Polymer Vol. 39 No. 17, pp. 4115–4122, 1998
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0032-3861/98/$19.00+0.00

PII: S0032-3861(97)10376-7

Effects of network segment structure on the phase homogeneity of crosslinked poly(ethylene oxide)/epoxy networks

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(Received 1 September 1997; revised 2 December 1997; accepted 2 December 1997)

Differential scanning calorimetry (d.s.c.), optical microscopy and scanning electron microscopy (OM and SEM), and Fourier Transform infrared (*FT*i.r.) studies have been performed to demonstrate several cases of cured poly(ethylene oxide)/(diglycidylether of bisphenol-A) epoxy networks. To evaluate effects of structural change of the crosslinked epoxy segments on the morphology of polymer/epoxy networks, three different types of hardening agents were used. An interesting miscible phase was observed in aromatic amine-cured PEO/DGEBA and anhydride-cured PEO/DGEBA. Structurally, it can be viewed that the PEO chains interpenetrate with entanglement into the crosslinked epoxy network. Thermodynamically, the glass transition results indicate that the PEO chains also intimately mingle with the epoxy-DDS network chain segments to achieve a homogeneous solid state. By comparison, aliphatic amine curing led to phase separation. Apparently, different structure of hardeners led to different chain segments of cured epoxy, which in turn could influence the ultimate phase morphology of cured PEO/epoxy solids. For the miscible polymer/epoxy networks, the cure temperature (thus cure kinetic rate) was found to exert no effects on influencing phase homogeneity. Factors controlling homogeneity of polymer/epoxy after cure were studied and discussed in this report. © 1998 Published by Elsevier Science Ltd. All rights reserved.

(Keywords: epoxy; miscibility; phase separation; PEO)

INTRODUCTION

Linear polymer–polymer blend systems have been of interest and widely studied. On the other hand, linear polymer–thermosetting polymer systems are relatively less understood. Miscible systems comprising of crosslinked thermosets and linear thermoplastics (amorphous or semi-crystalline) have been comparatively rare in comparison with polymer–polymer systems. Most initially homogeneous mixtures of polymers/epoxy eventually yield a phase-separated morphology upon sufficient curing. Most linear polymer-modified thermosetting resin systems that have been studied and reported in the literature exhibit a complex morphology, which can change rapidly with the state of cure starting early at initial curing. Upon reaching the gel point, the morphology is largely set and does not change much at further extended curing. Composition (polymer/thermoset ratios) significantly influences the final state of morphology, and phase continuity inversion has been common as the polymer content is changed. The critical content at continuity inversion can, however, be significantly different for different polymer/thermoset systems. Using an aromatic amine-cured poly(ether imide, PEI)/epoxy as the model system, a typical example of morphology development has been described in a recently published report by Woo *et al.*[1] Other than the extreme compositions, the morphology of PEI/epoxy intermediate compositions consists of inverted phase-in-phase domains, which can be viewed as partial inversion of phase continuity. The major characteristic of 'partial inversion' is more or less similar for most cured polymer/epoxy systems, which consists of scattered 'islands' representing PEI-rich phase domains, wherein the epoxy component is present as discrete spherical particles surrounded by the PEI-phase islands. These PEI/epoxy islands are in turn occluded by a much larger epoxy continuous phase domain. At low PEI contents below the intermediate compositions, the cured PEI/epoxy networks exhibited a discrete PEI/continuous epoxy structure, while at high PEI contents above the intermediate compositions of partial inversion, a complete inversion of phase continuity dictates the morphology, in which the epoxy exists as discrete spherical particles surrounded by continuous PEI domain.

A previous study[2] has demonstrated a poly(methyl methacrylate)/epoxy system can exhibit complete phase inversion at relatively low thermoplastic polymer (PMMA) loading. Other systems may require higher polymer contents for complete phase continuity inversion. It is interesting to note that a cured phenoxy/epoxy (diglycidyl ether of bisphenol-A) eventually develops a phase-separated network[3]. This is surprising if one considers that the chain structure of the linear phenoxy polymer is almost identical to that of the DGEBA epoxy chain segments; furthermore, phenoxy is capable of interacting with the epoxy network through potential hydrogen bonding between the hydroxyl groups. From the open literature, it is known that the number of miscible polymer/thermoset systems is much less than that of polymer–polymer systems. This dictates that factors governing the phase structure in crosslinked polymer/epoxy are probably more strict and perhaps different. Complete homogeneity, either due to physical miscibility or chemical copolymerization, in cured polymer/epoxy is rare. A recent

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report from our laboratory has revealed the detailed chemical reaction mechanisms in a rare homogeneous network formed by co-curing epoxy/DDS with bisphenol-A polycarbonate, with chemical exchange reactions between the epoxy and PC molecules[4]. In this system, PC is believed to undergo extensive transreactions or co-polymerization with the epoxy molecules during cure.

Ploy(ethylene oxide) is known to exhibit strong specific interactions and miscibility with several polymers possessing functional acid groups, such as poly(acrylic acid)[5] and poly(methacryic acid)[6]. In most of these miscible systems comprising PEO, complexion due to strong acid hydroxyl groups has been suggested. PEO is otherwise not known to form many miscible systems with polymers with non-acid hydroxyl groups. One known exception is the miscible polyblend of PEO with poly(hydroxyl ether of bisphenol-A) (phenoxy)[7,8]. Epoxy resins in general, or specifically DGEBA-type epoxies, possess a structure similar to phenoxy. It would be interesting to investigate the phase behaviour in crosslinked PEO/epoxy network. Lately, polyether-type polymers, such as polyacetal (polyoxymethylene) or poly(2,6-dimethyl-1,4-phenylene oxide), etc[9,10]. have been incorporated with crosslinking epoxy resins to investigate the phase structure of resulting cured networks. The results have shown that they yield a phase-separated morphology. However, another polyether, poly(ethylene oxide), has been demonstrated to exhibit miscibility with DGEBA cured with 4,4′-diaminodiphenylmethane (DDM)[11].

