Blends of Epoxy Resin with Amine-Terminated Polyoxypropylene Elastomer: Morphology and Properties

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ABSTRACT: A liquid diglycidyl ether of bisphenol A (DGEBA) epoxy resin is blended in various proportions with amine-terminated polyoxypropylene (POPTA) and cured using an aliphatic diamine hardener. The degree of crosslinking is varied by altering the ratio of diamine to epoxy molecules in the blend. The mixture undergoes almost complete phase separation during cure, forming spherical elastomer particles at POPTA concentrations up to 20 wt %, and a more co-continuous morphology at 25 wt %. In particulate blends, the highest toughness is achieved with nonstoichiometric amine-to-epoxy ratios, which produce low degrees of crosslinking in the resin phase. In these blends, the correlation between G_{IC} and plateau modulus (above the resin T_g), over a wide range of amine-to-epoxy ratios, confirms the importance of resin ductility in determining the fracture resistance of rubber-modified thermosets. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 427–434, 1999

Key words: blends; epoxy resins; polyoxypropylene; rubber toughening; stoichiometry

INTRODUCTION

There is now a very extensive body of literature on the preparation of rubber-toughened epoxy resins.[1–26] The method adopted by most authors has been to blend the liquid resin–hardener mixture with a functionalized liquid butadiene–acrylonitrile copolymer to form a single-phase solution and generate a phase-separated morphology during cure. Using this route, it is necessary to limit the rubber content because at concentrations above about 15–20% the rubber no longer separates as discrete particles but forms an interpenetrating network (IPN), which is co-continuous with the resin phase and, therefore, reduces the modulus of the blend.[3,24]

Mixtures of diepoxides with diamines form a crosslinked network on curing, because each primary amine group is capable of reacting with two epoxy groups, and diamines are therefore tetrafunctional. Domains containing functionalized elastomers become crosslinked in a similar way, as follows: the elastomer molecules react with dissolved epoxy molecules, which, in turn, react with tetrafunctional hardener molecules. Thus, the most widely used functionalized elastomer, carboxyl-terminated butadiene-acrylonitrile copolymer (CTBN), undergoes partial phase separation from epoxy resin and, at the same time, reacts through its acid end groups with the oxirane rings of the epoxy molecules, thereby forming a CTBN-rich crosslinked elastomer incorporating a minor proportion of epoxy and hardener units, which

constitute network points. In some cases, the CTBN is prereacted with epoxy resin before adding the hardener, effectively forming epoxy-terminated elastomer molecules (ETBN).[17,18,24] In others, the terminal —COOH units are replaced with primary amine —NH$_2$ or other functional groups.[7,11,23]

A key property of liquid butadiene–acrylonitrile copolymers is that over a narrow range of acrylonitrile contents, they are miscible with liquid epoxy resins but become immiscible as molecular weights rise during cure. Similar properties are exhibited by carboxyl-terminated ethyl hexyl acrylate oligomers[15] and by POPTA,[22] provided that their initial molecular weights are not too low. The present article examines the relationship between mechanical properties and composition in blends containing POPTA, including the effects of varying the hardener-to-epoxy ratio and, hence, the degree of crosslinking in the resin matrix phase. The results are compared with those of Pearson and Yee,[15] who varied the crosslink density of an epoxy resin by altering the molecular weight of DGEBA-based monomer molecules and showed that the toughness of epoxy–rubber blends increases rapidly with increased spacing between network points.

EXPERIMENTAL

The epoxy resin used in this work was Dow Chemical DER332, a diglycidyl ether of bisphenol A (DGEBA) having mol wt equal to 340, a hydroxyl-to-epoxy ratio equal to 0.015, and n equal to 0.03. The hardener was BASF Laromin C260 (4,4′-diamino-3,3′-dimethyl dicyclohexyl-methane), designated 3DCM in this article. The functionalized elastomer was Huntsman's Jeffamine T-5000, which is an amine-terminated polyoxypropylene (POPTA): H$_2$N [CH$_2$ CH(CH$_3$)O]$_n$ CH$_2$ CH (CH$_3$) NH$_2$. It has a molar mass of 5000 and $T_g \approx -75°$.

