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Morphology development in epoxy/polymer systems: thermosetting epoxy micro particles with a thermoplastic shell

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A novel method based on phase inversion and inter-boundary reaction in a reactive system comprising a thermoplastic phenoxy and a thermosetting epoxy has been proposed to design micro epoxy particles with a thermoplastic polymer shell. Due to the hydroxyl group in phenoxy, inter-domain reactions were found to lead to a chemical link between the polymer and the epoxy network. As cure progressed, the phenoxy component was first expelled out of the epoxy spheres at initial stages of cure and a phase-separated morphology was set. Subsequently, the pendant –OH groups in the phenoxy shells were grafted onto the outer surfaces of the epoxy core particles (3–4 μm) at high enough temperatures (187°C or higher) during later stages of cure. This paper describes the mechanisms and fundamental phenomenon under which this unique method of preparing polymer/epoxy spheres (epoxy cores/phenoxy shell) of controlled sizes can be realized. Several factors have been found to affect the geometry of the epoxy spheres and the chemical bondings between the polymer and epoxy. © 1997 Elsevier Science Ltd.

(Keywords: phase inversion; particles; phenoxy)

INTRODUCTION

Polymeric mixture systems comprising of linear high-molecular-weight thermoplastics and reactive thermosetting resins have attracted academic interest and curiosity due to the complex morphology development as cure reactions progress in multi-component, originally homogeneous, solutions. Traditionally, *in situ* phase separation in multiphase epoxy networks has been exploited for enhancing fracture resistance[1–5]. To explain the complex phase behavior, thermodynamic approaches have been used by a few researchers on the phase behavior of a polysulfone/epoxy system reported by Clarke *et al.*[6], as well as the poly(ether imide)/epoxy system by Riecardi *et al.*[7]. Lately an interesting review on morphology development by reaction-induced spinodal decomposition in poly(ether sulfone)-modified diglycidyl ether of bisphenol-A (DGEBA)/4,4'-diaminodiphenylmethane (DDM) systems is provided by Inoue[8], who observed that for 30 phr PES or higher in the cured PES/epoxy network, a connected-globule structure of the epoxy phase was resulted. Most polymer/epoxy systems after full cure develop a phase-separated morphology. There are only very few exceptions. A recent study from our laboratory has reported a homogeneous network structure in an amine-cured polycarbonate/epoxy system. However, there are extensive exchange reactions between the epoxy and the polycarbonate that account for the homogeneous structure[9,10].

We reported earlier a quite interesting case in which a complete phase inversion on a full scale occurred at relatively low thermoplastic contents (20 phr) in an epoxyl-polymer system comprising of poly(methyl methacrylate) (PMMA), diglycidyl ether of bisphenol-A (DGEBA), and 4,4'-diaminodiphenylsulphone (DDS)[11]. This is quite a low volume fraction considering that 20 phr PMMA (based on 100 part of epoxy) accounts for only about 14 vol.% in the cured PMMA/DGEBA/DDS network. Nevertheless, full-scale phase inversion occurs at this low thermoplastic loading, and all epoxy particles are independently separated and not interconnected at all.

Polymer spheres (or beads) are finding uses in chromatography column media or as substrates for medical diagnostic tests. Potential applications of polymer particles may also be in optimal design of toughened polymeric laminates. Suspension polymerization [12,13] or dispersion polymerization[14] has been traditionally used in industrial scales to produce small polymeric spheres of a controlled size distribution. Our recent report has also documented a novel method of preparing crosslinked epoxy micro spheres of controlled size from an amine-cured poly(methyl methacrylate) (PMMA)/diglycidylether of bisphenol-A (DGEBA) epoxy network by utilizing the full-scale phase inversion in the reactive polymer/epoxy systems[11].

In an earlier paper we reported the bulk cure versus inter-domain reactions in a phenoxy/epoxy system[15]. This paper reports more details on investigating the potential applications of inter-domain reactions for preparation of micro polymer/epoxy spheres. Investigative studies were performed to evaluate the factors that might influence the composition at which complete phase inversion occurred, geometry of particles, interconnection between particles, and bonding forces between crosslinked particles and the polymer shells.

EXPERIMENTAL

Materials and preparation

Two model epoxy resins were used in this study. One is

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tetraglycidyl-4,4'-diaminodiphenylmethane (TGDDM) (Ciba-Geigy MY-720), with an epoxide equivalent weight of approximately 109 g. The other epoxy resin used was diglycidyl ether of bisphenol-A (DGEBA) (Epikote-828, Shell Corp., USA), with an epoxide equivalent weight of 187 g. The phenoxy thermoplastic polymer used was poly(hydroxyl ether of bisphenol-A) (Union Carbide, PKHH, Mn = 20000–25000 g/mol). The base TGDDM or DGEBA epoxy resin and its mixtures with the phenoxy polymer of various compositions were all cured with an aromatic amine hardener, 4,4'-diaminodiphenylsulphone (DDS, Ciba-Geigy HT976), with an amino hydrogen equivalent weight of 62 g.

Phenoxy was weighed, pulverized into fine powder, and melt-dissolved (no solvent) in a pre-determined quantity of the liquid epoxy resin at a temperature of 100–120°C. The phenoxy contents in the phenoxy/TGDDM mixtures were varied within a range. The curing agent (DDS) was then added to the mixture, and mechanical mixing was continued for a few more minutes. The stoichiometry of the DDS used to cure the epoxy/polymer mixtures was maintained fixed at 30 phr to 100 parts of epoxy. At the end of melt-mixing operation, the liquid phenoxy/TGDDM/DDS mixtures were inspected. The mixing was not terminated until the mixtures appeared to be homogeneous and visually transparent.

