



Thermoplastic Toughened Epoxy Networks and Their Toughening Mechanisms in Some Systems

Metha Rutnakornpituk

Department of Chemistry, Faculty of Science, Naresuan University, Phitsanulok 65000, Thailand.

Corresponding author. E-mail address: methar@nu.ac.th (M. Rutnakornpituk)

Received 29 October 2004; accepted 12 April 2005

Summary

Epoxy resins have drawn a lot of attentions as construction materials in recent years due to their excellent mechanical and thermal properties. However, their brittleness is a major disadvantage which significantly limits their uses. Incorporation of thermoplastic polymers has found to overcome this drawback. Literature reviews in using various thermoplastic polymers, e.g., poly(phenylene oxide) (PPO), polysulfone (PSF) and polyetherimide (PEI), have been summarized herein. The toughening mechanisms that have been proposed and the measurement of their mechanical properties are also discussed.

Keywords: toughening, epoxy, network, thermoplastic

Introduction

Epoxy resins were first commercialized in 1946 and are now widely used in many applications such as adhesives, coatings, construction, and composite matrices in the aerospace and electronic industries (Riffle et al., 1983; Sue et al., 1996, 2000). This is due to their good mechanical and thermal properties, high chemical and corrosion resistance, excellent adhesion to various substrates and good electrical properties. However, their inherent brittleness is a major drawback and limits their use in high performance applications (de Nograra et al., 1996; Srinivasan et al., 1998). Enhancing the toughness of epoxy resins by addition of a second polymer such as an elastomeric or a thermoplastic modifier has been widely reported in last two decades (Huang et al., 1997). The phase separation of the second polymer from the polymer matrix causes toughening mechanisms that can shield the crack tip, resulting in improving the fracture toughness (Chikhi et al., 2002; van Overbeke et al., 2000, 2003; Poncet et al., 1999; Varley et al., 2000, 2001). The use of rubber modification of epoxy resins has been known and documented since 1960s (Sue et al., 2000). The rubber-modified epoxies showed surprisingly higher fracture resistance, but, at the same time, significant reductions in modulus, yield strength and the glass transition temperature (T_g) were observed (Li et al., 2004; Mimura et al., 2001). Fortunately, a new toughening technology has been discovered to avoid the reductions of the mechanical properties by using another type of toughening phase: rigid, thermoplastic particles (Girard-Reydet et al., 1999; Siddhamalli, 2000). Bucknall and Partridge first introduced high-performance thermoplastic modified epoxy networks in 1986 (Bucknall et al., 1986, 1989). These new materials disclosed an outstanding advantage over the elastomeric modified systems. Namely, their fracture toughness was increased without sacrificing the mechanical properties of the systems. Although thermoplastic modified epoxies were significantly developed in recent years, the fracture and toughening mechanisms in these modified epoxies are not well understood (Pearson et al., 1993).

In this review paper, the toughening mechanisms that have been proposed in literatures will be first addressed, followed by the results of fracture toughness and parameters used. The thermoplastic materials, e.g., poly(phenylene oxide) (PPO) (Pearson et al., 1993; Wu et al., 2000), polysulfone (PSF) (Min, Hodgkin et al., 1993; Min, Stachurski et al., 1993; Rajagopalan et al., 2000; Varley et al., 2000, 2001) and polyetherimide (PEI) (Li et al., 1999), which have been widely studied for the use as tougheners, will be then discussed.

Proposed Toughening Mechanisms in Thermoplastic-Modified Epoxy Networks (Pearson et al., 1993).

The particle bridging mechanism

The proposed role of the rigid plastic particles is to span two crack surfaces and apply surface tractions that effectively alleviate the stress applied at the crack tip. In other words, the energy is consumed when the crack deforms and tears the rigid plastic particles (Figure 1). Scanning electron microscopy (SEM) has been used to verify the crack bridging mechanism by examination of the fracture surfaces of damaged particles.

