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Cure kinetics and inter-domain etherification in an amine-cured phenoxy/epoxy system

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The aim of this study was to examine possible effects of the hydroxyl group (–OH) in phenoxy-type polymers on the cure reactions and network morphology of a crosslinking epoxy system, tetraglycidyl-4,4′-diaminodiphenylmethane (TGDDM) with diaminodiphenylsulfone (DDS). Similar to the case for a pure, unmodified TGDDM/DDS epoxy counterpart, an autocatalytic reaction kinetic model was found to describe the cure behaviour of the phenoxy/TGDDM/DDS mixtures up to the vitrification point. At the early stage of cure, the –OH group in the phenoxy might exert a catalytic effect for epoxide ring opening between epoxy and the amine. Subsequently, at later cure stages where phase domain boundaries were forming and the amine groups were largely depleted, the –OH groups of the phenoxy phase domain began to react with the residual epoxide groups in the epoxy domains. It is this later-stage reaction that led to interlinking chemical bonding between the phenoxy and epoxy phases at the domain boundaries. © 1998 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

Amorphous, glassy poly(hydroxyether of bisphenol A) (phenoxy), with a structure comprising bisphenol A and epichlorohydrin, is a widely useful thermoplastic. It contains a pendent hydroxyl group in each repeat unit and thus is capable of intramolecular self-associations or intermolecular interactions with other molecules through hydrogen bonding. Phenoxy has been demonstrated to be miscible with polyesters[1,2], polysulfone[3] and poly(ethylene oxide)[4,5], among others. Additionally, owing to potential specific interactions, polymer miscibility and phase behaviour in the pair phenoxy and poly(methyl methacrylate) (a-PMMA) have been the subject of many interesting studies[6,7]. The issue of complex phase changes upon heating of blends of phenoxy with bisphenol A polycarbonate (PC) has also drawn much attention[8,9]. In addition, phenoxy has also been used in the modification of thermosetting epoxy resins[10]. Most epoxy chains contain pendent hydroxyl groups, and thus are capable of interacting with phenoxy through hydrogen bonding. Some epoxies, such as diglycidyl ether of bisphenol A (DGEBA), possess a structure so similar to the structure of a phenoxy repeat unit that DGEBA may be viewed as a model compound for phenoxy. However, both the hydrogen bonding and the similarity in chemical structure may not be sufficient to observe miscibility between epoxies and phenoxy. The highly crosslinked nature of epoxies may expel the linear phenoxy molecules to separated domains upon cure. Furthermore, the hydroxyl group of phenoxy may participate in reactions with the epoxy at different stages of cure.

All applications of pure or modified epoxies require that the resins be subjected to an optimized cure for shape forming. Both empirical and mechanistic kinetic models have been derived for the cure of epoxy systems. Reaction mechanisms of pure tetrafunctional epoxides cured with amines have been widely reported[11–14]. Because of the complex chemistry of the epoxy curing process, study of epoxy–amine reactions by using model compounds has also been attempted[15]. While the cure kinetics and reaction mechanisms of various pure epoxy resins have been studied extensively by use of various methods including, most often, differential scanning calorimetry[16–18], the effects of polymers with special functional groups (such as a hydroxyl) on the cure kinetics of epoxy resins have been investigated in detail less often.

The introduction of modifiers into an epoxy system inevitably alters the cure mechanisms and/or phase morphology of the cured epoxy networks. Generally, introduction of thermoplastic linear polymers for co-curing with epoxies may quite likely alter the cure kinetics mechanisms of network building and morphology of the cured networks. It has been shown[19] that the presence of poly(ether imide) (PEI) does not alter the cure reaction mechanisms of epoxies, but that the polymer results in a systematic shift of the phase-separated morphology of the cured polymer/epoxy networks, the domain sizes and phase composition of which depend on the PEI content. Our recent studies have demonstrated that a PC-modified epoxy [tetraglycidyl-4,4′-diaminodiphenylmethane (TGDDM)/diaminodiphenylsulfone (DDS)] system exhibits an unexpected change of reaction mechanism of the epoxy cure[20]. More interestingly, the cured PC/TGDDM/DDS network was homogeneous with no phase separation[21], which is quite rare for most polymer-modified epoxy networks. This rare homogeneity in the polymer-modified network has been attributed to extensive transreactions between the carbonate group of PC and the hydroxyl group of the epoxy.

This study was initially motivated by curiosity, to

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understand what role the hydroxyl groups in the phenoxy polymer chains might play in interactions with the epoxy during cure. Ultimately, would the cure reaction and/or network morphology of the phenoxy–epoxy system be affected? Earlier, Fourier transfrom infra-red (*FT*i.r.) spectroscopy had been used in this laboratory primarily to probe possible effects of the hydroxyl groups of the phenoxy on epoxide reactions in epoxy/phenoxy mixtures (no amine hardeners) when heated at isothermal temperatures[22]. The *FT*i.r. study revealed that the presence of phenoxy in the epoxy does not exert any effect on the production of –OH groups, suggesting that the polymeric phenoxy hydroxyl group exerts almost no effect on the epoxide conversion rate in the absence of hardeners. For this reason, curing of epoxy/phenoxy mixtures with amine hardeners may be similarly unaffected by the phenoxy constituent. Effects on the phase morphology were, however, yet to be discovered. A subsequent continuing study provided preliminary information on cure of the phenoxy/TGDDM epoxy/DDS system leading to a network of phase-separated morphology with interesting epoxy core/phenoxy shell structure[23]. Critical issues yet to be investigated include how the rate and sequence of simultaneous reactions might determine the ultimate morphology. Specifically, interesting issues are how cure reaction kinetics and relative sequence of reactions might lead to a crosslinked network of a unique morphology *versus* how exchange reactions after phase separation might lead to interphase bonding. The aim of this current study was to gain better understanding of the role of the hydroxyl group of the phenoxy polymer on the cure reactions and phase morphology, especially in the inter-domain boundaries, of polymer-modified thermosetting epoxies by using phenoxy-modified TGDDM/DDS as a model system. Systems involving DGEBA (a difunctional epoxide resin) were not examined in this study as it had been demonstrated earlier that cured phenoxy/DGEBA/DDS systems do not exhibit the phenomenon of inter-domain links[23].

EXPERIMENTAL

Materials and sample preparation

The phenoxy polymer used was poly(hydroxyl ether of bisphenol A) (Union Carbide, PKHH; M_n = 20 000 to 25 000 g mol^{-1}). The main epoxy resin used in this study is tetraglycidyl-4,4′-diaminodiphenylmethane (TGDDM) (Ciba-Geigy, MY 720), with an epoxide equivalent weight of 109 g. The base TGDDM epoxy resin and its mixtures with the phenoxy polymer were cured with an aromatic amine hardener, 4,4′-diaminodiphenylsulfone (DDS) (Ciba-Geigy, HT 976), having an amino hydrogen equivalent weight of 62 g.