Apparatus and techniques

Fourier transform infrared spectroscopy. Fourier transform infrared spectra (FT-IR, Nicolet Magna IR 550 spectrometer) were obtained at 4 $\mathrm{cm^{-1}}$ resolution and the number of scans was 64. The recorded wave number range was 400–4000 $\mathrm{cm^{-1}}$. Depending on the state of the samples, the IR measurements were carried out either on thin films cast onto potassium bromide (KBr) disks or by a powder mixing technique.

Differential scanning calorimetry. The glass transition temperatures of the cured phenoxy/epoxy samples were measured with a differential scanning calorimeter (Perkin-Elmer DSC 7). All T_g measurements were made at a scan rate of 20°C/min within the temperature range of 25–250°C, and the T_g values were taken as the onset of the transition (the change of the specific heat) in heat flow curves.

Scanning electron microscopy. The morphology of the fracture surfaces of the amine-cured phenoxy/epoxy solids was examined using a scanning electron microscope (SEM) (JEOL JXA-840). To enhance the phase contrast and to expose the embedded spheres, another set of the amine-cured phenoxy/epoxy/DDS samples were first etched with methylene chloride or tetrahydrofuran (THF) before sputter-coating. The etched samples of crosslinked epoxy/polymer solids or the isolated epoxy spheres extracted from fully-phase inverted epoxy/polymer systems were coated with gold by vapor deposition using a vacuum sputterer.

RESULTS AND DISCUSSION

To determine whether there was mutual inclusion of one component in the other, T_g characterization was performed on the cured phenoxy/epoxy solids of various phenoxy contents. The characterization revealed that there were distinctly two T_g, each being easily attributed to the two separate phases of the thermosetting epoxy and the thermoplastic phenoxy, respectively, in the cured phenoxy/epoxy networks. The upper T_g is about 190–240°C for the epoxy phase depending on the cure temperature, while the lower T_g is about 60–89°C for the phenoxy phase, which is lower than the T_g of the neat phenoxy polymer (92°C). Clearly, the phenoxy phase in the cured phenoxy/epoxy network is initially plasticized by trace amounts of the uncured epoxy monomers dissolved in the phenoxy phase. However, at the higher cure temperatures of 187 and 197°C, the T_g of the phenoxy phase was found to elevate to that of neat phenoxy. These T_g results suggest that, other than plasticization of the phenoxy phase by residual monomeric epoxy, phase separation is quite complete and there is no evidence of partial miscibility of the phenoxy component in the crosslinked epoxy phase domain or vise versa.

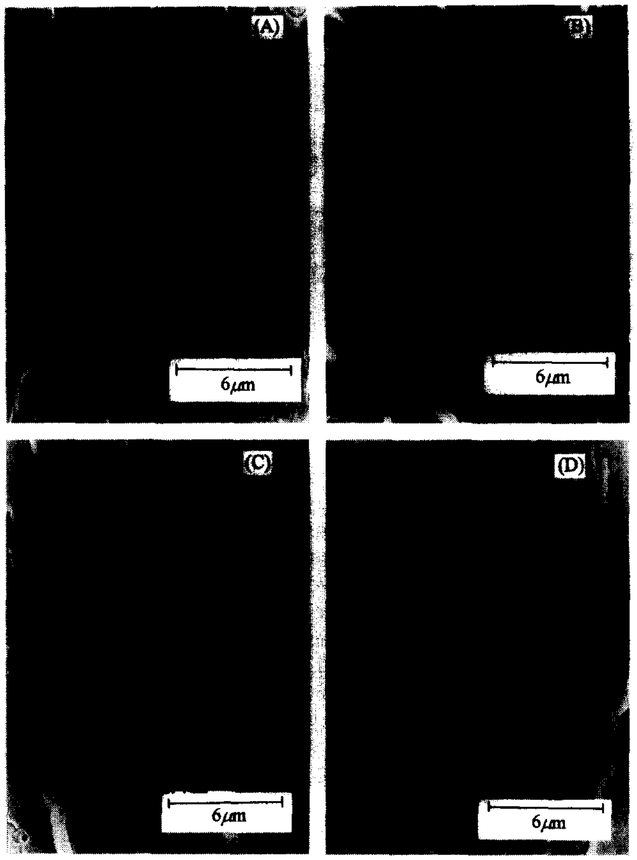


Figure 1 SEM micrographs of the fractured phenoxy/TGDDM/DDS (10/100/30) after heating at (A) 197, (B) 187, (C) 177, and (D) 167°C, respectively, for 2 h

Morphology of cured phenoxy/epoxy networks

The morphology of the as-fractured surface of various cured phenoxy/TGDDM/DDS was first characterized. Samples with the lowest phenoxy content (10 phr) were first examined. *Figure 1A–D* show the SEM micrographs of the fractured Phenoxy/TGDDM/DDS (10/100/30) after heating at (A) 197, (B) 187, (C) 177, and (D) 167°C, respectively, for 2 h. At this composition of 10 phr phenoxy, the continuous phase is apparently of thermosetting epoxy nature, while the discrete domains are identified as the phenoxy-rich phase, with domain sizes being 1 μm or smaller. A comparison of all four micrographs shows that the cure temperature did not seem to affect the size distribution or the geometry of the discrete particulate phenoxy domain.

To further prove the nature of these two phase domains, the fracture surfaces of the samples were etched with methylene or THF, and examined again using SEM.

