Tensile elongation (%)	4.5 ± 1.1	6.7 ± 1.3
Tensile toughness (MPa)	1.4 ± 0.4	3.2 ± 0.9
HDTUL, 1.82 MPa (°C)	146	170
Shore hardness	D/81/10	D/80/10

position. As evidenced by easy removal of phenoxy phase upon etching with methylene chloride, interfacial adhesion, that plays an important role in influencing the epoxy/phenoxy blend properties, is likely not due to the chemical bonding. It is rather due to the miscibility associated with the structural similarity between the two constituents.

Thermal Analyses

Figure 7 shows the DSC traces obtained for the PKHP-200 modified epoxy blends, indicating that the cure reaction was seemingly completed because there was no residual exothermic peak observed nor there was any endothermic peak due to the melting of DDS curing agent. The same phenomenon was noticed for the DDS-cured epoxy/PKHM-30 blend compositions.

DMTA has been used to measure the T_g and dynamic elastic modulus to qualitatively estimate the crosslinked density of the cured networks for both neat as well as the phenoxy modified epoxies. Some typical dynamic mechanical spectra for the DDS-cured epoxy modified with PKHP-

**Figure 7** DSC traces of DDS-cured epoxy/PKHP-200 blend compositions.

200 are illustrated in Figure 8. DSC and DMTA analyses confirm the presence of a second phase in most epoxy compositions containing phenoxy. Two transitions in the DSC thermograms and two-step decrease in E' (storage modulus) or dual peaks in $\tan \delta$ curve imply a two-phase character of the DDS-cured phenoxy modified epoxy blend compositions. The DSC curve for 10% PKHP-200 modified epoxy blend did not display the glass transition for the phenoxy component because of its low concentration in the blend. Also, the T_g of the PKHM component remained undetectable in the calorimetric studies of all blends, but it was clearly discerned in the DMTA measurements due to better sensitivity of the DMTA technique.

On the other hand, the MDA-cured 20% PKHP-200 modified epoxy blends showed only a single $\tan \delta$ peak (Fig. 9) suggesting that it is a single-phase blend. This has been confirmed by other techniques such as optical microscopy, SALS, and SEM as discussed above. The single phase T_g for the 20% PKHP modified epoxy blend (MDA-cured) is 157°C, whereas the value of 180°C was obtained for the two-phase blend (DDS-cured). The miscibility (compatibility at the molecular level resulting from “frozen-in” morphology) or

Table III Physical Properties of DDS-Cured, PKHM-30 Modified Epoxy

Property	Control	Phenoxy (%)			
		10	20	30	40
Flexural strength (MPa)	132 ± 10	86 ± 19	88 ± 4	47 ± 3	40 ± 2
Elastic modulus (GPa)	3 ± 0.1	3 ± 0.1	2.3 ± 0.2	2.1 ± 0.2	1.5
Tensile strength (MPa)	33 ± 3	48 ± 2	42 ± 3	27 ± 1	23 ± 1
Tensile elongation (%)	1.9 ± 0.6	2.9 ± 0.2	3.8 ± 0.2	4.8 ± 1	14 ± 1.7
Tensile toughness (MPa)	0.7	0.9 ± 0.1	1.1 ± 0.1	1.4 ± 0.3	2.9 ± 0.9
HDTUL, 1.82 MPa (°C)	173	133	160	41	39
Shore hardness	D/84/10	D/84/10	D/80/10	D/78/10	D/73/10

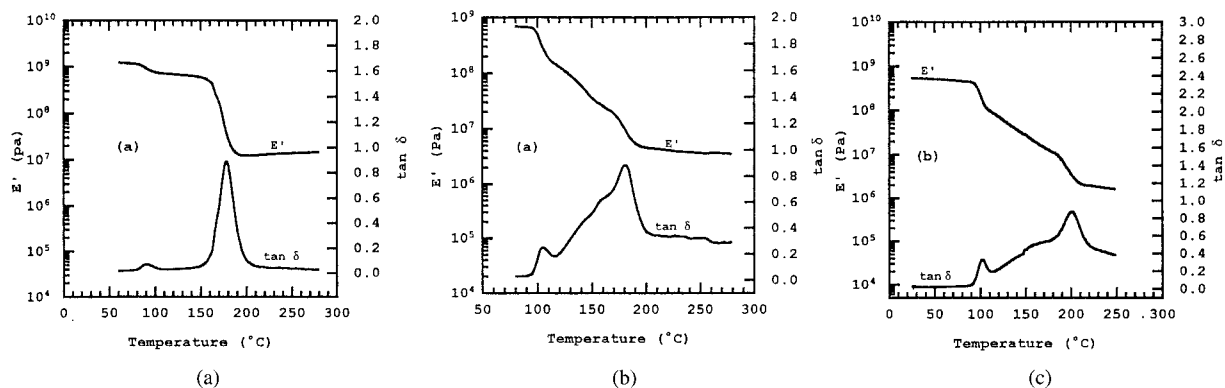


Figure 8 DMTA traces for DDS-cured epoxy modified with PKHP-200 (a) 20 wt %; (b) 30 wt %, and (c) 40 wt % phenoxy.

single-phase character of the MDA-cured 80:20 epoxy/PKHP-200 blend may be responsible for deterioration in thermal and mechanical property in contrast to the phase separated 80:20 blend that displayed superior properties. Chen et al.¹⁹ also found that the DDS-cured system has higher flexural strength and modulus than those of the MDA-cured system because of the greater chain rigidity of the former.