Prior to introduction of the hardener, phenoxy/TGDDM mixtures were first prepared with various compositions of 0, 20, 30 and 40 phr phenoxy, where 'phr' is parts of phenoxy polymer per hundred parts of epoxy resin. First, the phenoxy was weighed and pulverized into a fine powder to aid the melt-dissolution process. The resulting polymer powder of weighed proportions was mixed with the liquid epoxy by heating and mechanical stirring at a temperature of about 120°C. Subsequently, 30 phr of powdered DDS (0.53 stoichiometric equivalent) was slowly added to the already homogenized liquid polymer/epoxy mixture with further mechanical stirring in an isothermal oil bath at 120°C, until it was well mixed in.

Apparatus

Differential scanning calorimetry (d.s.c.) (Perkin–Elmer DSC-7) was used for characterization of glass transition temperatures (T_gs), isothermal cure experiments and kinetic analysis. The temperature and enthalpy were calibrated with indium and zinc standards. Samples (5–8 mg) were placed in aluminium pans. The calorimeter, with its precise, small size of the sample/reference cells and accurate temperature control, provided a unique capability of bringing the samples of polymer/epoxy mixtures rapidly to designated temperatures. The cure reaction, which generally took 1 to 2 h, was considered to be complete when the isothermal d.s.c. thermogram levelled off to the baseline. The total area under the exotherm curve, on the basis of the extrapolated baseline at the end of the reaction, was used to calculate the isothermal heat of cure, ΔH_I (J g^{-1}). After the isothermal cure reaction was completed in the calorimeter, the sample was cooled to 40°C. To determine the residual heat of reaction, ΔH_R (J g^{-1}), the samples after isothermal cure were scanned at 10°C min^{-1} from 40 to 300°C. Kinetic analysis was performed on the isothermal d.s.c. data obtained by using standard procedures. Specific procedures leading to the evaluation of kinetic parameters are discussed in Section Section 3 below.

The morphology of the amine-cured phenoxy/epoxy samples was examined by scanning electron microscopy (SEM; model JSM-35 or JXA-840 from JEOL). To investigate the morphology of the cured phenoxy/epoxy networks, samples were cured by heating the well-prepared phenoxy/TGDDM/DDS mixtures in an oven at 177, 187 or 197°C; the cure time for all samples was constant at 2 h. The cured samples were then fractured and sputter-coated with gold by vacuum sputtering. All samples possessed relatively high T_gs and were fractured at ambient temperature. One set of samples was fractured and sputter-coated without solvent etching while another set of samples was fractured and etched with solvent (methylene chloride) prior to being sputter-coated and examined by SEM. The purpose of this comparison was to more clearly identify the thermoplastic domains by fully exposing the crosslinked regions. Additionally, bonding strength between the thermoplastic (TP) and thermosetting (TS) domains could also be examined.

RESULTS AND DISCUSSION

T_g and morphology

Our previous study has shown that, regardless of the similarity in structure between the phenoxy and epoxy, the nature of the network as a result of curing of epoxy with DDS leads to eventual phase separation in cured phenoxy/epoxy/DDS systems[23]. More exactly, T_g characterization might reveal the extent of phase separation of the networks. *Figure 1* shows the T_gs of the phenoxy and epoxy phases in the samples of cured phenoxy/epoxy networks of various phenoxy contents, which were cured at 177, 187 and 197°C. Apparently, there are two distinct T_gs, which can be attributed to the two separate phases in the cured phenoxy/epoxy network. Additionally, the T_g values for these two phases are dependent on the cure temperatures. The figure shows that the upper T_g is about 190–240°C for the epoxy-rich phase, while the lower T_g is about 60–89°C for the phenoxy-rich phase; in comparison, the T_g of the pure phenoxy polymer is about 92°C. Clearly, the figure also shows that, at higher cure temperatures, the T_gs of these two

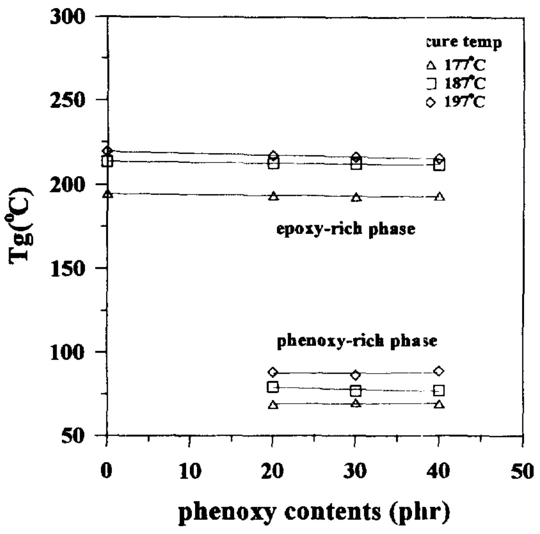


Figure 1 T_gs of the phenoxy and epoxy phases as a function of phenoxy content in the phenoxy/epoxy/DDS networks cured at 177°C (△), 187°C (□) and 197°C (◇)

phases are both elevated. The elevation of T_g in the epoxy-rich phase is easy to understand since the crosslinked density of the epoxy phase is higher at higher cure temperatures. On the other hand, the phenoxy phase is initially plasticized by the epoxy monomers or oligomers dissolved in the phenoxy phase. Elevation of the T_g of the phenoxy phase is believed to be associated with the originally dissolved epoxy monomers being cured or expelled out of the phenoxy phase. At lower cure temperatures, the T_g of the phenoxy-rich phase is lower than that of pure phenoxy polymer because of partial plasticization. At higher cure temperatures, however, the plasticizing epoxy monomer component is either expelled from the phenoxy phase domains or homopolymerized *in situ*. Thus, the T_g of the phenoxy phase gradually approaches that of the pure phenoxy. Overall, the results of thermal analysis demonstrated that, within the crosslinked phenoxy/epoxy networks, there exist two completely separated phases.

Clearly, the results show that the T_g of the epoxy-rich phase in the phenoxy-modified epoxy networks remains the same as that of the pure cured epoxy. This suggests that, as the epoxy was cured by reacting with DDS and gradually became a separate phase, no phenoxy polymer molecules remained in the epoxy phase. The –OH groups of the phenoxy showed little reactivity with epoxide at early stages of cure. Thus, there was no chemical driving force for the phenoxy to remain in the crosslinked epoxy phase. As the epoxy gelled or crosslinked, the phenoxy component was completely expelled from the bulk of the epoxy particulate domains owing to unfavourable thermodynamic factors.