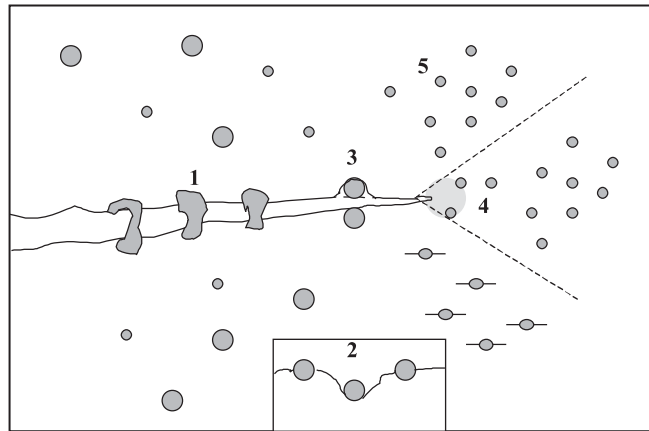


Figure 1 Schematic diagram of toughening mechanisms proposed for thermoplastic-modified epoxy; (1) particle bridging, (2) crack pinning, (3) crack path deflection, (4) particle yielding-induced shear banding, (5) particle yielding, and (6) microcracking (Pearson et al., 1993).

Although the amount of toughness from the bridging of the crack by rigid thermoplastic particles is still ambiguous, it can be estimated from two other types of modified epoxies: rubber-modified and glass-filled epoxies. In the rubber-modified epoxies, the model is stated as:

$$K_c/K_0 = \varphi (1-f) + [f E^* \Gamma_t] / [2\varphi (1-f) K_0^2]$$

where K_c is the fracture toughness of the glass-filled epoxy, K_0 is the fracture toughness of the unmodified epoxy, φ is a correction factor that accounts for crack bowing, f is the volume fraction of rubber particles, E^* is the stiffness of the particles and Γ_t is the tearing energy of the rubber particles. In the glass-filled epoxies, the model is stated as:

$$K_c/K_0 = [(2s/\lambda) + (2r/\lambda)(K_L/K_0)^2]^{1/2} / F_1$$

where K_c is the fracture toughness of the rubber-modified epoxy, K_0 is the fracture toughness of the unmodified epoxy, $2s$ is the surface-to-surface obstacle spacing, $2r$ is the diameter of the particles, λ is the center-to-center obstacle spacing, K_L is a limiting stress intensity factor that specifies the failure of the trailing end of the reinforced zone, and F_1 is an interpolating function constructed to reproduce the correct asymptotic expansions for soft springs and for hard springs.

Evidence for crack bridging in thermoplastic-modified epoxies has been reported in many papers. For example, Bucknall and colleagues showed that torn particles could be observed from a post-mortem analysis of fracture surfaces (Bucknall et al., 1989).

Crack pinning

The proposed role of the rigid thermoplastic particles is to behave as impenetrable objects that slow down the crack, resulting in consuming extra energy as the crack propagates (Figure 1). The quantitative amount of toughness from this mechanism is still uncertain. However, the model used for glass-filled system has also been applied for the rigid thermoplastic particles. The model is stated as:

$$K_c/K_0 = [\pi / (2 + d_p / C)]^{1/2} [\tan \{\pi / (2 + d_p / C)\}]^{1/2}$$

where K_c is the fracture toughness of the modified epoxy, K_0 is the fracture toughness of the unmodified epoxy, C is the surface-to-surface obstacle spacing, and d_p is the diameter of the particles (Pearson et al., 1993).

Evidence for crack pinning mechanism in thermoplastic-modified epoxies exists. For example, SEM micrographs show 'tails' near the particles on the fracture surfaces (Kinloch et al., 1985).

Crack path deflection

The proposed role of the rigid thermoplastic particles is to cause the crack to deviate from its original direction (Figure 1). Consequently, surface area of the crack is increased and the mode I character of the opening of the crack is reduced, resulting in increasing energy to propagate such a crack. SEM is again used to verify the occurrence of crack path deflection mechanism by observing its fracture surfaces. Quantitative amount of fracture toughness from this mechanism is stated as:

$$K_c/K_0 = [(E_0 / E_c) (1 + 0.87 V_f)]^{1/2}$$

where K_c is the fracture toughness of the modified epoxy, K_0 is the fracture toughness of the unmodified epoxy, E_c is the Young's modulus of the modified epoxy, E_0 is the Young's modulus of the unmodified epoxy, and V_f is the volume fraction of spheres.