Using poly(ethylene oxide) (PEO) as a model polymer to be incorporated with an epoxy network, this study attempted to probe molecular structure factors that may influence the ultimate phase morphology in cured polymer/epoxy network. The same base epoxy was used while several different hardeners were investigated to assess their effects on the cure network phase behaviour. This paper reports on an interesting phenomenon of complete miscibility in aromatic amine-cured poly(ethylene oxide)/epoxy networks in one example case, as well as in an anhydride-cured network in another case, but complete phase separation in other cases when a different amine hardener was used. Factors relating to the rare miscibility in this crosslinked epoxy/polymer system are discussed. In addition, structural factors of curing agents controlling phase homogeneity in the cured PEO/epoxy networks were investigated and reported. The role of specific interactions *versus* structural polarity match is discussed.

EXPERIMENTAL

Materials

Poly(ethylene oxide) was obtained from a specialty laboratory polymer supplier (Polymer Science, Inc., $M_w = 2 \times 10^5$ g/mol, M.P. = 62–67°C), and was used in the as-received state. The epoxy resin used in this study was diglycidylether of bisphenol-A (DGEBA) (Epikote-828, Shell Corp., USA), with a degree of oligomerization $n = 0.12$ and an epoxide equivalent weight of 187 g.

For curing the PEO/epoxy mixture resins, this study first employed one of the commonly used curing agents, 4,4′-diaminodiphenylsulfone (DDS, Ciba-Geigy, HT-976) with an amino hydrogen equivalent weight of 62 g. When used at 30 phr of DDS per 100 parts of DGEBA, the stoichiometric amino-H/epoxide ratio is 0.91 for the DDS/DGEBA. DDS (30 phr) was used in most samples of DDS-cured PEO/epoxy samples; however, for comparison purposes, DDS was also used at higher loading (up to 40 and 50 phr). This was indicated specifically wherever a different DDS phr was used in curing. As the hardener molecules eventually become part of the cured network through cure reactions, it can be expected that structural changes can be effected by simply changing the type of curing agents. Thus, other curing agents were also investigated while the epoxy resin was kept the same. One was an aliphatic amine, diethylene triamine (DETA) (Lancaster Chem. Co.) with a H-equivalent wt. of 17.2 g, and the other was an aromatic anhydride, pyromellitic dianhydride (PMDA, Tarde Chem. Co.).

Preparation

PEO was weighed, pulverized, and mixed in a pre-determined quantity of the epoxy resin at 100–120°C temperature by hot-melt blending until the liquid epoxy/polymer mixtures appeared homogeneous. The curing agent (DDS, in powder form) was then added into the liquid mixture, and mechanical mixing was continued on the epoxy/polymer/DDS for a few more minutes until the ternary mixtures appeared homogeneous. The as-blended (by hot melting, no solvent) epoxy/polymer/DDS mixtures appeared to be homogeneous and visually transparent, indicating no phase separation prior to curing with the hardener agent. The stoichiometry of the DDS used to cure the epoxy/PEO mixtures was fixed at 30 phr (parts per 100 parts) to the base epoxy resin. At 30 phr DDS to the epoxy, it is equivalent to 0.61 stoichiometry of amino-H/epoxide for the TGDDM/polymer/DDS system and 0.91 for the DGEBA/polymer/DDS one. The compositions of PEO in the mixtures were varied between 0 and 70 phr to the base epoxy resin. It became difficult to melt-blend the mixtures as PEO loading in the epoxy mixtures was greater than 70 phr. Curing of the epoxy/PEO/DDS mixtures was performed at 177°C for 4 h. For comparison, some samples were cured at 187°C for 4 h. Thermal and morphology characterization was then performed on the cured samples.

Apparatus

Fourier transform infrared spectroscopy (*FT*-i.r., Nicolet Magna-560) was used for investigating possible molecular interactions between the constituents. Spectra were obtained at 4 cm^{-1} resolution, and averages were obtained from at least 64 scans in the standard wavenumber range of 400–4000 cm^{-1}.

The glass transition temperatures and other thermal transitions of the epoxy/PEO mixtures before and after curing with the hardener were measured with a differential scanning calorimeter (Perkin-Elmer DSC 7). All d.s.c. measurements of glass transition 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.

The morphology of the fracture surfaces of the amine-cured epoxy/PEO networks was examined using a scanning electron microscope (SEM, Model JEOL JXA-840). The samples of crosslinked networks of various compositions were fractured across the thickness and coated with gold by vapour deposition using a vacuum sputterer prior to SEM characterization.

In addition, a polarized-light optical microscope (Nikon Optiphot-2 POL) with UFX-DX automatic exposure was used to confirm the phase structure of the polymer mixtures before and after curing. The objective was to examine the optical homogeneity of the epoxy/PEO mixtures before and after curing was examined to provide additional evidence of phase structures. Heating and temperature control were provided by using a microscope heating stage (Linkam THMS-600 with TP-92 temperature programmer). The samples were placed between two micro glass slides, which were then heated at constant temperatures and gently pressed until the liquid polymer/epoxy mixtures was made into thin films. The liquid mixture was cured in the final form of thin solid films on the heating stage and ready for examination.

RESULTS AND DISCUSSION

Cure network morphology

The morphology of cured epoxy/PEO networks was first preliminarily examined using optical microscopy. The cured networks of all compositions appeared visually transparent and homogeneous. The resulted micrographs are plain with no discernible phase boundary at 800 × , and thus not shown. This is similar for the samples of four different PEO contents in the PEO/epoxy networks (177°C cured for 4 h): 10, 30, 50 and 70 phr. The optical micrographs show that all compositions investigated are transparent and homogeneous with no discernible phase boundaries, indicating no apparent phase separation.