In addition to thermal properties, morphology characterization was expected to provide some critical clues for the discussed phase separation. Furthermore, the presence of inter-domain reactions in the interfaces of the epoxy and phenoxy phases might be examined. An earlier study[23] revealed that, at low phenoxy contents (*ca.* 10 wt% and higher), phase separation readily takes place in the cured phenoxy/TGDDM/DDS and evidence of inter-domain exchange reactions during later stages of cure is present. To investigate fully the surface morphology at the interfaces between the crosslinked epoxy phase and the thermoplastic phase, the microscopy characterization in this study focused on samples of compositions where complete phase inversion occurred (high phenoxy contents). Of particular interest was the phase morphology and surface characteristics in the inter-domain regions of the cured phenoxy/epoxy/DDS samples of two compositions (30 and 40 phr), where complete phase inversion occurred. There was experimental difficulty in the preparation of samples of even higher phenoxy content (> 50 phr).

Figures 2A–D show SEM micrographs of as-fractured (unetched) surfaces of the 30 phr phenoxy-modified epoxy samples, all cured for 120 min, at 197, 187, 177 and 167°C, respectively. At the end of cure (120 min), the epoxy-rich domain clearly exists as fine, dispersed, spherical particles (*ca.* 5 μm) surrounded by a continuous phenoxy phase domain. The fractured surfaces are all quite rough, indicating some levels of chemical linkage between the two phase domains. The roughness of the fractured surface of the epoxy particles increased clearly with the cure temperature from 167 to 197°C. The roughness of the boundary morphology may be taken to reflect the strength of the interfacial chemical links, which is apparently dependent on the cure temperature. It was possible that inter-phase chemical interactions occurred at the epoxy surfaces with the surrounding phenoxy phase. Our SEM results showed that at phenoxy contents lower than 30 phr, the crosslinked epoxy network formed the continuous phase in which the phenoxy component existed as particulate domains. At 30 phr of phenoxy, the cured phenoxy/TGDDM/DDS networks exhibited a fully inverted phase morphology. That is, the major crosslinked epoxy component (weight fraction = 0.81) constitutes the discrete domain and exists as spherical particles, being surrounded by a vast,

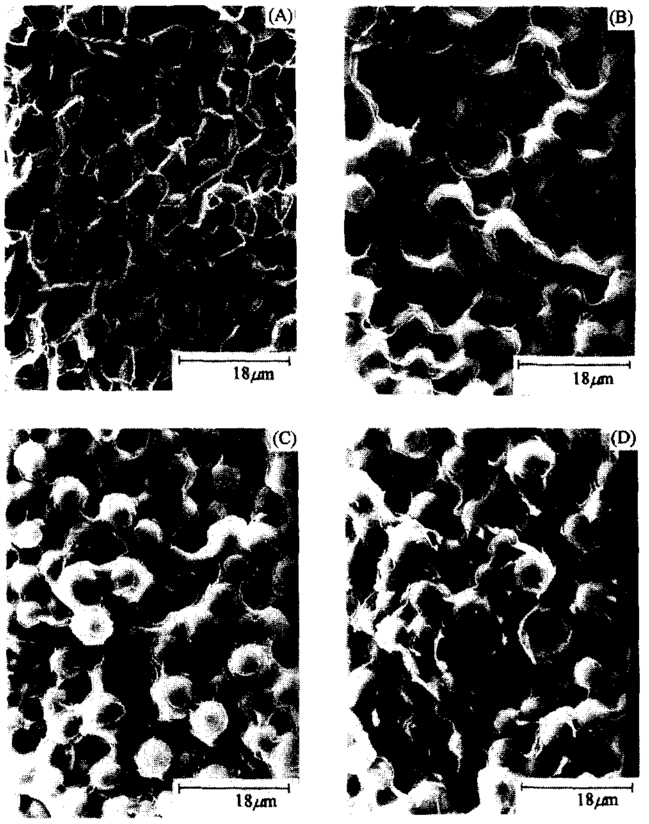


Figure 2 SEM micrographs of as-fractured (unetched) surfaces of the 30 phr phenoxy-modified epoxy samples cured for 120 min at 197°C (A), 187°C (B), 177°C (C) and 167°C (D)

continuous phase of the minor phenoxy component (30 phr, or phenoxy weight fraction of 0.19).

Another composition of the phenoxy/epoxy sample of higher phenoxy content (40 phr) was also examined. *Figures 3A–D* shows SEM micrographs of as-fractured surfaces (unetched) of the 40 phr phenoxy-modified epoxy samples cured for 120 min at 197, 187, 177 and 167°C, respectively. Again, at the end of cure (120 min), the epoxy-rich domain clearly existed as fine, dispersed, spherical particles surrounded by a continuous phenoxy phase domain. The epoxy particles, however, are smaller at about 2–3 μm. The fact that the epoxy particles became smaller with greater contents of phenoxy is in agreement with our earlier findings reported for a PMMA/DGEBA/DDS system[24], where an increase in the volume fraction of the continuous TP phase (PMMA) favours the formation of more crosslinked epoxy particles, thus decreasing the average sizes of the epoxy particles. For the present phenoxy/TGDDM/DDS system, the trend of variation of average size of the phase-inverted epoxy particles is consistent. Other than the noted difference in the size of epoxy particles for different phenoxy contents, the inter-domain surfaces of 40 phr phenoxy/TGDDM/DDS are all similarly quite rough, and are not unlike those in the 30 phr phenoxy/TGDDM/DDS sample. The result of rough surfaces suggests again that there exists some level of chemical interlinks between the two phase domains for this cured sample of 40 phr phenoxy.

Inter-phase bondings and morphology

To expose further the surface characteristics of the spherical epoxy particles and to test the solvent resistance of the inter-phase constituents, the fractured surfaces of the cured phenoxy/epoxy samples were etched with tetrahydrofuran or methylene chloride solvent. The thermoplastic phenoxy domains, if not bonded sufficiently strongly with the crosslinked epoxy particles, could be stripped out and a smooth surface of the epoxy particles was exposed. Thus, solvent etching helped reveal the inter-phase bonding strengths by enabling examination and comparison of the smoothness of the epoxy particles before and after etching.