Particle yielding-induced shear banding

This mechanism of thermoplastic-modified epoxies is similar to that of rubber-modified epoxy. Namely, the rigid plastic particles would yield and produce a significant stress concentration, which initiates shear banding in the matrix (Figure 1). The particle-induced shear banding has been proposed according to a result of a finite-element method (FEM) model, which considered the non-linear deformation of a rigid sphere embedded in a rigid matrix. The quantitative amount of fracture toughness from this mechanism has not been studied.

Determination of Fracture Toughness

Fracture toughness can be measured by investigating the critical stress intensity factors, K_{Ic} , using three-point bending specimens according to ASTM E399 (Figure 2) (Huang et al., 1997). High values of K_{Ic} indicate high fracture toughness. K_{Ic} is calculated using the equation

$$K_{Ic} = P_c S / B W^{3/2} f(A/W)$$

where P_c is the load at crack initiation, B is the thickness of specimen, S is the span width, W is width of the specimen and A is crack length.

Another parameter indicating toughness properties is G_{Ic} , fracture energy. High values of G_{Ic} also indicate high fracture toughness. G_{Ic} is calculated from K_{Ic} as

$$G_{Ic} = (1 - \gamma^2) K_{Ic}^2 / E$$

where γ is Poisson's ratio and E is the flexural modulus.

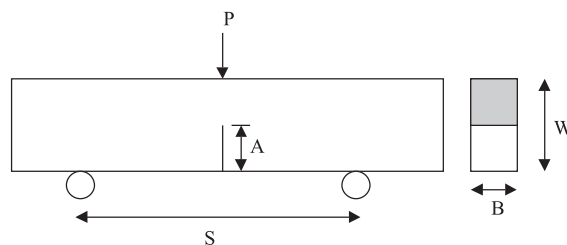


Figure 2 Schematic diagram of three-point bending specimen measuring fracture toughness.

Thermoplastic-Toughening Epoxy Networks

Poly(phenylene oxide) (PPO) toughened epoxy networks

Studies of toughening mechanism and morphology of the blends of PPO with diglycidyl ether of bisphenol A (DGEBA, commercial name 'Epon828') have been reported by Pearson and colleagues (Figure 3) (Pearson et al., 1993). A series of PPO-modified networks with different PPO contents (M_n 34,000 g/mol) were cured with piperidine at 160°C for 2 hours. During the formation of the network, if the solubility parameters of PPO and epoxy matrix structure differ sufficiently, it would be possible to develop microphase separated PPO-modified epoxy networks. Therefore, small domains of PPO phase, which was the minority component, should be dispersed in the continuous matrix composed of the epoxy resins. Transmission electron micrographs (TEM) reveal two-phase morphology containing discrete PPO particles. However, the morphology was not uniform and some large heterogeneous PPO particles containing occlusions of smaller epoxy particles were observed throughout the materials. In order to eliminate the occurrence of occluded PPO particles, styrene-maleic anhydride (SMA) copolymers (M_n 260,000 g/mol) were utilized as a compatibilizing agent for PPO-DGEBA blends. The addition of SMA copolymers with a 10:1 ratio of styrene to maleic anhydride can significantly improve the uniformity of these two-phase materials, resulting in spherical PPO particles (2 μ m in diameter) embedded in the epoxy continuous matrix.