In addition, the fractured surfaces of the PEO/epoxy cure networks were examined using scanning electron microscopy (SEM) to provide further evidence of phase homogeneity across the sample thickness. *Figure 1* shows the SEM micrographs of the fracture surface of the 10-and 30-phr PEO/epoxy networks (cured at 177 and 187°C, respectively, for 4 h). for both cure temperatures, the fracture surfaces demonstrate that the morphologies of DDS-cured PEO/epoxy samples are all homogeneous and similar to that of neat cured epoxy/DDS sample.

Furthermore, SEM was also performed on other compositions of DDS-cured PEO/epoxy network samples, 10 and 50 phr PEO, respectively. The SEM micrographs are all similar to those in *Figure 1* and not shown again here. The morphology of the fractured surfaces of these other compositions was all similarly homogeneous, demonstrating no discernible phase separation within the resolution limit of SEM. Note that these SEM microscopy results were for the as-fractured samples of cured PEO/epoxy. To further demonstrate that the evidence of no phase separation was not obscured by lack of depth or shade contrast, the as-fractured samples were etched with dichloromethane (a good solvent for PEO) before additional SEM examination was performed.

SEM was also performed on the samples of cured 30- and 50-phr PEO/epoxy that were further etched with dichloromethane (a good solvent for PEO) to more clearly expose the PEO domains if existing. The samples again exhibited a homogeneous structure (not shown for brevity), further indicating that the PEO component is dispersed in a homogeneous state with the crosslinked epoxy network. Similarly, other compositions (e.g., 10-phr PEO) were also investigated, and the resulting SEM micrographs are all similar and thus not shown again. Had the PEO component been in phase-separated domains, the SEM examination on the solvent-etched PEO/epoxy networks would have revealed craters (cavities) of various sizes occupied by the PEO component, which presumably can be easily etched out and dissolved in the solvent. The fact that the etched

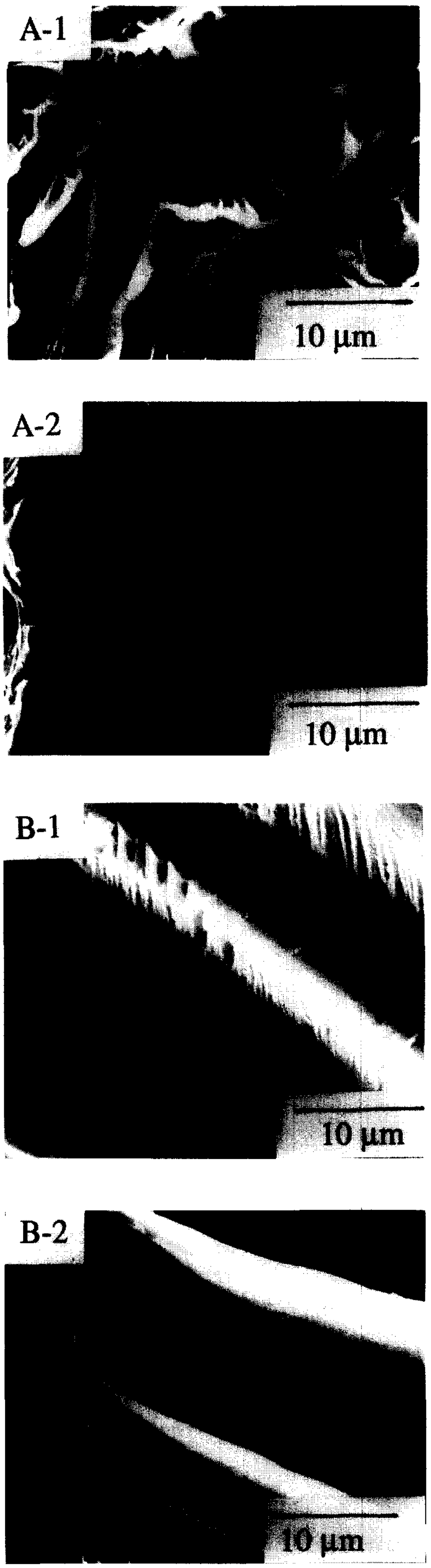


Figure 1 SEM micrographs of the fracture surface of the DDS-cured PEO/epoxy samples: (A-1) 10-phr PEO and 177°C cure; (A-2) 10-phr PEO and 187°C cure; (B-1) 30-phr PEO, 177°C cure; and (B-2) 30-phr PEO and 187°C cure, all cured for 4 h

morphology of the cured PEO/epoxy is smooth and homogeneous demonstrates that the polymeric PEO chains are molecularly dispersed in the crosslinked epoxy network.

Glass transition behaviour

Figure 2 shows the d.s.c. thermograms for the 30-phr DDS-cured PEO/epoxy samples (177°C cured for 4 h) of 10-, 30-, 40-, 50-, and 70-phr PEO contents (top to bottom), respectively. Other than being slightly broadened, a single T_g that is also composition-dependent within the range investigated (10–70-phr PEO) can be easily seen in the DSC curves. Note that the minor tiny peak at about 60°C is associated with the melting of trace crystalline phase of PEO, which is observed only in the cured PEO/epoxy samples with higher PEO contents (e.g., greater than 40 phr). Thus, other than trace amount of crystalline PEO that may exist in a separate crystalline phase, the amorphous portion of linear PEO polymer chains is in a miscible state with the crosslinked epoxy network. Structurally, it can be viewed that the PEO chains interpenetrate with entanglement into the crosslinked epoxy network. Thermodynamically, the PEO chains also intimately mingle with the epoxy-DDS network chain segments to achieve a homogeneous solid state.