Figures 4A–D show SEM micrographs of the etched fracture surfaces of 30 phr phenoxy-modified epoxy samples cured for 120 min at 197, 187, 177 and 167°C, respectively. The samples were all etched with methylene chloride solvent prior to sputter-coating and SEM examination. The etching clearly exposed the discrete epoxy particles, with traces of polymer (phenoxy) coatings remaining on the particles. The micrographs presented in *Figures 4A* and *4B* are for the phenoxy/epoxy samples cured at 197 and 187°C, respectively, the surfaces of which remained quite rough after solvent etching. On the other hand, *Figures 4C* and *4D* were obtained for the phenoxy/epoxy samples cured at the relatively lower temperatures of 177 and 167°C, respectively. The surfaces of the epoxy particles in these latter two samples are apparently much smoother after solvent etching, indicating fewer chemical links.

Another etched sample of a different composition was also examined microscopically. *Figures 5A–D* show SEM micrographs of the 40 phr phenoxy-modified epoxy samples (etched with methylene chloride), which were cured for 120 min at 197, 187, 177 and 167°C, respectively. A consistent trend can be noted. Once again, the micrographs

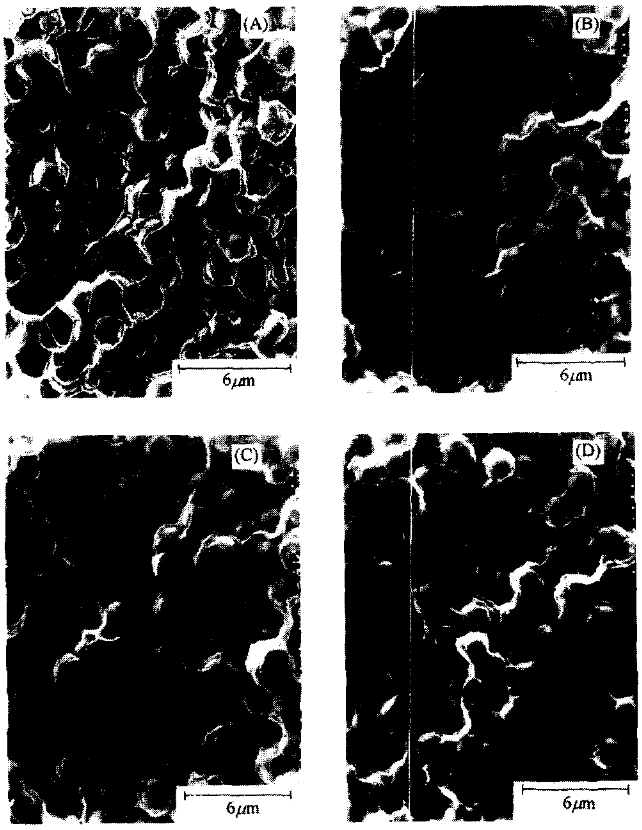


Figure 3 SEM micrographs of as-fractured surfaces (unetched) of the 40 phr phenoxy-modified epoxy samples cured for 120 min at 197°C (A), 187°C (B), 177°C (C) and 167°C (D)

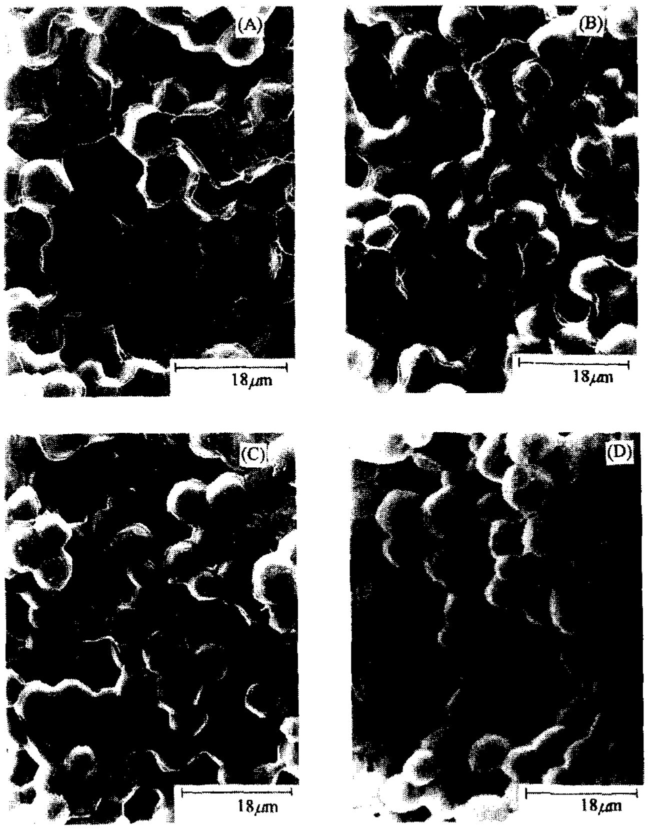


Figure 4 SEM micrographs of the fractured and etched phenoxy/TGDDM/DDS (30/100/30) samples cured for 120 min at 197°C (A), 187°C (B), 177°C (C) and 167°C (D)

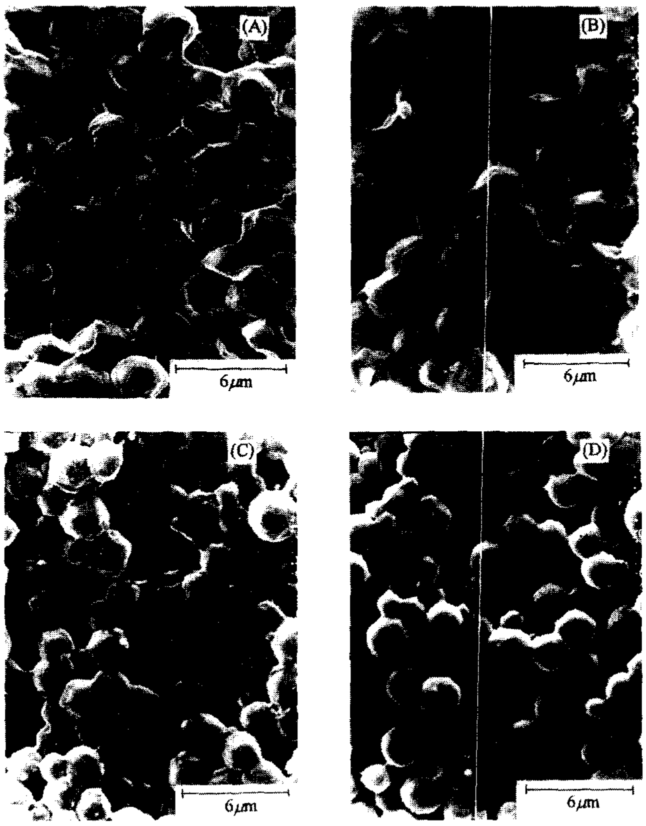


Figure 5 SEM micrographs of the fractured and etched phenoxy/TGDDM/DDS (40/100/30) samples cured for 120 min at 197°C (A), 187°C (B), 177°C (C) and 167°C (D)

for the phenoxy/epoxy samples cured at the higher temperatures (197 and 187°C) demonstrate that the surfaces of the epoxy particles in these two samples remained rough after solvent etching, providing evidence of chemical bonding in the inter-phase boundaries. For the phenoxy/epoxy samples cured at relatively lower temperatures of 167°C or 177°C, the surfaces of the epoxy particles in this case are visibly less rough than for the other two samples (cured at 187 and 197°C).