As discussed above, the DSC and DMTA curves for the DDS-cured phenoxy modified epoxy resin blends can be characterized by two distinct transitions (or peaks) attributable to the T_g of the epoxy-rich phase and the T_g of the phenoxy-rich phase. These two peaks are not well separated for the 30 and 40% phenoxy modified epoxy compositions suggesting that there might exist some partial compatibility (brought about by structural similarity) between the phenoxy and epoxy components. However, we have to admit that the $\tan \delta$ peak width broadens with increasing phenoxy concentration.

In principle, crosslinking density of a cured network can be obtained from DMTA data using theory of rubber elasticity,²⁰ viz.,

$$\phi\rho/M_c = E/3RT \quad (1)$$

where E is the elastic modulus, R is the universal gas constant, ρ is the density, M_c is the average molecular weight of the chain segments between crosslink points, T is the absolute temperature at which the modulus in the plateau region was measured, and ϕ is the front factor which can be assumed to be unity assuming the Gaussian network.²⁰ In this study, rubbery modulus of the epoxy network was defined as the value of dy-

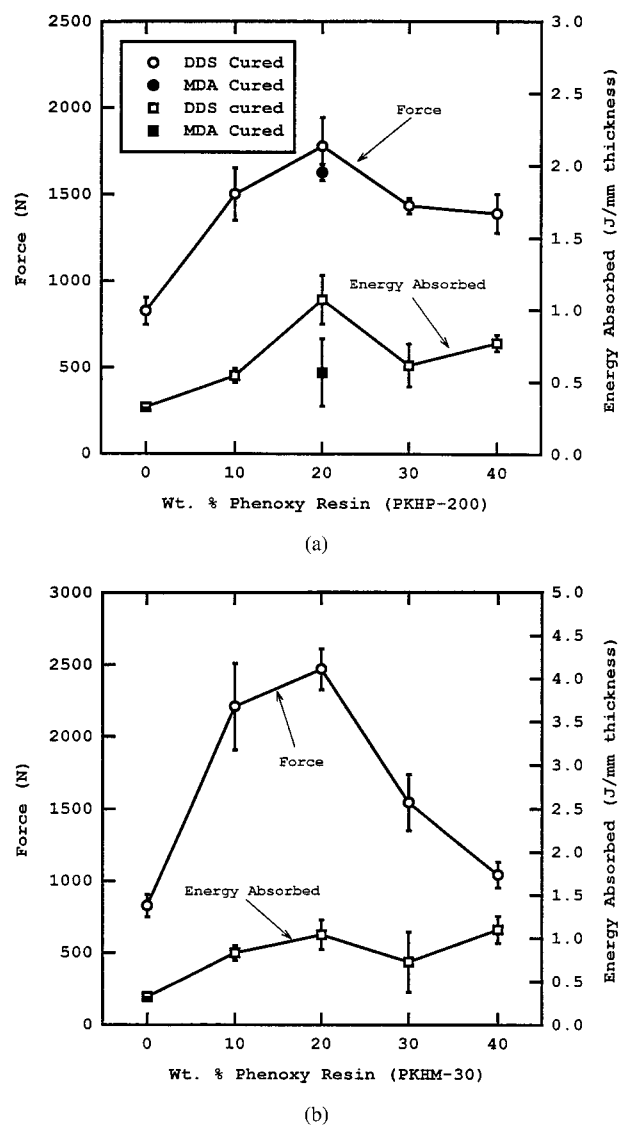


Figure 9 Instrumented falling weight impact properties of DDS-cured (a) PKHP-200 modified and (b) PKHM-30 modified epoxy blends.

dynamic storage modulus at 50°C ^{21,22} above its α relaxation peak, i.e., T_g . Assuming that the density was constant for all compositions, E' at the rubber plateau region is, as a first approximation, considered to be inversely proportional to M_c . The modulus values (proportional to the crosslink density) decreased with increasing amount of phenoxy resin. This is due to the unreacted phenoxy, which diluted the crosslinking density of the epoxy resin.

IFWI Test

The IFWI method has been well practiced in testing of composites. The development of instrumented impact testing has greatly improved the understanding of the detailed history of the impact event.²³ Two values of IFWI were reported. First is the maximum force necessary for penetration of the test specimen. The second value is the total energy absorbed during the impact event. These parameters are of practical importance because absorbing the incident energy of the impacting object is the key to damage tolerance. The fractured energy is equal to the area under the load-deflection curve.