The same compositions were cured at a slightly higher temperature of 187°C and the glass transition was characterized again. A similar single T_g was revealed in each of those investigated. In general, cure temperatures other than 177°C were investigated and it was found that all other cure temperatures similarly led to a miscible interpenetrating network of linear PEO/crosslinked epoxy. On the other hand, for phase-separated polymer/epoxy networks, earlier studies[1–3] (phenoxy, PMMA, etc.) have demonstrated that cure kinetics can influence the domain sizes, especially in the composition range where complete phase inversion takes place. The crosslinked epoxy component is inverted (from an original continuous phase) into discrete particles surrounded by a continuous linear-polymer phase. The particle sizes have been reported to change slightly with the cure temperatures.

Regarding the composition dependence of the glass transition temperature of the DDS-cured PEO/epoxy networks, additional clarification must be provided to exclude the effect of changing DDS concentration as the PEO is added into the epoxy formulation. Some may argue that, in addition to the molecular chain interaction effect that may cause changes in the network T_g, the presence of PEO may cause dilution of the hardening agent, which may induce an independent down shift of the network T_g. First of all, it must be pointed out that the hardening agents do not react with the polymeric PEO molecules. Although adding PEO into an epoxy/hardener mixture may result in a lower volume fraction of the hardening agent in the PEO/epoxy/hardener mixture, the amino-H/epoxide ratio is not altered.

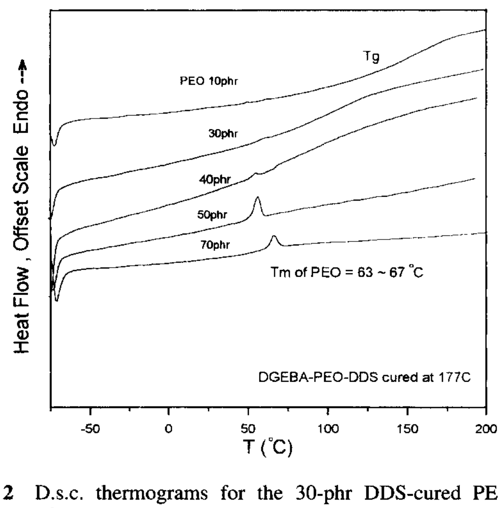


Figure 2 D.s.c. thermograms for the 30-phr DDS-cured PEO/epoxy samples (177°C cured for 4 h) of 10-, 30-, 40-, 50-, and 70-phr PEO contents (top to bottom)

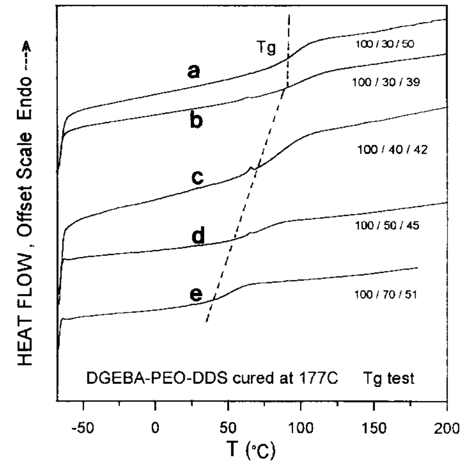


Figure 3 T_g results of these DDS-cured PEO/epoxy samples of various epoxy/PEO/DDS compositions as indicated (*a*) 100/30/50, (*b*) 100/30/39, (*c*) 100/40/42, (*d*) 100/50/45, and (*e*) 100/70/51, all cured at 177°C for 4 h

To verify this, several polymer/epoxy compositions were prepared and characterized to demonstrate how T_g may shift in cases involving re-adjustment of the hardener loading in order to account for decreased volume fraction of the hardener in the PEO/epoxy/DDS system. In one case, the PEO content was fixed at 30 phr in the PEO/epoxy/DDS mixture and the DDS was varied at two different levels: 39 and 50 phr. D.s.c. was then performed on these two cured samples (both cured 177°C for 4 h). The d.s.c. thermograms (*a*) and (*b*) in *Figure 3* show the T_g result of these two cured compositions. Apparently, the T_g values of these two cured 30-phr PEO/epoxy network compositions are similar, nevertheless the DDS concentrations are different ((*a*) DDS = 50 phr; (*b*) DDS = 39 phr). T_g characterization was also performed on a series of PEO/epoxy/DDS samples which were prepared where the DDS loading was adjusted in accordance with the increasing PEO content, so that the volume fraction of DDS in the PEO/epoxy/DDS mixtures remained approximately the same. Thus for PEO contents of 30, 40, 50, and 70, respectively, in the mixtures, the DDS was loaded at 39, 42, 45, and 52 phr. The calculated volume fraction of DDS in the mixtures was at an approximate constant of 0.23 for all four compositions. The T_g results are shown in *Figure 4* (curves *b–e*), which illustrate that, regardless of the adjustment of DDS concentration, the T_g of the cured networks decreases monotonously with increasing PEO content. The slanted dashed line intersecting with the four d.s.c. curves indicates where the onset T_g would be for each of the four indicated network compositions. Clearly, the T_g decrease is dependent on the increasing PEO content.

Interestingly, if one compares the d.s.c. curves in *Figure 3* with those in *Figure 2*, a difference in the clarity of transition signal can be observed. In general, *Figure 2* shows that as PEO content is increased, the T_g decreases but the transition signal becomes gradually less apparent. The T_g transition appears to be somewhat more 'broadened' as a result. However, by observing the d.s.c. curves in *Figure 3*, one finds that if the decreased DDS volume fraction is compensated for by increasing DDS in proportional to the increased PEO content, the transition signal sharpness is enhanced. The temperature location of T_g remains the same for the compositions of the same PEO content regardless of increased DDS. Clearly, the network T_g, is dependent on the PEO content but not the DDS. The compensated adjustment of DDS, however, helped to enhance the sharpness and restrict the breadth of the T_g transition.