Another interesting feature should be noted for the morphology of the phenoxy/TGDDM/DDS system. The solvent-exposed epoxy particles seem to be interconnected, rather than discrete and separate. This morphology is similar to that reported for a poly(ether sulfone) (PES) modified epoxy system (DGEBA/diaminodiphenylmethane) by Inoue[25]. Since the epoxy particles are interconnected and surrounded by a continuous matrix of phenoxy, the phase morphology is actually a co-continuous structure, with the epoxy component forming a continuous phase of a connected, globular shape and the phenoxy forming another continuous phase surrounding the connected globules. Experiments were also performed with another solvent as the etching agent. Etching with THF yielded similar results, and the micrographs are not shown. These results all suggest that reactions between the –OH groups of the phenoxy and the residual epoxides might be more complete at higher cure temperatures, leading to stronger inter-phase chemical links between the two phase domains.

Analysis of reaction kinetics

To evaluate possible effects of the phenoxy hydroxyl groups on the cure kinetics and morphology, a basic kinetic analysis was performed. It was assumed that cure of the epoxy/phenoxy mixtures might follow either an autocatalytic or *n*th order mechanistic model. The assumption would then be tested against the experimental data. First of all, a conventional model of autocatalytic cure reactions was assumed and investigated, which for most amine-cured epoxy systems is generally expressed as follows[26–28]:

$$\mathrm{d}\alpha/\mathrm{d}t = \left(k_1 + k_2\alpha^m\right)(1-\alpha)^n \tag{1}$$

where α is the conversion, k_1 and k_2 are the apparent rate constants, and m and n are the kinetic exponents of the reactions. The constant k_1 in equation (1) can be calculated from the initial reaction rate near $\alpha = 0$. The kinetic constants, k_1 and k_2, are assumed to be of the Arrhenius form: $k_1 = A_1\exp(-E_{a1}/RT)$ and $k_2 = A_2\exp(-E_{a2}/RT)$, where A_i is the pre-exponential constant, E_{ai} is the activation energy, R is the gas constant and T is absolute temperature. Detailed kinetic analysis procedures used in this study were similar to those described in our previous studies[13]. Briefly, an iteration approach aided with computer codes was used in obtaining a first guess of the reaction order, n. Equation (1) is re-written as the following form:

$$\ln(\mathrm{d}\alpha/\mathrm{d}t) = \ln\left(k_1 + k_2\alpha^m\right) + n\ln(1-\alpha) \tag{2}$$

or, alternatively, as

$$\ln\left\{\left[(\mathrm{d}\alpha/\mathrm{d}t)/(1-\alpha)^n\right] - k_1\right\} = \ln\left(k_2\right) + m\ln(\alpha) \tag{3}$$

The first term of equation (3) can be computed from the previously estimated values of k_1 and n. If the left term of equation (3) is plotted against $\ln(\alpha)$, a straight line is yielded whose slope and intercept allow the estimation of m, and kinetic constant, k_2, respectively. Preliminary kinetic parameters can be obtained on the first trial. The kinetic parameters, k_2, m and n can be estimated from the stated procedures. To obtain more precise values, an iterative procedure should be utilized. The equation can be further rearranged to give the following form:

$$\ln(\mathrm{d}\alpha/\mathrm{d}t) - \ln\left(k_1 + k_2\alpha^m\right) = n\ln(1-\alpha) \tag{4}$$

The left terms of the above equation can be plotted against $\ln(1-\alpha)$. A new value of the reaction order n can be obtained from the slope. The same iterative procedure can be repeated until apparent convergence of m and n values.

The rate of cure reactions of the phenoxy/TGDDM/DDS mixtures as a function of time are shown in *Figures 6a–6c*. These three diagrams represent the rate curves obtained at three isothermal temperatures, 177, 187 and 197°C, respectively, for the polymer/epoxy mixtures of various compositions from 0 to 40 phr phenoxy. There are several major characteristics in these curves. First of all, these rate curves remain distinctly autocatalytic in nature, regardless of mixing with phenoxy. This result suggests that the hydroxyl groups of the phenoxy polymer did not effect a change in the autocatalytic nature of the epoxy resin. Second, the time at which the maximum reaction rate occurred is seen to decrease steadily with increasing phenoxy content in the polymer/epoxy mixtures. The overall cure reaction rate of the epoxy is apparently enhanced by the presence of these hydroxyl groups. The figures show that the same effect on the cure reaction rate is also observed for all the three isothermal cure temperatures investigated in this study.

Table 1 lists the total heats of cure reactions for all the phenoxy/epoxy mixtures investigated at three isothermal