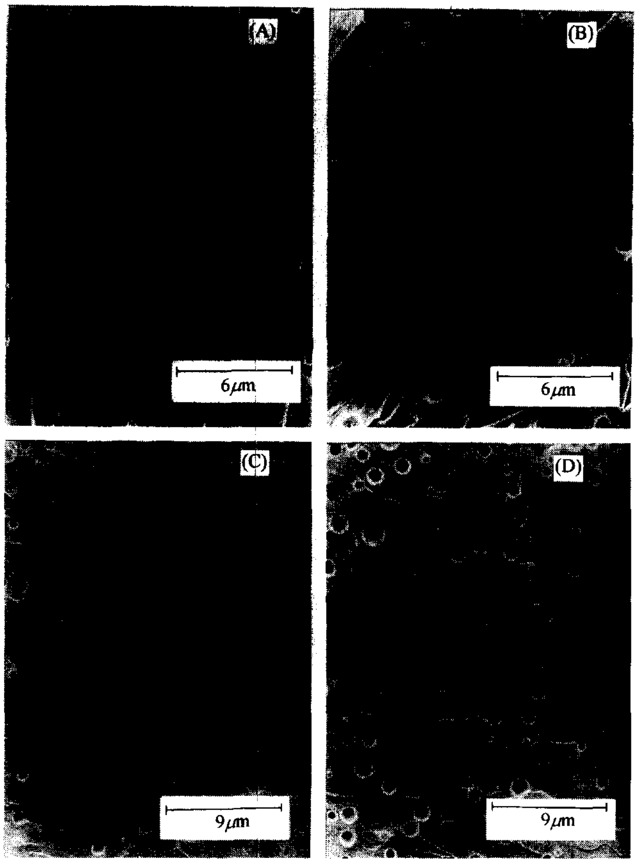


Figure 2 SEM micrographs of the solvent-etched phenoxy/TGDDM/DDS (10/100/30) samples after curing for 2 h at (A) 197, (B) 187, (C) 177, and (D) 167°C, respectively

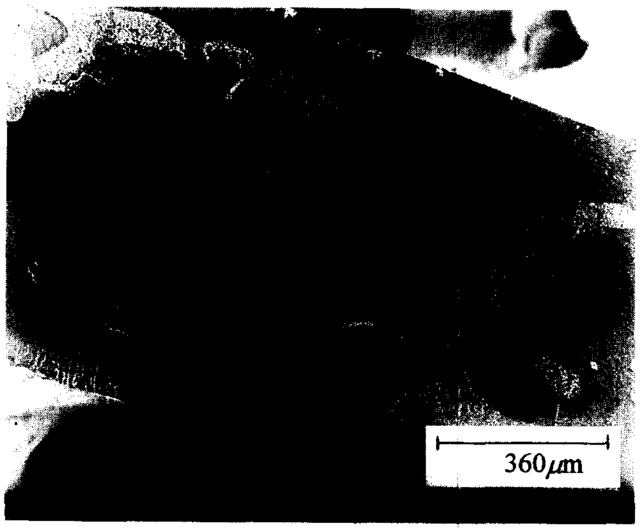


Figure 3 SEM micrograph (50X) of the 197°C-cured phenoxy/TGDDM/DDS (20/100/30) showing the overall phase-in-phase structure

Figure 2A–D shows the SEM micrographs of the solvent-etched counterparts of the same samples, which were cured at (A) 197, (B) 187, (C) 177, and (D) 167°C, respectively. A direct comparison was made between *Figures 1 and 2*. Clearly, for the samples cured at the two higher temperatures of 197 and 187°C, the morphology remained relatively unchanged with or without solvent etching. The situation is quite different for the sample cured at the lowest temperature of 167°C. *Figure 2D* shows that after etching, most of the discrete particulate domains are replaced by hollow craters of the same sizes as a result of solvent etching on the 167°C-cured sample. This observation demonstrated first that at low phenoxy contents (10 phr or smaller), the continuous phase is of crosslinked epoxy nature. The thermoplastic phenoxy, being the minor component, forms the discrete phase. Secondly, low cure temperatures obviously resulted in less extents of bonding between the thermosetting and thermoplastic domains.

Beginning at 20 phr phenoxy, an apparent shift in the phase continuity in the cured phenoxy/epoxy networks was observed. *Figure 3* shows the SEM micrograph (at a low magnification of 50 ×) of the fractured Phenoxy/TGDDM/DDS (20/100/30) after heating at 197°C for 2 h. It should be noted here that the polymer/epoxy samples cured at the other temperatures (187, 177, and 167°C) also exhibited a similar morphology; thus, the micrographs are not presented here. Low magnification was used to glance over the complete distribution of phase continuity, showing apparently a phase-in-phase morphology. The epoxy is still the continuous phase, within which the phenoxy component is dispersed as irregular-shaped islands with sizes of 100–300 μm. The thermoplastic 'islands' however, are not all phenoxy component. A closer inspection reveals that within the phenoxy islands, tiny crosslinked epoxy particles of micron-meter sizes are dispersed. To examine how the epoxy particles are imbedded in the phenoxy islands, focus was placed on the regions in the island and a greater microscopy magnification was used for further investigation.