Blends were made by dissolving the POPTA in the stirred liquid resin under vacuum at room temperature and then adding the required amount of DCM hardener, also at room temperature. All blend solutions were transparent at this stage, indicating complete miscibility. The POPTA content of the overall mixture was varied from 0 to 25 wt % for stoichiometric compositions and held at either 0 or 15 wt % for nonstoichiometric formulations. Plaques with a thickness of

5 mm were cast between preheated glass plates coated with Frekote 44 release agent and cured at 80°C for 2 h, including degassing under vacuum for 30 min. They were then post-cured at 190°C for 14 h and finally cooled slowly by switching off the oven.

Scanning electron microscopy (SEM) was carried out on specimens fractured at liquid nitrogen temperatures. Fracture surfaces were etched with dichloromethane and coated with gold–palladium. Sections for transmission electron microscopy (TEM) were made on a Reichert-Jung Cryotome equipped with a diamond knife. Dynamic mechanical analysis was carried out at 10 Hz in three-point bending, over the temperature range 20 to 250°C, on rectangular bar samples measuring 60 × 12 × 5 mm, using a Metravib Viscoanalyseur at a heating rate of 3°C min^{-1}.

The flexural properties of the cured materials were measured at 23°C, using an Instron Model 4206 machine, under conditions specified in ASTM standard D-790. The fracture toughness K_{IC} was measured according to the testing protocol issued by the European Structural Integrity Society (ESIS).[27] Tests were carried out in three-point bending using sharply notched specimens. The fracture energy G_{IC} was calculated from the following relationship:

$$G_{IC} = \frac{K_{IC}^2(1 - \nu^2)}{E} \tag{1}$$

where E is Young's modulus, and ν is the Poisson's ratio of the epoxy resin, which was taken to be 0.40.

RESULTS AND DISCUSSION

Effects of POPTA Content on Stoichiometric Resin

As noted earlier, the initial transparency of the blends indicates a high degree of miscibility between POPTA and the uncured resin–hardener mixture. However, demixing during cure is clearly indicated in the dynamic mechanical data. Figure 1 compares dynamic mechanical loss curves for cured stoichiometric mixtures of DGEBA–3DCM with 0, 20, and 25 wt % POPTA. The neat resin shows an α peak at 199.5°C, which is clearly related to the glass transition of the epoxy resin. Addition of up to 20% POPTA has little effect upon the temperature of the peak and only a minor effect upon its height; but at

Figure 1 Dynamic mechanical curves for stoichiometric resin with: (○) 0%; (□) 20%; (●) 25% POPTA.

25 wt %, there is a small downward shift in T_α and a marked decrease in peak height, which is caused by a sharp fall in storage modulus E'. These results confirm that epoxy–POPTA blends undergo almost complete phase separation during cure.

Both SEM and TEM were used to investigate the morphology of the cured blends. The POPTA forms discrete spherical particles, which increase in size with increasing concentration, following a similar pattern to other epoxy–rubber blends.[18] However, as illustrated in Figure 2, increasing the POPTA concentration from 20 to 25 wt % causes the onset of phase inversion, again repeating the pattern of behavior seen in earlier studies of epoxy–rubber blends.[3,24] At 25% POPTA, large domains with a continuous POPTA-rich phase enclosing epoxy-rich particles coexist with domains having a continuous epoxy-rich phase enclosing POPTA-rich particles.

This phase inversion explains the relationship between Young's modulus E and POPTA content shown in Figure 3. Between 0 and 20% POPTA, E decreases steadily with modifier content; but between 20 and 25% POPTA, there is a steep drop in

Figure 2 Sections of blends containing (a) 20 wt % POPTA and (b) 25 wt % POPTA. Transmission electron micrographs (no staining).

Figure 3 Effects of POPTA on Young's modulus of stoichiometric resin.