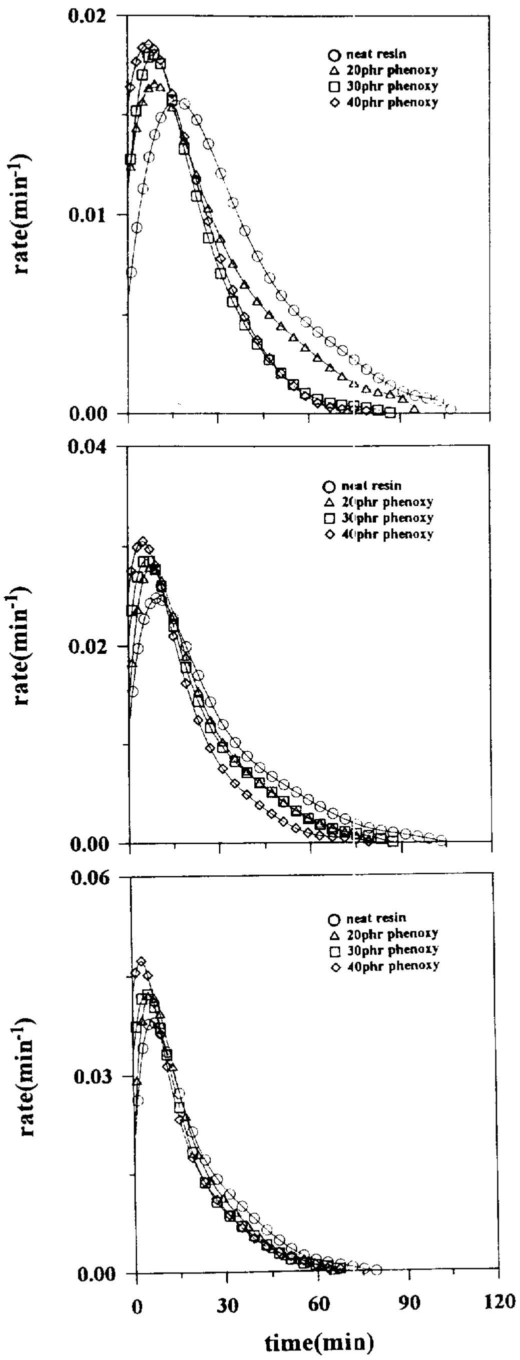


Figure 6 The rate of cure reactions of the phenoxy/TGDDM/DDS mixtures as a function of time at three temperatures: (a) 177°C, (b) 187°C and (c) 197°C. The curve indicates the continuous trend of data, not a model fitting

cure temperatures. The heat of cure at each of the isothermal cures, labelled ΔH_I, was determined by integrating the heat under the peak of isothermal cure exotherm. Owing to vitrification, the cure did not progress to complete conversion. The sample after isothermal treatment was then subjected to d.s.c. heating scans from ambient temperature to 250°C for determining the residual heat of reaction, labelled ΔH_R. The total heat of cure is the sum of ΔH_I and ΔH_R.

The kinetic parameters for the phenoxy/epoxy system were then determined by using the assumed autocatalytic model. Since there are two kinetic constants, k_1 and k_2, two activation energies, ΔE_1 and ΔE_2, could be obtained by plotting ln k_1 and ln k_2, respectively, *versus* $1/T$. The slopes of these plots were then used to estimate the activation energies of these two steps. *Figure 7* shows the plots of ln k_1 or ln k_2 *versus* $1/T$, from which the activation energies for k_1 and k_2 were determined for the pure epoxy as well as for the phenoxy-modified epoxy mixtures.

The rate constants obtained through considerable iteration and graphic procedures are listed in *Table 2*. The reaction orders, m and n, are approximately 0.5–0.7 and 1.0–1.7, respectively. The orders vary slightly with the isothermal temperature, but do not seem to change much with the phenoxy content of the mixtures. The values of ΔE_1 and ΔE_2 obtained in this study for the pure, amine-cured TGDDM epoxy were 97 and 43 kJ mol^{-1}, respectively, which agree reasonably well with those reported in the literature[29].

Compared with the pure TGDDM/DDS epoxy, the amine-cured phenoxy/TGDDM mixtures exhibited lower activation energies (by about 10 kJ mol^{-1}) for k_1. The activation energy for k_2 of the phenoxy/epoxy mixtures remained much the same ($\Delta E_2 = 50$ kJ mol^{-1}) as that of the pure epoxy system. Since k_1 governs the early-stage autocatalytic reaction and k_2 affects the reaction after the initial autocatalytic stage, this suggests that the rate increase might be due to an accelerated autocatalytic process at the

Table 1 Heats of cure reaction for phenoxy/epoxy/DDS mixtures

Cure temperature (°C)	Phenoxy in mixtures (phr)	ΔH_0 (J g^{-1})	ΔH_R (J g^{-1})	ΔH_T (J g^{-1})	α (%)
177	0	381.9	138.8	520.7	73.3
	20	237.7	138.0	375.7	63.3
	30	186.6	167.3	353.9	52.7
	40	200.9	161.6	362.5	55.4
187	0	522.0	62.3	584.3	89.4
	20	367.5	81.1	448.6	81.9
	30	322.3	74.1	396.4	81.3
	40	250.9	95.2	346.1	72.5
197	0	525.0	14.0	539.0	97.4
	20	375.2	27.2	402.4	93.2
	30	317.4	40.7	358.1	88.6
	40	329.0	34.4	363.4	90.5

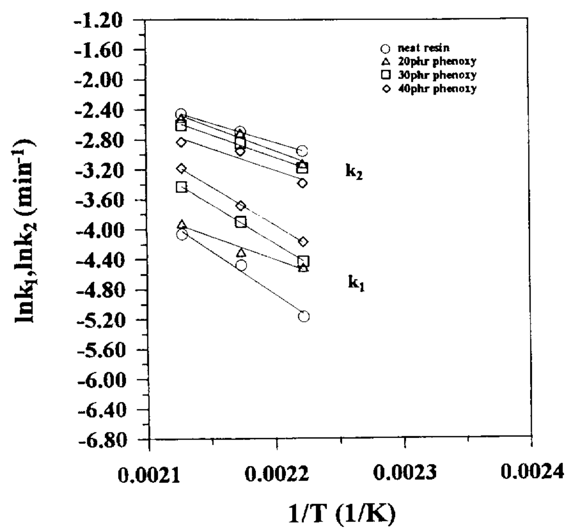


Figure 7 Plot of ln(k_1) and ln(k_2) against $1/T$ for pure TGDDM/DDS epoxy sample and 20, 30 and 40 phr phenoxy-modified systems

Table 2 Model constants for cure kinetics of phenoxy-modified TGDDM/DDS systems

T (°C)	m	n	$k_1 \times 10^3$ (min^{-1})	$k_2 \times 10^3$ (min^{-1})	ΔE_{a1} (kJ mol^{-1})	ΔE_{a2} (kJ mol^{-1})	ln A_1	ln A_2
Pure TGDDM/DDS								
177	0.69	1.65	5.7	52.2	97.1	43.4	20.8	8.7
187	0.66	1.38	11.3	67.7	97.1	43.4	20.8	8.7
197	0.58	1.04	17.1	85.5	97.1	43.4	20.8	8.7
20 phr phenoxy in epoxy/DDS								
177	0.69	1.89	11.1	44.2	51.8	53.5	10.3	11.2
187	0.59	1.56	13.5	66.6	51.8	53.5	10.3	11.2
197	0.53	1.15	19.9	81.0	51.8	53.5	10.3	11.2
30 phr phenoxy in epoxy/DDS								
177	0.61	1.74	11.9	41.5	87.8	50.7	19.1	10.4
187	0.65	1.63	20.2	58.0	87.8	50.7	19.1	10.4
197	0.67	1.42	32.4	73.9	87.8	50.7	19.1	10.4
40 phr phenoxy in epoxy/DDS								
177	0.73	1.60	15.5	33.9	87.0	48.8	19.1	9.7
187	0.68	1.68	25.1	52.0	87.0	48.8	19.1	9.7
197	0.66	1.37	41.6	59.0	87.0	48.8	19.1	9.7

initial stages. This is just the opposite to the case of the PEI-modified epoxy system[19], where the PEI component exhibits no catalytic effect and the rate increase is confined to the later-stage reaction. The post-phase separation rate increase in the PEI/TGDDM/DDS system has been attributed to DDS aggregation in the epoxy-rich phase during cure.