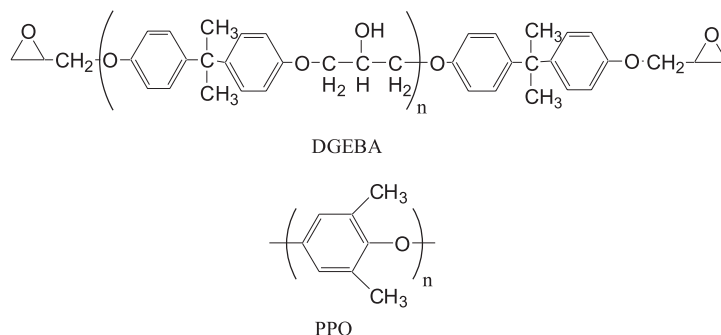


Figure 3 Chemical structure of diglycidyl ether of bisphenol A (DGEBA, commercial name 'Epon828') and poly(phenylene oxide) (PPO)

The tensile yield strengths of the PPO-modified networks containing SMA as a surfactant were found independent of PPO contents. On the other hand, the fracture toughness (K_{Ic}) improved as increasing PPO contents, indicating improving in toughness properties. Microcracking and crack deflection were thought to be the mechanisms for improvement in toughness, which is different from rubber-modified epoxies mainly toughened by shear banding mechanism.

Wu and associates have also studied the morphology and mechanical properties of melt blends of poly(2,4-dimethyl-1,4-phenylene oxide), PPO with DGEBA resins using multifunctional cyanate ester as a curing agent (Wu et al., 2000). The blends were cured at 200°C for 2 hours. A series of reactions using various PPO contents (0-50 wt%) were performed in order to study the effect of PPO contents on phase separation and morphology of the blends via scanning electron microscopy (SEM) and dynamic mechanical analysis (DMA). The similar results to those of Pearson and colleagues have been found (Pearson et al., 1993). Namely, all the blends exhibited heterogeneity and their morphology was found dependent on the PPO contents. Addition of triallylisocyanurate (TAIC) used as a compatibilizer for epoxy/PPO blends can eliminate the occurrence of the large PPO particles in the blends. In addition, DMA and SEM indicated that adding TAIC improved not only the miscibility, but also solvent resistance of the epoxy/PPO blends (after etching with dichloromethane).

Insignificant change in tensile strength and modulus was observed as increasing PPO contents in the blends. Toughness properties of the TAIC-modified epoxy/PPO networks were significantly improved as PPO started to form the continuous phase (20 wt% PPO or more). It is thought that the particle-yielding induced shear banding of the PPO continuous phase was the main toughness mechanism in this system.

Polysulfone (PSF) toughened epoxy networks

The morphology and toughness properties of DGEBA epoxy networks modified with phenolic hydroxyl-terminated polysulfone (PSF) in the presence of diaminodiphenyl sulfone (DDS) hardener have been reported as a function of the molecular weight and concentration of PSF by Min and colleagues (Min, Hodgkin et al., 1993; Min, Stachurski et al., 1993) (Figure 4). Two phenolic hydroxyl-terminated polysulfones of Mn 6,400 and 10,000 g/mol were prepared from bisphenol A and dichlorodiphenyl sulfone monomers. The desired amount of DGEBA, PSF and DDS were blended at 140°C and cured in an air oven at 140°C for 2 hours and postcured at 180°C for 2 hours. SEM micrographs revealed that the microstructure changed from the typical particulate structure (spherical PSF particles in epoxy matrix) at 5 and 10 wt% of PSF to the partially phase-inverted structure at 15 wt% of PSF to the completed phase-inverted structure eventually at 20 wt% of PSF.

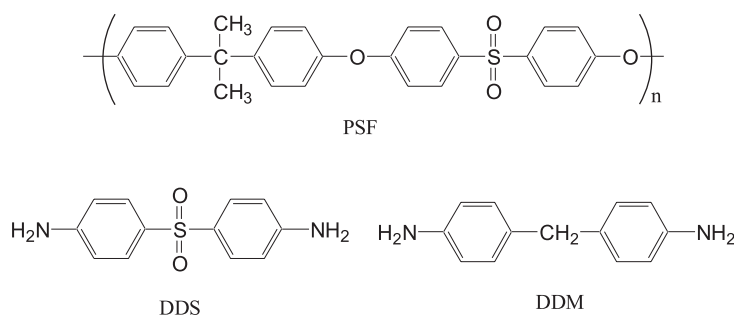


Figure 4 Chemical structure of polysulfone (PSF), diaminodiphenyl sulfone (DDS) and diaminodiphenyl methane (DDM)