Figure 4A–D show the SEM micrographs of the regions within the phenoxy islands for the phenoxy/TGDDM/DDS (20/100/30) sample after heating at 197, 187, 177, and 167°C, respectively, for 2 h. A phase-in-phase morphology is evident in that the phenoxy-rich domain exists as discrete,

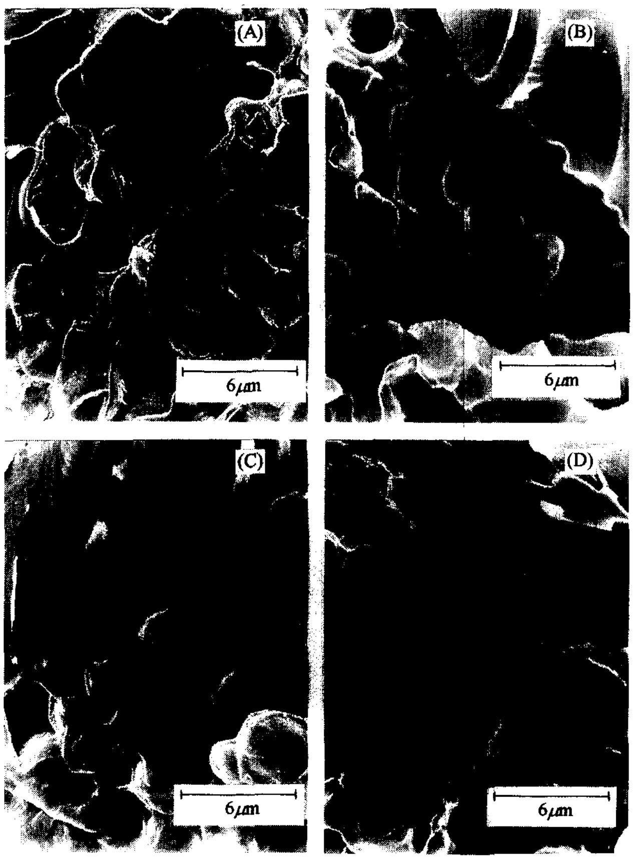


Figure 4 SEM micrographs of the phenoxy islands for the as-fractured phenoxy/TGDDM/DDS (20/100/30) after heating 2 h at temperature indicated

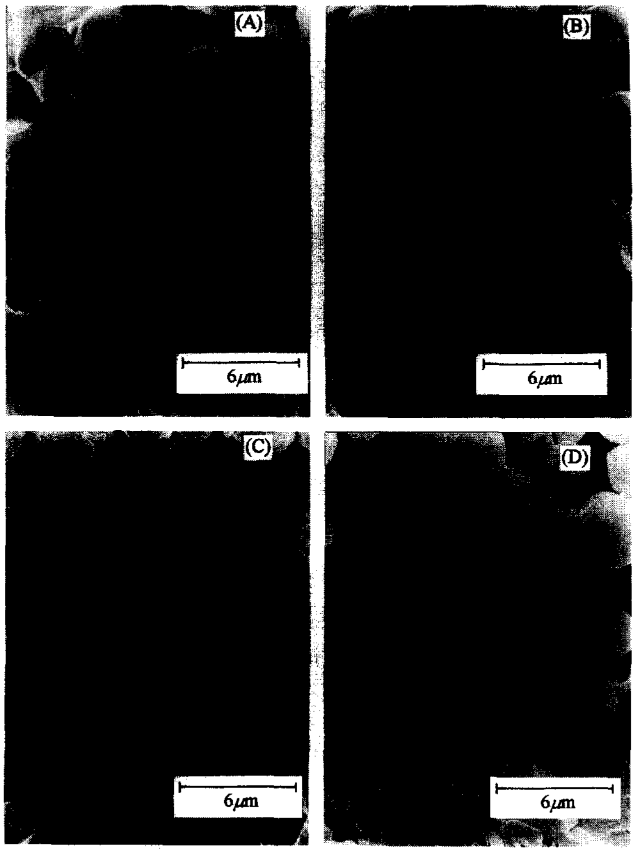


Figure 5 SEM micrographs of the solvent-etched phenoxy/TGDDM/DDS (20/100/30) sample after heating 2 h at (A) 197, (B) 187, (C) 177, and (D) 167°C

irregular-shaped islands, which in turn are imbedded in a continuous matrix, whose fracture characteristics could be identified as the brittle crosslinked epoxy. Within the islands, there is phase inversion. Exactly speaking, there is localized phase inversion. Phase inversion at this composition is not complete since outside the phenoxy islands, the continuous phase is still the dominant epoxy component. Only within the irregular phenoxy-rich islands, tiny epoxy spherical particles (3–4 μm) are dispersed and imbedded in the phenoxy continuous phase. The sizes of the discrete epoxy particles are about 3–4 μm for all cure temperatures. Interestingly, a closer inspection of the epoxy nature revealed that the outer shell of the epoxy particles are covered with a continuous shell with a rough surface characteristic. The cure temperature has little observable effect on the average diameters of the epoxy spheres in the phenoxy islands. However, at higher cure temperatures, the extent of grafting between the phenoxy and epoxy is more complete. Thus, the interfacial reactions between the phenoxy and epoxy phase led to more extensive chemical links.

This observation suggested that there might be chemical interactions between the epoxy and the polymer component. Solvent etching was performed to reveal the nature of the shells that covered the epoxy particles. *Figure 5A–D* show the SEM micrographs of the solvent-etched phenoxy/TGDDM/DDS (20/100/30) sample after heating at (A) 197, (B) 187, (C) 177, and (D) 167°C, respectively, for 2 h. Again, only the regions within the phenoxy islands are shown for details at large magnifications. Clearly, for the samples cured at the two higher temperatures of 197 and 187°C, the shells covering the epoxy particles remained relatively unchanged with or without solvent etching. The outer shells remain intact and the surface of the covered epoxy particles appear to be rough and interconnected. The situation is quite different for the samples cured at the two lower temperatures of 177 or 167°C. *Figure 5C* and *D* show that after etching, the outer shells are more easily removed by the solvent and most of the discrete epoxy particles are exposed with a smoother surface. This observation suggests that the extents of chemical interlinks between the polymer shells and epoxy particles might be dependent on the temperature. A high temperature might result in a more complete extent of reactions that led to chemical bondings between the two thermoplastic and thermosetting domains.