The autocatalytic kinetic model and the rate constants obtained (*Table 2*) were then used to calculate empirical curves of conversion *versus* time for the phenoxy/epoxy mixtures of various compositions at the three isothermal cure temperatures. *Figures 8a–c* show that the empirical conversion curves fit the experimental data quite well up to the vitrification point. Apparently, the mechanistic model describes the cure kinetics well but diffusion of species might be a controlling factor in the vitrified state, which limits the reactions from going any further. After vitrification, the progress in the cure reaction almost comes to a stop and therefore the extent of cure is limited[30,31]. This indicates that the cure kinetics in the later stage were indeed subjected to diffusion control as a consequence of vitrification.

Roles of phenoxy hydroxyl groups

Earlier, by performing *FT*i.r. characterization on phenoxy/TGDDM mixtures (no hardeners) subjected to several cure temperatures[22,23], it was shown that the phenoxy hydroxyl groups exert little effect on epoxide ring opening. In this study, the kinetics results further suggested that the autocatalytic nature of epoxy cure was preserved in the phenoxy/epoxy/DDS mixtures, and that catalytic effects of phenoxy –OH were not found to be significant in this system. In essence, this is to say that during early stages of cure of the phenoxy/TGDDM/DDS mixtures, the phenoxy –OH groups exhibit little reactivity toward TGDDM monomers or polymerizing TGDDM–DDS oligomers. Although the phenoxy/TGDDM/DDS mixtures were initially homogeneous and the components were intimately mixed in one phase, the phenoxy molecules stayed out of the initial cure reactions (between TGDDM and DDS) until phase separation was initiated, beginning at relatively low conversions. Once phase separation started, the polymeric phenoxy component was gradually expelled from the crosslinking epoxy–DDS domains. That is, the phenoxy –OH groups do not participate in the cure reaction within the bulk of epoxy–DDS. This conclusion could be partially demonstrated in the above cure kinetics analysis.

Chemical links between phase domains

After the phenoxy was expelled from the epoxy domain and DDS was almost depleted during the later stages of cure, the residual epoxide groups—upon proper catalysing effects—might exhibit reactivity towards the phenoxy hydroxyl groups. An epoxide reaction that is known to occur at later-stage cure is etherification[32], which is the reaction between an epoxide and the –OH group of the intermediate epoxy products from addition reactions with the amine. This reaction usually occurs at the later stages of cure, where the amine functional groups have been depleted. Additionally, etherification can occur intermolecularly to form crosslinks or intramolecularly to form cyclic rings (cyclization).

For the phenoxy/TGDDM/DDS system, upon cure, the phenoxy component was indeed gradually excluded from the crosslinked epoxy–DDS network and eventually a phase-separated morphology resulted. Similar phenomena have also been found in most other polymer-modified epoxy systems. In the phenoxy/TGDDM/DDS system, phase separation took place early on, before the gel state was reached. A similar phase separation phenomenon has also been reported for a PEI/TGDDM/DDS system[13], where phase separation takes place when the cure extent reaches only 5–10%. As the cure progresses in the PEI/TGDDM/DDS mixtures, phase separation becomes more evident and the morphology undergoes a gradual transformation. In this study, similar phenomena were also observed for the phenoxy/epoxy network system, except that its final morphology is different from that of the cured PEI/epoxy system. A major thermodynamic difference between these two systems is in the solubility parameters of phenoxy *versus* PEI. More specifically, the phenoxy molecules contain –OH groups which, owing to their delayed reactivity with the epoxides until domain formation after phase separation, may restrict the sites of chemical links within the inter-domain regions of the thermoset epoxy and thermoplastic phenoxy.

Interestingly, the SEM micrographs showed that inter-domain links were more evident in the phenoxy/TGDDM/DDS system, but not in the phenoxy/DGEBA/

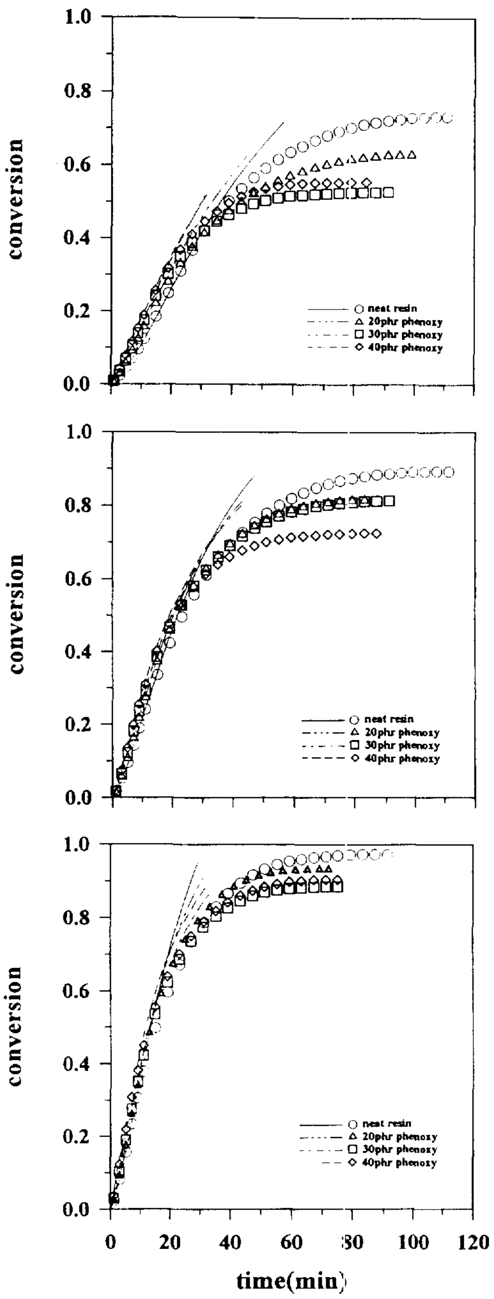
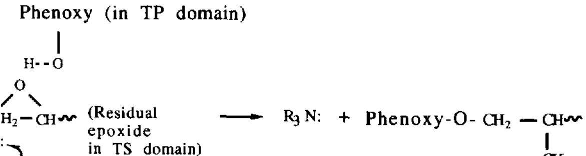


Figure 8 Fitting of the model—calculated conversion–time curves with the experimental data at three temperatures: (a) 177°C, (b) 187°C and (c) 197°C