Figure 4 shows a plot of T_g–composition dependence for the DDS-cured PEO/DGEBA network system (DDS = 30 phr, 177°C cured 4 h). In this figure, the on-set value of glass transition was used as T_g. Interestingly, the T_g dependence on composition for this system appears to be quite smooth and symmetric. This glass transition result further suggests that the cured PEO/epoxy networks are distinctly homogeneous and miscible. Note that the T_g data for the DDS-cured PEO/epoxy compositions with greater PEO contents are not available due to experimental difficulty in preparing those samples. However, within the experimentally obtainable range of compositions (0–70-phr PEO), the T_g data are quite consistent and yield a clear trend of monotonous decrease with increasing PEO content in the cured PEO/epoxy networks.

Note on the same graph, two commonly known empirical T_g models (Fox and Gordon-Taylor equations) were also plotted for comparison. Although not by significant deviation, the composition dependence relationship for this system is slightly over-predicted by the Fox equation[13]: $1/T_g = \omega_1/T_{g1} + \omega_2/T_{g2}$. Another model, the Gordon-Taylor equation, has been commonly used for describing the T_g–composition relationship of miscible systems[14]:

$$T_g = (\omega_1 T_{g1} + k\omega_2 T_{g2})/(\omega_1 + k\omega_2) \qquad (1)$$

where ω_i is the mass fraction of component i, and $k = \Delta C_{p2}/\Delta C_{p1}$, i.e., ratio of heat capacity change of PEO polymer (i = 1 for the low-T_g component, T_{g1} = − 57°C) to the change of crosslinked DGEBA (i = 2 for the high-T_g component, T_{g2} = 172°C) at T_g of polymer/epoxy network. The extra parameter (k) in the Gordon-Taylor equation allows one more additional dimension of adjustment than the Fox equation, and the value of k has been suggested to correlate with the intensity of interaction forces between the constituent molecular segments[15]. Best fitting was performed by fitting the Gordon-Taylor equation with the T_g data, and the best-fitted value of parametric k was found to be 0.39. The low-to-medium value of k suggested that the interaction forces were only moderate at the best. A quick inspection of the molecular structures of the crosslinked epoxy network and PEO reveals that potential hydrogen bonding might exist between potential group pairs, such as –OH of epoxy and the ether group (–O–) of PEO. However, structural hindrance due to rigid crosslinked epoxy chains might have limited the accessible number of specific interactions that can be expected. Another contribution to the observed miscibility might have been due to close match between the molecular polarities of PEO and epoxy. The matched polarity may be sufficient to result in physical miscibility, but probably not enough to generate significant specific interactions.

Similarly, the T_g data of the same PEO/DGEBA system cured at a higher temperature of 187°C were plotted. *Figure 5* shows such a plot of T_g–composition dependence for the DDS-cured PEO/DGEBA network system (DDS = 30 phr, 187°C cured 4 h). This glass transition result is similar to that in the previous figure for the 177°C-cured data. Note that the cure rates are substantially different for these two cure temperatures. Yet the phase behaviours of both systems are distinctly the same, indicating that cure kinetic rates were not a dominating factor in affecting the phase structure. Evidently, the thermodynamic factor is overwhelmingly favouring phase homogeneity. A fitting with the Gordon-Taylor equation led to a new value of parametric k = 0.40, which is almost the same as the value (k = 0.39) for the 177°C-cured system (*Figure 4*), suggesting that the intermolecular interaction forces were likely similar for the networks cured at these two different temperatures.

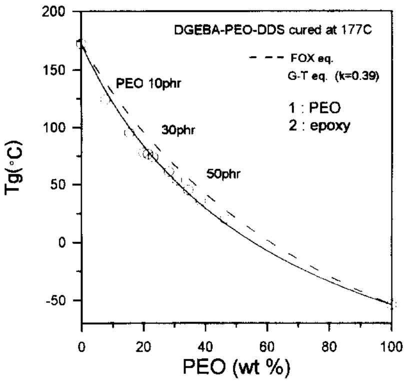


Figure 4 Plot of T_g–composition dependence for the DDS-cured PEO/DGEBA network system (DDS = 30 phr, 177°C, 4 h). Gordon-Taylor and Fox equations are also plotted for comparison

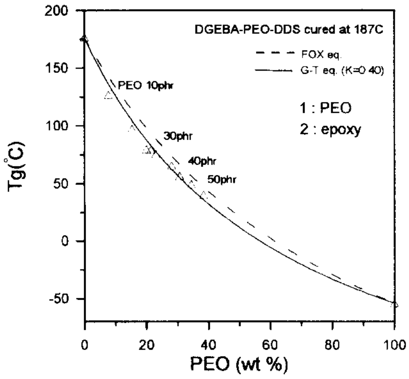


Figure 5 T_g–composition dependence for the DDS-cured PEO/DGEBA network system (DDS = 30 phr, 187°C, 4 h). Gordon-Taylor and Fox equations are also plotted for comparison

Effect of structures of epoxy and curing agents

The phase structure was investigated on the systems where aliphatic amine curing agents were used to cure the PEO/epoxy mixtures. Diethylene triamine (DETA) was used to cure the PEO/DGEBA mixtures of several different compositions. Instead of phase homogeneity in the DDS-cured PEO/epoxy system, the aliphatic curing agent led to a phase-separated morphology in the cured network. *Figure 6* shows the SEM micrographs of the fracture surface of three different PEO contents in the DETA amine-cured PEO/epoxy networks (177°C cured for 4 h): 10, 30 and 40 phr, respectively. To enhance the contrast, all fractured samples were etched with dichloromethane solvent prior to SEM characterization. The fractured surfaces of these four compositions exhibited a phase-separation morphology that is typical for most polymer/epoxy networks[16–18]. The