Figure 5 Effects of POPTA on G_{IC} of stoichiometric resin.

modulus, as the soft modifier begins to form a continuous phase. The flexural strength σ_f follows a similar pattern, as shown in Figure 4, but with a smaller drop in magnitude between 20 and 25% POPTA. These trends in E and σ_f are similar to those reported for other modified epoxy resins. They reflect the low modulus and strength of POPTA in comparison with epoxy resin. Bussi and Ishida[25] have shown that, at low rubber concentrations (<6%), the dependence of E and σ_f upon rubber content can be reduced dramatically by introducing functional groups into the rubber chain and prereacting them with the epoxy resin before adding hardener. Instead of forming particles, the prereacted rubber becomes incorporated into the resin matrix.

Fracture mechanics data for the blends are shown in Figures 5 and 6. Measurements of G_{IC} indicate that addition of POPTA has a significant toughening effect on epoxy resin, although the levels of toughness achieved in this study are quite modest in comparison with optimized epoxy–CTBN blends, especially when the properties of the resin matrix are taken into consideration: a G_{IC} of 300 J m^{-2} is relatively high for neat epoxy resin. The blends yield during flexural tests, exhibiting an increasing ductility with POPTA content, whereas the neat resin fails by brittle fracture. However, the potential of the matrix to absorb energy ahead of a crack tip is not fully exploited in any of the POPTA blends. Indeed, when the fracture resistance is expressed in terms of K_{IC}, the critical stress field intensity at

Figure 4 Effects of POPTA on flexural strength of stoichiometric resin.

Figure 6 Effects of POPTA on K_{IC} of stoichiometric resin.

Figure 7 Dynamic mechanical curves for resin containing 15% POPTA, with differing stoichiometric ratios r: (□) 0.6, (■) 0.8, (○) 0.9, and (●) 1.0.

the crack tip, it can be seen that there is a slight decrease with increasing POPTA content, especially at concentrations above 15%.

The reason for this contradictory behavior is that $K_{IC}^2 \approx EG_{IC}$, as shown in eq. (1), and in the present series of POPTA blends, the increase in fracture energy G_{IC} is offset by a decrease in stiffness E. Physically, G_{IC} can be regarded as a more fundamental measure of toughness because it represents the material's ability to dissipate energy ahead of a crack tip and, thus, reflects changes in deformation behavior with composition and morphology, whereas K_{IC} essentially measures strength, that is, the material's ability to sustain high stresses. However, in choosing toughening additives, it is of course preferable to achieve substantial increases in both G_{IC} and K_{IC}.

Effects of Stoichiometry on Neat Resin and 15% POPTA Blends

The stoichiometric ratio r of amine to epoxy units has a marked effect upon the α transition in the epoxy resin, as illustrated in Figure 7. Following the practice adopted in previous articles, r is defined as $4A/2E$, where A and E are, respectively, the numbers of moles of diamine (including POPTA) and diepoxide present in the initial mixture; thus, it is assumed, for purposes of calculation, that each primary amine group is capable of forming two new bonds, whereas each epoxy group forms only one. Both in the neat resin (not included in the illustrations) and in the 15%

POPTA blend (Fig. 7), T_α reaches a maximum and the loss peak area a minimum, when $r = 1$. These changes reflect the reduced mobility of the epoxy chains as the degree of crosslinking in the resin is increased.

The relationships between T_α and stoichiometric ratio r for both neat resin formulations and blends containing 15 wt % POPTA are compared in Figure 8. Previous work has demonstrated the dependence of the matrix T_g upon stoichiometry in epoxy resin blends[28] and has shown that the glass transition temperature reaches a maximum at $r = 1$. In addition to lowering T_g, the reduced level of crosslinking in nonstoichiometric resins lowers the plateau modulus reached by these materials in the elastomeric state at temperatures well above T_g. This point is illustrated well in Figure 9, which presents data on storage modulus E' for three resins with differing stoichiometric ratios. It is convenient to use the plateau modulus, here defined as the value of E' at $(T_g + 40)$K, as a measure of crosslink density in the resin. In applying this definition, T_g is taken as the temperature of the tan δ peak.