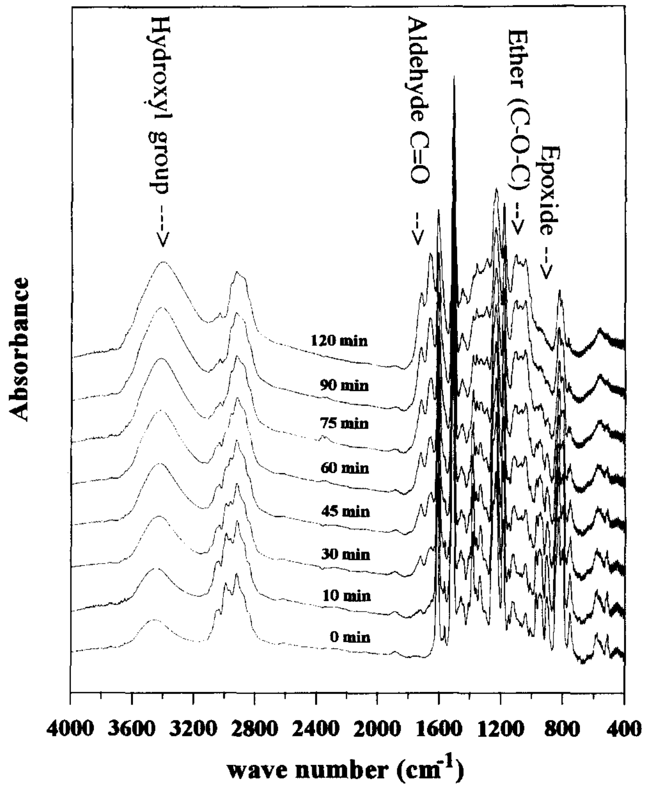


Figure 6 FTIR spectra for the phenoxy/TGDDM (20 phr phenoxy, no DDS) sample after heating at 177°C for various times

Chemical bondings

FTIR characterization was performed, with the focus being placed on probing interactions between the phenoxy and the TGDDM epoxy. The DDS component was excluded for this purpose since TGDDM could readily react with DDS, which, if present, may significantly complicate the observation. *Figure 6* shows the FTIR spectra for the phenoxy/TGDDM (20 phr phenoxy) sample upon heating at 177°C for various times as indicated on the respective spectra. Three notable changes are observed in the spectra. First, the spectra shows that the intensity of the hydroxyl group (3450–3400 cm^{-1}) absorbance steadily increases with increasing heating time at 177°C. Secondly, the aldehyde group absorbance (1640 and 1720 cm^{-1}) increases with heating time as well. Thirdly, the epoxide group absorbance (905, 970 cm^{-1}) decreases with heating time. In the absence of DDS, the increase of –OH groups may come from several sources: (1) homopolymerization of TGDDM; and (2) isomerization of TGDDM molecules. It has been pointed out that neat TGDDM by itself can produce –OH groups upon heating[13]. One possible source of the hydroxyl groups is TGDDM homopolymerization, which is present

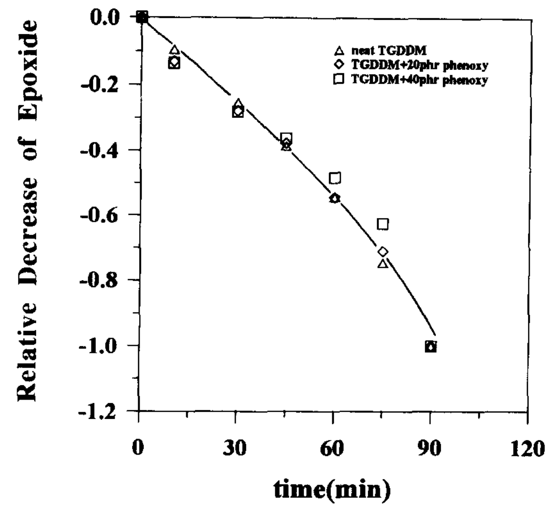


Figure 7 Depletion of the epoxide group as a function of heating time at 177°C for three systems: (1) neat TGDDM; (2) 20 phr phenoxy/TGDDM; and (3) 40 phr phenoxy/TGDDM

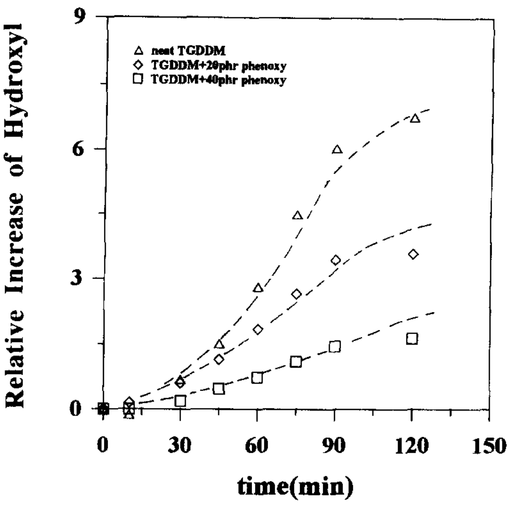


Figure 8 Relatively increase of the hydroxyl group as a function of heating time at 177°C for phenoxy/TGDDM mixtures with (1) 0 phr, (2) 20 phr and (3) 40 phr phenoxy

but the extent is quite limited. Related studies[16] have pointed out that isomerization of TGDDM can proceed at high temperatures and produce various low-M_w species with an –OH or aldehyde C=O group.