G_{Ic} values of the PSF-modified DGEBA/DDS networks were increased as increasing PSF contents in the materials, indicating that toughness properties were improved. This means that the fracture toughness was improved as microstructure changed from the particulate structure to the phase-inverted structure. In addition, the fracture toughness of a high molecular weight ($M_n = 10,000$ g/mol) PSF-modified system was higher than those of the one with low molecular weight PSF ($M_n = 6,400$ g/mol). SEM micrographs suggest the particle bridging was a main toughening mechanism and the shear banding was a minor toughening mechanism. More interestingly, the flexural modulus of the PSF-modified epoxy resins did not decrease significantly. Unlike typical rubber-modified epoxy resins, the modulus of this system thus was not sacrificed.

The mechanical properties of PSF-modified DGEBA/ diaminodiphenylmethane (DDM) networks were investigated as a function of PSF contents by Huang and colleague (Huang et al., 1997) (Figure 4). To prepare the networks, the blends of DGEBA, PSF and DDM curing agents were cured at 80°C for 2 hours, 150°C for 2 hours and postcured at 200°C for 2 hours. The homogeneity of the blends was determined using SEM and by observing the glass transition temperatures (T_g 's) of the blends using differential scanning calorimetry (DSC). DSC studies showed that the PSF-modified networks had only one T_g indicating the uniformity of the blends, which was in agreement with SEM. Unlike the case of the rubber-modified epoxy networks, the T_g 's of the PSF-modified networks were not significantly depressed. K_{Ic} and G_{Ic} of the PSF-modified networks increased about 20% as increasing the PSF content in the blends from 0 to 15 wt%. In addition, both tensile and flexural properties (strength and modulus) of the blends with PSF modifiers slightly improved compared to those of the unmodified networks. The possible toughening mechanism for this system was not revealed.

Yoon and colleagues have reported the investigations of mechanical properties and morphology of the aminophenyl terminated reactive or *t*-butyl terminated non-reactive PSF toughen epoxy networks (Yoon et al., 1995). Aminophenyl functional reactive PSF was synthesized by using bisphenol A and dichlorodiphenylsulfone with aminophenol endcappers whereas, for *t*-butyl terminated non-reactive PSF, *t*-butylphenol was used as endcapper (Hendrick et al., 1991; McGrath et al., 1993). The amount of endcappers used were calculated in order to obtain PSF with molecular weight 5,000, 10,000, 15,000 and 20,000 g/mol. The network samples were prepared by incorporating curing agents, DDS to the DGEBA with PSF loadings varied from 5 to 30 wt% and cured at 130°C for 4 hours and postcured at 220°C for 2 hours. The fracture toughness properties of the reactive PSF toughened epoxy networks improved as a function of the molecular weight and loadings of the PSF toughener. The maximum obtainable K_{Ic} values of epoxy networks toughened with the reactive PSF was about 2.2 MPa-m^{1/2}, which is approximately the K_{Ic} of the neat PSF. SEM micrographs reveal the particulate structure with PSF spheres of about 0.5 μ m in diameter in epoxy matrix at low loadings of PSF (up to 10 wt%) and changed to a phase inverted morphology, at high loading of PSF (15 wt% or more).