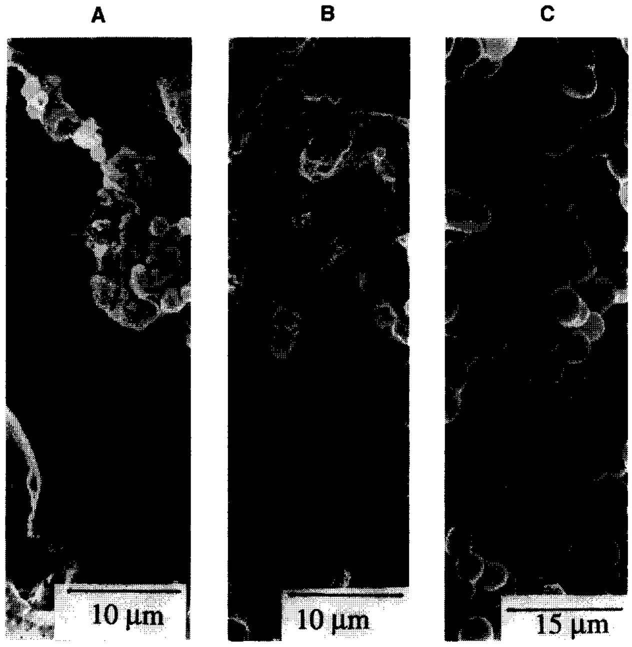


Figure 6 SEM micrographs of the fracture surface of three different PEO contents in the DETA amine-cured PEO/epoxy networks (177°C cured for 4 h): 10, 30, and 40 phr, respectively

network structure gradually shifted from a continuous epoxy/discrete PEO morphology to partial phase inversion, eventually to a complete phase inversion at higher PEO contents.

Phase structure was further investigated on systems where anhydride-type curing agents were used to cure the PEO/epoxy mixtures. Again, to enhance the contrast, all fractured samples were etched with dichloromethane solvent prior to SEM characterization. The SEM micrographs of the fracture surface for the PMDA anhydride-cured PEO/epoxy networks (10-, 20-, 30- and 40-phr PEO) cured at 177 and 187°C for 4 h, respectively, are all similarly homogeneous and resemble those illustrated in *Figure 1*. To avoid redundancy, they are not shown again. The fractured surfaces of these four compositions demonstrate that the morphologies are all homogeneous and similar to that of the neat cured epoxy/PMDA sample. The homogeneous, smooth structure of the etched morphology for the anhydride-cured PEO/epoxy demonstrates miscibility in this PEO/epoxy network, and indicates that the polymeric PEO chains are molecularly dispersed in the anhydride-crosslinked epoxy network. This result is strikingly similar to another anhydride-cured PEO/epoxy reported by Luo *et al.*[19], where in their study a different anhydride (phthalic anhydride) instead of PMDA was used as the curing agent. This should not, however, be generalized to a view that all anhydride-cured epoxy/PEO mixtures lead to homogeneous networks. Within a window of polarity, aromatic anhydrides of similar structures can lead to a crosslinked epoxy network that intimately interacts with PEO polymer chains and they co-exist as a homogeneous system.

Evidence of physical interactions

In certain demonstrated cases of cured polymer/epoxy networks with a single-phase structure reported in the literature, it has been also proven that the polymer(s) may participate in various extents of chain exchanges and/or transreactions or alcoholysis with the chain segments of epoxy networks. Most notable examples are found in polycarbonate/epoxy systems[4]. However, such homogeneous PC/epoxy-cured networks actually involve chemical linkages between several functional groups or even copolymerization between the polymer segments and the epoxy molecules during curing. Thus, strictly speaking, physical miscibility is not a proper term to describe them if extensive chemical bondings/exchanges are partially or completely responsible for the observed network homogeneity.

For the present DDS-cured PEO/DGEBA networks, evidence needs to be provided to verify the physical miscibility in the observed homogeneous morphology. The following procedures were taken. The DDS-cured PEO/epoxy solids of several compositions were pulverized into fine powder. The fine powder was then thoroughly extracted with the dichloromethane solvent. The solidified epoxy component would not dissolve while the linear polymer component of PEO molecules, if only physically interpenetrating in the network, could be dissolved and extracted. The solid powder was then filtered from the solutions. Several drops of the extracted solutions were then carefully deposited onto a KBr disk for *FT*i.r. characterization after proper drying treatment to get rid of the solvent.

Figure 7 shows the full i.r. spectra (labelled *a–d*) for the extracted solution samples that had been extracted from the cured PEO/DGEBA solids with four PEO contents: 10, 30, 50, and 70 phr, respectively. For direct comparison, the *FT*i.r. spectrum of the neat PEO sample is placed on the bottom of the graph. Apparently, the spectra of all four extracted samples coincide quite well with that of the neat PEO sample. The result shows that, firstly, the PEO component could be extracted freely from the original PEO/epoxy network, which suggests that PEO was physically interacting and/or interpenetrating with the epoxy network. It further suggests that the extracted PEO polymer component possesses exactly the same molecular structure before and after curing. Most likely the PEO component is not chemically bonded in any way to the epoxy network as a result of curing reactions.

Discussion on the role of hydrogen bonding

It has been argued that the hydrogen bonding between the ether groups of PEO and the hydroxyl group of the epoxy network is responsible for the observed miscibility in the DDS-cured PEO/epoxy network[20]. While the possibility of hydrogen bonding between the two groups is likely and cannot be precluded, one must be careful in assessing the factors for miscibility, especially in thermoplastic/thermoset systems involving a linear-chain polymer and cross-linked chains of epoxy.