It must be pointed out that our separate FTIR results (spectra not shown for brevity) indicated that the aldehyde group was not observed in the DDS-cured TGDDM system upon heating, indicating that the normal amine-curing reactions suppressed and dominated the isomerization of TGDDM. Thus, the fact that the 20 phr phenoxy/TGDDM mixture produced aldehyde groups upon heating suggested that at 177°C, phenoxy did not significantly promote homopolymerization or crosslinking of TGDDM. Evidently, the depletion of the epoxide group came primarily from isomerization of TGDDM into aldehyde-containing species, and the likelihood of chemical interactions between phenoxy and TGDDM at 177°C or lower was limited. The FTIR result for another composition (40 phr phenoxy/TGDDM) revealed similar results and is thus not shown or discussed again here.

Figure 7 shows the depletion (relative decrease) of the epoxide group as a function of heating time at 177°C for three systems: (1) neat TGDDM; (2) 20 phr phenoxy/TGDDM; and (3)40 phr phenoxy/TGDDM. In constructing the plot, the epoxide absorbance peak (905 cm^{-1}) was normalized with the aromatic C–C absorbance peak at 1600 cm^{-1}. The figure shows that apparently the rate of epoxide depletion is not affected by the content of phenoxy in TGDDM since the rate of decrease is about the same for all three phenoxy/TGDDM systems with different phenoxy contents from 0 to 40 phr.

Figure 8 shows the relative rate of increase of the hydroxyl group as a function of heating time at 177°C for three polymer/epoxy compositions: (1) neat TGDDM; (2) 20 phr phenoxy/TGDDM; and (3) 40 phr phenoxy/TGDDM. In the plot, the relative rate of hydroxyl group increase was calculated using the following expression:

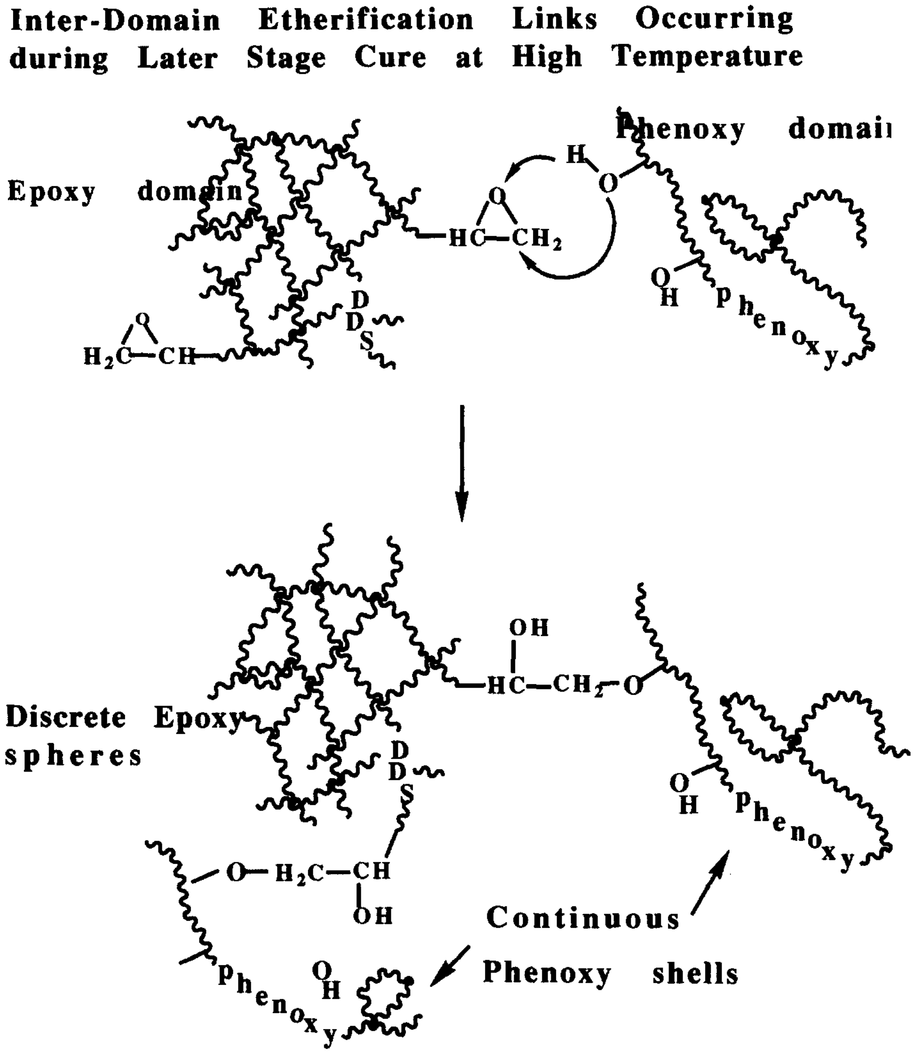
$$r = [(\mathrm{OH})_t - (\mathrm{OH})_0]/(\mathrm{OH})_0 \qquad (1)$$

where the subscripts t and 0 indicate the absorbance intensity at time t and 0, respectively. The plot shows that the phenoxy component does not promote the rate of increase of –OH group. On the other hand, the relative rate of increase of the hydroxyl group seems to be depressed by the presence of phenoxy in TGDDM. However, this interpretation may not be correct. The phenoxy/TGDDM mixtures before heating contain a higher initial hydroxyl group content, $(\mathrm{OH})_0$, owing to the pendant –OH group in the repeat unit of the phenoxy molecules. A greater value of the denominator in equation (1) for the phenoxy/TGDDM mixture systems results in a slower relative rate of –OH increase. By taking this into account, it can be reasoned that the presence of the phenoxy component does not seem to affect the –OH group production from isomerization of TGDDM molecules upon heating at 177°C. The results in *Figures 7 and 8* together suggest that there might be little direct chemical interaction between phenoxy and TGDDM epoxy at the temperature of 177°C or lower.