Figures 9(a) and 9(b) show the mechanical impact properties of the DDS-cured epoxy resins modified with PKHP-200 and PKHM-30, respectively. It is obvious from the figures that the breakdown energy increases with increasing content of phenoxy resin up to 20 wt %. For a phenoxy content of 20 wt % the value of energy absorbed by the sample to failure increases 2.5 times (for PKHP-200) and 3 times (for PKHM-30) with respect to the reference (neat epoxy matrix). Thereafter, the energy curves decrease in value at 30 wt % and then increase again at 40 wt % phenoxy content, whereas, the force necessary for penetrating the sample decreases with increasing phenoxy content. It is reasonable to infer that a better impact property was achieved when the content of phenoxy resin (both PKHP-200 and PKHM-30) was 20 wt % in the modified epoxy resin network, cured with DDS. It has been already established by SEM that the morphology thus obtained for the 80:20 epoxy/PKHP-200 blend was co-continuous, characteristic of spinodal decomposition. The same morphology has been shown to give better tensile strength, elongation, and toughness at little or no expense of flexural modulus, glass transition or heat deflection temperature. It may be speculated that the strong interaction between phases in co-continu-

ous morphologies may facilitate a more uniform stress distribution in the material under load and thereby avoid premature failure due to localized stress concentrations.¹⁷ Also, Bagheri and Pearson²⁴ in their study on the core/shell rubber modified epoxy, observed the blend with a connected microstructure provides significantly higher fracture toughness. They gave a similar reason for the above observation that the connected morphology enables the shear bands to grow further from the crack tip and thus consume more energy before failure occurs. SEM micrograph [Fig. 5(a)] shows the stretching of phenoxy phase and thus the ductile drawing and tearing of the thermoplastic phase is the dominant toughening mechanism in this epoxy/phenoxy composite.

The aforesaid result follows the trends apparent in the literature,²¹⁻²⁸ i.e., the toughness in such blends is significantly improved only when bicontinuous or phase-inverted structures are generated. However, the IFWI data and other thermo-mechanical properties obtained for epoxy/PKHM-30 blend compositions indicated that the 80:20 blend gave the optimum result with no adverse effect on modulus and high deflection temperature. However, the toughening effect may be interpreted in light of morphological analyses performed on the fractured surfaces. Obviously, the only observation of fractured surfaces is not sufficient to attribute the failure to any particular toughening mechanism. But on the basis of more comprehensive works in this field,²⁻⁴ a plausible scenario may be proposed. Unlike most reports on epoxy/thermoplastic systems which involve high modulus and high strength thermoplastics, the PKHM grade of phenoxy used in this study has relatively low modulus and yield stress that make the phenoxy particle yielding and tearing easier than for most high yield strength thermoplastics during fracture. The modulus mismatch (high modulus epoxy matrix and soft, low T_g PKHM-30 thermoplastic with a high shore D hardness) can also create a stress concentration, which in turn initiates yielding around the phenoxy particles in the epoxy matrix, thereby enhancing toughness. Girard-Reydet et al.¹¹ showed the particle-induced shear yielding of the epoxy matrix to be a contributing factor to toughening of the 10% polyether imide modified epoxy blend (particulate morphology).

The present situation is similar to that in the rubber-toughened epoxies, i.e., the PKHM-30 particles yield before the matrix undergoes yielding. As these materials do not show strain hardening,

a stress concentration occurs in the epoxy, which will initiate localized yielding between the particles. The fractured surfaces [Fig. 4(c,d)] also show some evidence of localized plastic deformation (stress whitening) and thus the crack-blunting mechanism is probably the major toughening mechanism prevalent in this epoxy/phenoxy composite system.

CONCLUSIONS

It has been demonstrated that all epoxy/phenoxy blends cured with DDS exhibited heterogeneity with droplet morphology at 10% PKHP-200 and up to 20% PKHM-30 content; co-continuous or interconnected globular structures at the 20% PKHP-200 and phase inverted morphology at >30%. In the case of MDA-cured epoxy/phenoxy blends, the viscosity build-up rate was so high due to the fast curing rate of MDA that no phase separation was observed for the epoxy/PKHP-200 blend. The mechanical properties of phenoxy modified epoxy networks varied with the blend morphology generated by reaction-induced phase separation. The 80:20 epoxy/PKHP-200 blend gave the optimum results for tensile strength, elongation, and tensile toughness with little or no loss of flexural modulus, T_g , and heat deflection temperature. The energy absorbed during drop weight impact measurement was also improved 2.5-fold as compared with the neat epoxy. The observed interconnected globular morphology probably contributes to property enhancement in this 80:20 epoxy/PKHP-200 blend in which the stretching and tearing of the phenoxy phase may be responsible for toughening of the epoxy matrix.

In regard to the epoxy/PKHM-30 blends, the composition having 20% phenoxy also afforded the highest physical and mechanical properties. That is to say, the impact energy absorbed by the sample during IFWI testing was three times the value for the control (epoxy). This toughness enhancement was achieved at a slight loss of flexural modulus and heat deflection temperature, but virtually with no reduction in T_g . The toughening mechanism possibly involves yielding of the PKHM-30 phenoxy modifier particles initiating local yield in the epoxy matrix. It is this yielding mechanism occurring as the main deformation process in the epoxy matrix.

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