Figure 8 shows the *FT*i.r. spectra of a 30-phr PEO/DGEBA mixture upon heating at 177°C for times between 0 and 120 min. DDS was excluded for purpose of simplification. Upon heating, the DGEBA can homopolymerize and lead to oligomers/polymers with increasing –OH contents. There are doublet hydroxyl absorbance peaks in the PEO/epoxy sample with no heating. Note that a small amount of –OH probably was originally present in the epoxy monomers even without any heat-induced oligomerization. The doublet peaks indicate that some of the –OH groups were originally hydrogen bonded and some were probably not. With increasing heating time, the hydroxyl peak becomes gradually pronounced in the samples heated for longer times, suggesting homopolymerization producing epoxy oligomers with generation of more –OH groups. Note

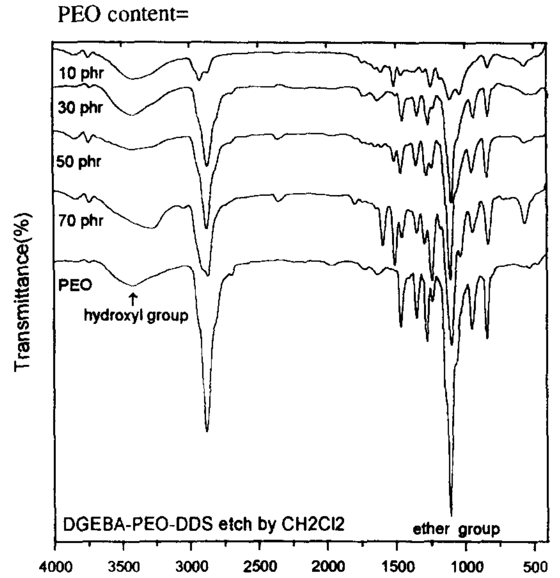


Figure 7 Full i.r. spectra (labelled a–d) for the extracted solution samples that had been extracted from the cured PEO/DGEBA solids with four PEO contents: 10, 30, 50, and 70 phr, respectively. For comparison, i.r. spectrum of neat PEO is also plotted and labelled as (e)

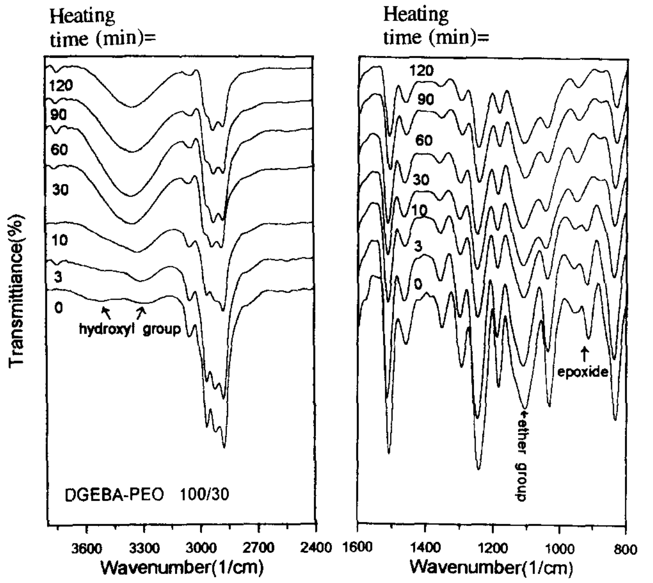
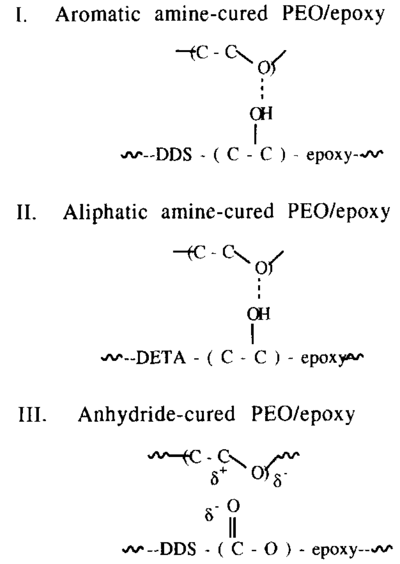


Figure 8 *FT*i.r. spectra of a 30-phr PEO/DGEBA mixture upon heating at 177°C for times between 0 and 120 min

that generation of –OH eventually masks the doublet. We thus cannot comment on the –OH peak shift as a result of cure-induced changes. If the changes of the –OH groups of epoxy could not be easily observed, focus was placed on observing possible changes of the ether groups of PEO. The figure shows that the ether (–O–) absorbance (1100 cm^{-1}) remains at the same frequency regardless of heating-induced –OH generation in the epoxy molecules. Thus, although possibility of ether–hydroxyl interactions of hydrogen bonding could not be ruled out, evidence was not particularly strong for the present PEO/epoxy system.

Similar hydrogen bonding characteristics may be expected to exist in the DDS- or aliphatic-cured PEO/epoxy systems, and there is no question that hydrogen bonding may well exist in both systems. This is illustrated in *Scheme I* and *Scheme II*, respectively. However, the former exhibited a single-phase structure, while the latter was shown to be a phase-separated system. A question thus arises. Is the presence of some hydrogen-bonding sites between specific functional groups in polymers/epoxy systems responsible for phase homogeneity? The result seems to suggest that it is neither a sufficient nor necessary condition. The anhydride PMDA-cured PEO/epoxy system also resulted in a homogeneous structure, where hydrogen bonding is not expected to exist as anhydride curing of epoxies does not lead to pendant –OH groups. Rather, closely matched polarity between the PEO polymer and the epoxy chains after curing might be a determining factor. This is illustrated in *Scheme III*.