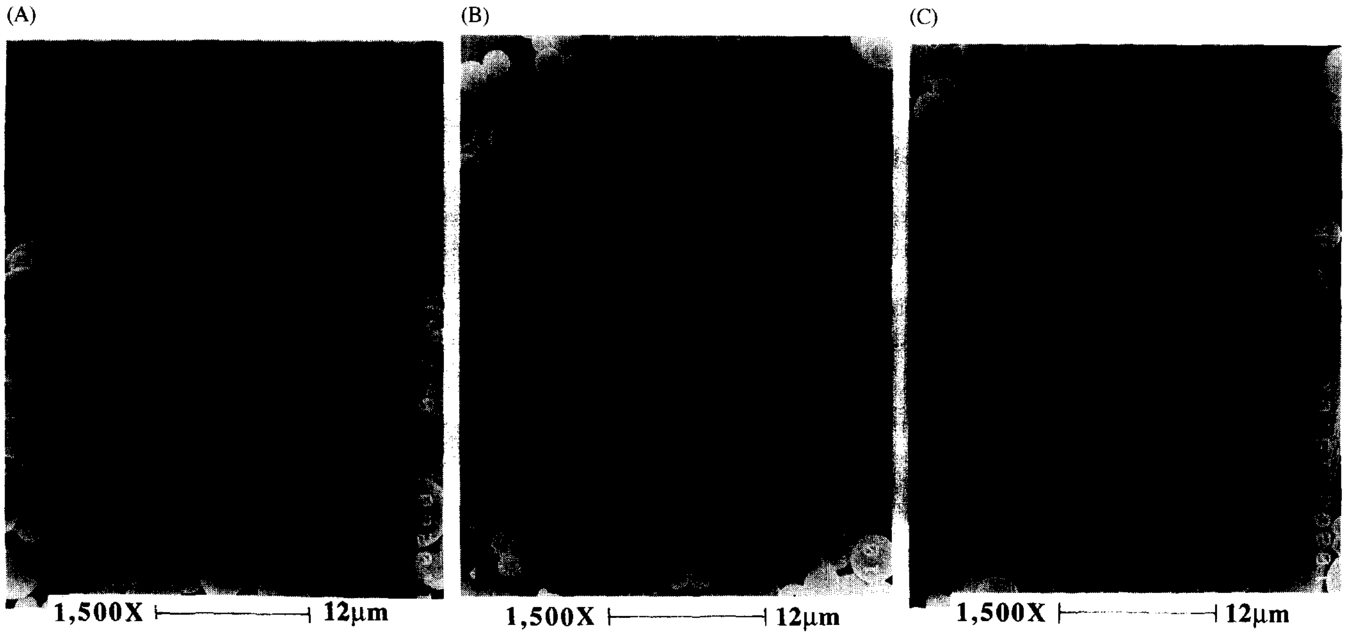
At higher temperatures, the situation might be different. In amine-cured phenoxy/TGDDM mixtures, the early-stage cure is dominated by normal cure reactions between amine and epoxide. It has been postulated in our previous study[15] that at higher temperatures and during later stages of cure where there are still ample excess epoxide groups, the residual epoxide groups in the epoxy particles may begin to react with the pendant –OH groups in the phenoxy domain. Since a phase-separated morphology is already formed, the later-stage reaction is confined to the outer surfaces of the spherical epoxy phase domain and phenoxy domain, thus leading to chemical links between the epoxy particles and the phenoxy shells. This is depicted in *Scheme 1*[15].

The above mechanism assumes that there are excess epoxide groups left for reactions with phenoxy at high temperatures. At 30 phr DDS in 100 parts of epoxy, the stoichiometric amino-H/epoxide ratio is 0.57 for the phenoxyTGDDM/DDS mixture system. Thus, at 30 phr DDS, there are apparently plenty of excess epoxide groups in the phenoxy/TGDDM/DDS system. There might be some epoxide groups consumed in side isomerization of TGDDM, but this is supposed to be minimal in the epoxy systems where DDS is present. However, 30 phr of DDS in the phenoxy/DGEBA/DDS mixture system, has a stoichiometric amino-H/epoxide ratio of 0.91. Apparently, there would be not many residual epoxide groups left in the 30 phr DDS/DGEBA system at later stages of cure. Thus, chemical bondings would not be expected in phenoxy-modified DGEBA/DDS epoxy systems.

Thus, samples of phenoxy/DGEBA/DDS were prepared



Scheme 1



DGEBA/DDS/Phenoxy (100/30/30) 167°C, 2h (Solvent-etched)

DGEBA/DDS/Phenoxy (100/30/30) 177°C, 2h (Solvent-etched)

DGEBA/DDS/Phenoxy (100/30/30) 187°C, 2h (Solvent-etched)

Figure 9 SEM micrographs of the solvent-etched phenoxy/DGEBA/DDS (30/100/30) sample after heating 2 h at (A) 167, (B) 177, and (C) 187°C and the morphology was examined. *Figure 9* shows the SEM micrographs of the solvent-etched phenoxy/DGEBA/DDS (30/100/30) sample after heating at (A) 167, (B) 177, and (C) 187°C, respectively, for 2 h. All micrographs show that the epoxy particles (3–4 μm), after solvent etching, are fully exposed with no phenoxy shell at all. The results demonstrate that although the morphology of the phenoxy/DGEBA/DDS systems is similar to the phenoxy/TGDDM/DDS, there is no evidence of chemical interaction between the phenoxy domains and the epoxy domain. Interestingly, interconnection between the epoxy particles in the phenoxy/DGEBA/DDS was not observed. This is opposite to that observed in the phenoxy/TGDDM/DDS system, where severity of interconnection between the particles was more apparent.