The effects of stoichiometry on flexural properties at 23°C are shown in Figures 10 and 11. Both the Young's modulus and strength of the neat resin reach a minimum at the stoichiometric ratio $r = 1$. A similar pattern of behavior was reported in an earlier article,[28] for the same epoxy resin, DER332, with a different hardener, diamino–diphenylmethane (DDM). In that article, the higher stiffnesses of nonstoichiometric resins were shown to correlate with increases in the density of the cured epoxy mixture. By contrast, the moduli of

Figure 8 Effects of stoichiometric ratio on T_g of (○) neat resins and (●) resins containing 15% POPTA.

Figure 9 Dynamic mechanical curves showing storage modulus in the plateau region for epoxy resins containing 15 wt % POPTA, with differing stoichiometric ratios r: (○) 0.6, (●) 0.8, and (□) 1.0.

Figure 11 Effects of stoichiometric ratio on flexural strength of resin containing (○) 0% and (●) 15% POPTA.

blends containing 15 wt % POPTA are almost independent of r, and strength reaches a maximum at $r = 1$. This pattern of behavior is very different from that observed in blends containing 15 phr polyethersulfone, which followed the same trends as the neat resin. A possible explanation of these data for POPTA blends is that stoichiometry affects not only the stiffness of the epoxy resin phase but also the distribution of resin molecules between the continuous resin phase and the disperse POPTA-rich regions. This point requires further investigation.

Resistance to crack propagation shows a marked dependence upon stoichiometric ratio, as

illustrated in Figures 12 and 13. Because E is almost independent of r in neat resin formulations, G_{IC} and K_{IC} increase together as the resin composition shifts away from the stoichiometric ratio, especially at low r. The controlling factor is the degree of crosslinking in the resin phase, which can be related to the plateau modulus of the corresponding neat resin, defined as Young's modulus in the elastomeric state, at a temperature 40°C above T_g (see Fig. 9). Figure 14 shows that when G_{IC} is plotted against this plateau modulus, data for high and low values of r fall approximately upon a single curve.

The effects discussed in this article, on toughening of epoxy resins of varying ductility, are similar to those reported by Pearson and Yee, who varied

Figure 10 Effects of stoichiometric ratio on Young's modulus of resin containing (○) 0% and (●) 15% POPTA.

Figure 12 Effects of stoichiometric ratio on G_{IC} of resin containing (○) 0% and (●) 15% POPTA.

the degree of crosslinking in their epoxy resin systems not by altering the stoichiometry but by selecting epoxy oligomers of differing molecular weight.[15] In both neat resin and rubber-modified blends, they found an increase in G_{IC} with M_c, the molecular weight between crosslinks. However, the increase in toughness with M_c was much more marked in the blends.

CONCLUSIONS

This work has shown that functionalised polyoxypropylene elastomers of medium molecular weight can be effective toughening agents for epoxy resin. They are soluble in liquid resin–hardener mixtures, undergo phase separation during cure, and produce an increase in G_{IC}. However, when mixed at or near the stoichiometric ratio r, the resin–hardener combination chosen for the present series of experiments is too highly crosslinked to allow high levels of toughness to develop in blends with rubber. Consequently, the effectiveness of POPTA as a toughening agent becomes clear only when the level of crosslinking in the resin matrix is reduced substantially by varying r. These observations suggest a simple procedure for evaluating candidate toughening agents for epoxy resins. By varying the stoichiometry of the resin, it is possible to determine whether the characteristics of the rubber phase, including chain structure, reactivity, particle size, and interfacial adhesion, significantly limit the performance of the additive as a toughening agent or whether any limitations on toughness arise mainly from the restricted ductility of the resin matrix.

Figure 14 Relationship between G_{IC} and plateau modulus at $(T_g + 40)$K for resins containing (○) 0% and (●) 15% POPTA.

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Figure 13 Effects of stoichiometric ratio on K_{IC} of resin containing (○) 0% and (●) 15% POPTA.

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