Schemes I–III

Guo[21] reported similar observation in his study on a phenoxy/DGEBA mixed system cured with a series of different hardeners. In all, five different hardeners were used: (1) 4,4′-diaminodiphenylmethane (DDM), (2) maleic anhydride (MA), (3) hexahydrophthalic anhydride (HHPA), (4) DDS, and (5) phthalic anhydride (PA). The former three yielded a homogeneous system, while the latter two resulted in phase separation. Again, there seems no clear trend in assessing that a greater density of hydrogen-bonding sites might lead more readily to a homogeneous crosslinked structure upon curing. The structures of the epoxy and hardening agent must be such that, after curing, the crosslinked segments possess closely matched polarity with the polymer chains. To induce miscibility in the polymer/epoxy systems, the sensitivity of the hardener in adjusting the chain structure and polarity of the crosslinked segments is believed to be more critical than whether or not the hardener leads to hydrogen bonding sites in the epoxy. The hydrogen bonding itself does not seem to be sufficient to guarantee an intimate and strong interaction leading to phase homogeneity.

Interestingly, PEO has been known to be miscible with PMMA as numerously reported in the literature[22–24]. Clearly, hydrogen bonding is absent in this binary polymer blend, but polar interactions between these two components are likely, and believed to be responsible for the noted miscibility. Thus, although hydrogen bonding under favourable conditions might enhance the likelihood of building a miscible system, interactions between closely matched polar segments are necessary and fundamental.

CONCLUSION

An interesting miscible phase was observed in DDS- and anhydride-cured PEO/DGEBA systems. T_g–composition relationships in a wide composition range were shown to follow what would be expected for a miscible system. Physical miscibility, not through chemical linkages and/or co-polymerization, was proven in the cured networks showing a homogeneous morphology. Structurally, it can be viewed that the PEO chains interpenetrate with entanglement into the crosslinked epoxy network. Thermodynamically, the PEO chains also intimately mingle with the epoxy-DDS network chain segments to achieve a homogeneous solid state.

On the other hand, aliphatic amine curing led to phase separation and so did the DDS-cured PEO/TGDDM system. Apparently, the structures of both epoxies and hardeners could influence the ultimate phase structure of cured networks. For the miscible polymer/epoxy networks, the cure temperature (thus cure kinetic rate) was found to exert no effects on influencing phase homogeneity. This is different for phase-separated cases, where earlier studies have proven that cure kinetics influences the domain sizes.

By using a variety of hardeners on the same polymer/epoxy system, this study revealed that the cured polymer/epoxy with potential hydrogen sites is not necessarily more likely to lead to a miscible network in comparison to the systems where hydrogen bonding is clearly absent from the structure. Thus, although hydrogen bonding under favourable conditions might enhance the likelihood of building a miscible system, interactions between closely matched polar segments are necessary and fundamental. Further studies are needed to shed more light and provide more quantitative views.

ACKNOWLEDGEMENTS

The authors appreciate the financial support kindly provided by National Science Council (NSC) of Taiwan. (Grant #NSC 86-2216-E006-007 and #NSC 87-2216-E006-005).

REFERENCES

1. Su, C. C. and Woo, E. M., *Polymer*, 1995, **36**, 2883.
2. Hseih, H. K. and Woo, E. M., *J. Polym. Sci., Polym. Phys. Edn.*, 1996, **34**, 2591.
3. Woo, E. M. and Hseih, H. K., *Polymer*, 1998, **39**, 7.
4. Su, C. C. and Woo, E. M., *Macromolecules*, 1995, **28**, 6779.
5. Smith, K. L., Winslow, A. E. and Peterson, D. E., *Ind. Eng. Chem.*, 1959, **51**, 1361.
6. Osada, Y. and Sato, M., *J. Polym. Sci., Polym Lett.*, 1976, **14**, 129.
7. Robeson, L. M., Hale, W. F. and Merriam, C. N., *Macromolecules*, 1981, **14**, 1644.
8. Coleman, M. M. and Moskala, E. J., *Polymer*, 1983, **24**, 251.
9. Venderbosch, R. W., Meijier, H. E. H. and Lemstra, P. J., *Polymer*, 1994, **35**, 4349.
10. Pearson, R. A. and Yee, A. F., *J. Appl. Polym. Sci.*, 1993, **48**, 1051.
11. Zheng, S., Zhang, N., Luo, X. and Ma, D., *Polymer*, 1995, **36**, 3609.
12. Inoue, T., *Prog. Polym. Sci.*, 1995, **20**, 119.
13. Fox, T. G., *Bull. Am. Phys. Soc.*, 1956, **2**, 123.
14. Kwei, T. K. J., *Polym. Sci., Polym Lett.*, 1984, **22**, 307.
15. Gomez, C. M. and Bucknall, C. B., *Polymer*, 1993, **34**, 2111.
16. Bucknall, C. B., Gomez, C. M. and Quintard, I., *Polymer*, 1994, **35**, 353.
17. Pearson, R. A. and Yee, A. F., *Polymer*, 1993, **34**, 3658.
18. Pak, S. J., Lyle, G. D., Mercier, R. and McGrath, J. E., *Polymer*, 1993, **34**, 885.
19. Luo, X., Zheng, S., Zhang, N. and Ma, D., *Polymer*, 1994, **35**, 2619.
20. Zheng, S., Zhang, N., Luo, X. and Ma, D., *Polymer*, 1995, **36**, 3609.
21. Guo, Q., *Polymer*, 1995, **36**, 4753.
22. Liberman, S. A. and Gomes, A. De S., *J. Polym. Sci., Polym. Chem. Edn.*, 1984, **22**, 2809.
23. Li, X. and Hsu, S. L., *J. Polym Sci., Polym. Chem.*, 1984, **22**, 1331.
24. Makhija, S., Pearce, E. M. and Kwei, T. K., *J. Polym. Sci., Polym. Chem. Edn.*, 1992, **30**, 2693.