No mechanical or other macroscopic characterization was performed on these two interesting phenoxy/epoxy systems since the main objective of this study was limited to providing microscopic structural or molecular interpretation. Although not exactly the same material systems or directly comparable, an earlier study on polymers as interlaminar toughening agents for epoxy/fiber composites has demonstrated that the phenoxy can improve the interlaminar fracture toughness, G_{IC} and G_{IIC}, nearly three-fold (unidirectional laminates) when used at an areal density of 21.5 g/m^2 (phenoxy weight/prepreg area ratio) in the interlaminar ply of epoxy/carbon fiber composites[17]. Similar toughening effects may be expected for the phenoxy/TGDDM/DDS and phenoxy/DGEBA/DDS systems in neat resin forms as a result of the interesting morphology and interfacial bonding characteristics developed upon co-cure.

CONCLUSION

Morphology in aromatic amine-cured phenoxy/epoxy mixtures reacted for 2 h at 167, 177, 187, and 197°C, respectively, was investigated using SEM. Full-scale phase inversion was observed in the cured phenoxy/epoxy networks as the phenoxy content was about 30 phr or more. DSC measurements on the T_g of the cured phenoxy/epoxy networks suggested that phase separation was complete with no partial miscibility between the phenoxy polymer and the crosslinked epoxy domains. Two epoxy/polymer systems were investigated for comparison. One phenoxy/epoxy system included phenoxy and TGDDM cured with 30 phr DDS. An interesting phenomenon has been demonstrated where inter-domain chemical links between phenoxy and the epoxy phases in the phase-separated phenoxy/TGDDM/DDS networks of various compositions. At later stages of cure where a phase-separated morphology was already set, etherification occurred at high temperatures (e.g. 187°C or higher) between the pendant hydroxyl group of the phenoxy shells and the residual epoxide of the crosslinked epoxy core particles. However, at lower cure temperatures (e.g. 177°C or lower), the extent of etherification might be too low, leading to less evident etherification-induced chemical links between the polymer shells and epoxy cores. The FTIR results also supported the interpretation obtained from the SEM morphology results.

Additionally, sufficient conditions for development of inter-domain chemical bondings also included that the polymer/epoxy mixtures should contain reasonable amounts of epoxide groups at later stages of cure. Studies were performed on another polymer/epoxy system comprising of phenoxy and DGEBA cured with the same amounts of DDS, where the epoxide group was in about the same stoichiometric ratio as the amine. Similar morphology was found in the cured network; however, the thermoplastic polymer shells were easily and completely etched out from the epoxy particles using THF or methylene. This is attributed to the fact that no chemical links developed across the TP–TS domains due to lack of residual epoxide groups available for reacting with the –OH groups of the phenoxy.

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REFERENCES

1. Su, C. C. and Woo, E. M., *Polymer*, 1995, **36**, 2883.
2. Pak, S. J., Lyle, G. D., Mercier, R. and McGrath, J. E., *Polymer*, 1993, **34**, 885.
3. Pearson, R. A. and Yee, A. F., *Polymer*, 1993, **34**, 3658.
4. Gomez, C. M. and Bucknall, C. B., *Polymer*, 1993, **34**, 2111.
5. Bucknall, C. B., Gomez, C. M. and Quintard, I., *Polymer*, 1994, **35**, 353.
6. Clarke, N., Mcleish, T. C. B. and Jenkins, S. D., *Macromolecules*, 1995, **28**, 4650.
7. Riccardi, C. C., Borrajo, J., Williams, R. J. J., Girard-Reydet, E., Sautereau, H. and Pascault, J. P., *J. Polym. Sci., Polym. Phys. Ed.*, 1996, **34**, 349.
8. Inoue, T., *Prog. Polym. Sci.*, 1995, **20**, 119.
9. Su, C. C. and Woo, E. M., *Macromolecules*, 1995, **28**, 6779.
10. Su, C. C., Kuo, J.-F. and Woo, E. M., *J. Polym. Sci., Polym. Phys. Ed.*, 1995, **33**, 2235.
11. Hseih, H. K. and Woo, E. M. J., *Polym. Sci., Polym. Phys. Ed.*, 1996, **34**, 2591.
12. Chiang, J. and Prud'homme, R. K. J., *Colloid Interface Science*, 1988, **122**, 284.
13. Tamai, H., Nishida, Y. and Suzawa, T. J., *Colloid Interface Science*, 1991, **146**, 288.
14. Hattori, M., Sudol, E. D. and El-Aasser, M. S. J., *Appl. Polym. Sci.*, 1993, **50**, 2027.
15. Woo, E. M., Hseih, H. K., J. Polym. Sci., Polym. Chem. Ed., submitted 1996.
16. Attias, A. J., Bloch, B. and Lauprete, F. J., *Polym. Sci., Polym. Chem. Ed.*,, 1990, **28**, 3445.
17. Woo, E. M. and Mao, K. L., *Composites*, 1996, **27A**, 625.