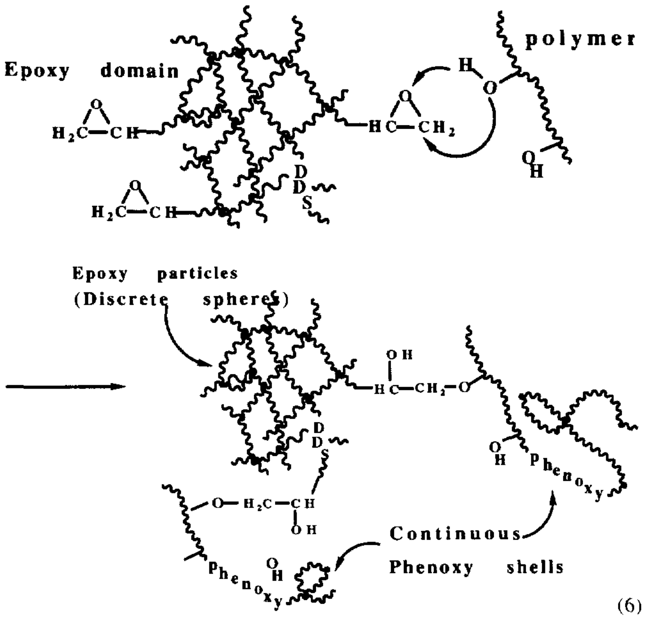
DDS counterpart, which has been demonstrated in one of previous reports[23]. The differences are clear. The TGDDM molecules possess a tertiary amine structure while DGEBA does not. In addition, at the same content of hardener (DDS at 30 or 40 phr to epoxy weight) used in both systems, the one with tetrafunctional TGDDM epoxy is more likely to possess residual epoxide groups than the other with difunctional DGEBA during the later stages of cure. However, during later stages of cure, phase separation has resulted in a morphology of two distinct domains of crosslinked epoxy–DDS and thermoplastic phenoxy, respectively. Thus, hydroxyl exchange, if occurring between the epoxide and phenoxy –OH, is restricted to the inter-domain regions. A likely mechanism leading to hydroxyl exchange between the residual epoxide and the –OH groups of phenoxy, with a catalysing effect from the TGDDM molecules of a tertiary amine structure, is proposed as follows:



(5)

As shown above, with a catalysing effect from the tertiary amine (TGDDM), the epoxide groups (with DDS being depleted) can be opened and reacted with the phenoxy hydroxyls, leading to inter-domain links between the epoxy and phenoxy phase boundary.

With the catalysed hydroxyl exchange reaction taking place during the later stage of cure, a chemical link across the two domains can be anticipated. The following schematic equation illustrates how a unique inter-domain morphology with mutually interlinked epoxy–polymer phases can be built[23]:



(6)

As the cure approached later stages where the epoxide concentrations in the curing network might be significantly depressed, the phenoxy –OH groups (now confined primarily in the exterior surfaces of continuous shells of phenoxy domains) begin to react with the residual epoxide groups of the epoxy network chains. Note that these were confined at the outer surfaces of the spherical epoxy phase domain. Subsequently, in the interfaces of the phase-separated domains, the pendent –OH groups of the phenoxy domain began to react with the residual epoxide groups of the epoxy/DDS networks. A competition thus may occur between intramolecular reaction of the residual epoxide with –OH in the crosslinked epoxy *versus* inter-phase reaction between epoxide of the epoxy phase and –OH of the phenoxy phase. Accordingly, cure reaction mechanisms might be altered. Furthermore, reactivity of the –OH in the phenoxy polymer with the epoxy molecules might also affect the morphology of the finally cured polymer/epoxy networks. It may be expected that the interfaces of the polymer domain and the epoxy domain might be chemically interlinked through the pendent –OH groups of the phenoxy. This was justified by the results of SEM morphological characterization.

CONCLUSION

Effects of the hydroxyl group (–OH) of a polymeric phenoxy on the cure reactions and network morphology of a crosslinking epoxy/phenoxy system were examined in this study. An autocatalytic reaction kinetic model was found to describe the cure behaviour of the phenoxy/TGDDM/DDS mixtures up to the vitrification point. Although the reaction mechanism of the phenoxy/epoxy system remained autocatalytic and unchanged, the initial cure reaction rates of the phenoxy-modified epoxy were found to be comparatively higher than that of the pure epoxy, suggesting that the –OH group in the phenoxy chains exerts a catalytic effect for epoxide ring opening.

At initial stages of cure where DDS (curing agent) was still abundant, the phenoxy –OH groups showed little reactivity towards the epoxide. Thus, the –OH groups in the phenoxy did not react with the epoxide groups of the epoxy during the pre-gel stages of cure. As a result of lack of chemical bonding between the phenoxy and epoxy components, phase separation readily took place in the originally homogeneous mixtures as the epoxy was being cured by the amine to form a distinct crosslinked phase of spherical domains. In the meantime, as the epoxy/DDS component reacted to form a crosslinked domain in the curing network, the phenoxy component was gradually expelled to form a distinctly separate phase. The morphology of the cured epoxy/phenoxy network exhibited a systematic variation with changes of phenoxy content in the polymer/epoxy mixtures. The phenoxy component became the discrete domain (about 1 μm or less) at low phenoxy contents ($<$ 10 phr). An islands-and-sea (partial phase inversion) morphology was observed for the samples with 10–20 phr phenoxy. For mixtures with the phenoxy content equal to or greater than 30 phr, the phenoxy component formed the continuous phase with the epoxy component being dispersed as tiny, connected, globular particles. This phenomenon was designated as complete phase inversion. Furthermore, the discrete epoxy particles were found to be dependent on the phenoxy volume fraction constituting the continuous domain. The same trend has been found in many other cured thermoplastic/epoxy networks. The only difference is in the values of critical TP volume fraction at which complete phase inversion is initiated. In addition, the average particle sizes of the discrete epoxy domain vary for different TP or epoxy components. At later cure stages as DDS was sufficiently depleted, phase boundaries between the TP phenoxy and crosslinked epoxy domains gradually became distinct. Only at this stage did the –OH groups of the the phenoxy phase domain begin to react with the residual epoxide groups in the epoxy domains. The morphology in the phase boundary was found to be influenced by the reactivity of the phenoxy –OH groups and the residual epoxide groups of the epoxy domain surfaces. The later-stage reactions between –OH and residual epoxide groups in the gradually vitrified network, however, were confined in the phase boundary regions owing to the existence of relatively immobilized chains at these stages of cure. These later-stage exchange reactions led to chemical bonding between the continuous phenoxy-rich and spherical epoxy-rich domains.

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