The non-reactive PSF toughened epoxy networks exhibited K_{Ic} values of about 0.75 to 0.85 MPa-m^{1/2} at low loadings of PSF, but as the loading increased, K_{Ic} significantly increased and then dropped to approximately 0.5 MPa-m^{1/2}. SEM micrographs reveal the particulate morphology with the size of PSF spheres approximately 1-2 μ m in diameter at low loadings of PSF (up to 10 wt%) and phase inverted morphology at high loadings of PSF (15-20 wt%). The larger PSF spheres in the non-reactive PSF system were attributed to better phase separation behavior of the non-reactive PSF than those in the reactive PSF (1-2 and 0.5 μ m in diameter, respectively). However, in the epoxy networks containing of 25-30 wt% of PSF (or lower in case of high molecular weight PSF), SEM micrographs indicate that most of the PSF spheres disappeared, which is attributed to poor adhesion between epoxy phase and PSF spheres due to the absence of chemical bonds. This is in agreement with the significant descent of K_{Ic} values at high contents of

PSF in the epoxy networks.

It was proposed that the particle bridging is the main toughening mechanism in the reactive-PSF toughened epoxy networks due to the presence of covalent bonds between two phases. Namely, the reaction between the amine-functional groups in aminophenyl-terminated PSF and epoxy-functional groups in DGEBA took place. SEM micrographs support this idea as the broken PSF spheres were observed at the equator. In contrast, there was no covalent bond between epoxy and PSF phases in the epoxy networks toughened with the non-reactive PSF. Therefore, particle bridging toughened mechanism can not fully contribute in the system due to no chemical interaction between two phases, as observed in the networks with high contents of PSF.

Polyetherimide (PEI) toughened epoxy networks

Gilbert and Bucknall have reported the investigation of phase separation behavior in PEI-modified epoxy networks (Gilbert et al., 1991). Tetrafunctional epoxy resins (DGDDM) was blended with PEI toughening agents and using DDS as curing agents and then cured at 120°C for 16 hours, 150°C for 2 hours, 180°C for 2 hours and postcured at 200°C for 4 hours. SEM micrographs reveal spherical PEI domains in epoxy matrix at 5 wt% PEI used and these domains became larger as the PEI contents were increased up to 20 wt%. At 30 wt% PEI contents in the networks, the phase inversion occurred, e.g., the PEI phase was effectively continuous throughout the materials. K_{Ic} of the PEI-modified networks increased from 0.48 to 1.53 MPa.m^{1/2} as the PEI contents increased from 0 to 30 wt%, respectively. This is in agreement with the fracture energy measurements indicating the increase of G_{Ic} values from 0.055 to 0.530 kJ.m⁻² as the PEI contents increased from 0 to 30 wt%, respectively. Moreover, there was a slight increase in modulus upon addition of PEI in the networks, compared with the unmodified system. According to SEM, it is thought that the particle bridging was the major toughening mechanism and crack pinning was a minor toughening mechanism in this system.

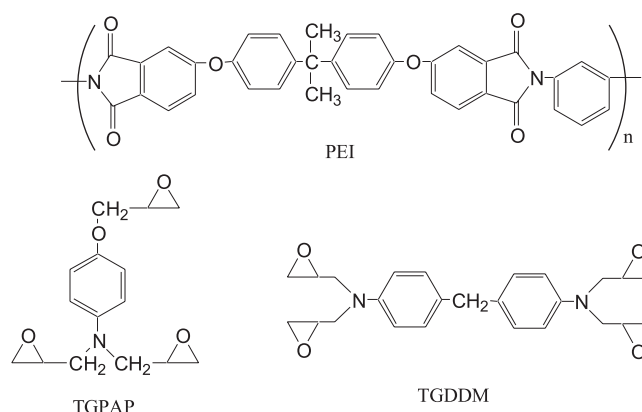


Figure 5 Chemical structure of polyetherimide (PEI), triglycidyl-p-aminophenol (TGPAP) and tetraglycidyl-diaminodiphenyl methane (TGDDM)

Murakami and colleagues have studied the phase separation and fracture behavior of PEI-modified epoxy networks as a function of PEI contents (Murakami et al., 1992). The mixture of DGEBA and PEI resins were blended with dicyanodiamide used as a curing agent at 150°C for 4 hours and postcured at 200°C for 2 hours (Figure 5). There was no increase in K_{Ic} when only 10 wt% of PEI was added in the blends, whereas in 20 wt% PEI networks, K_{Ic} increased dramatically from 0.8 to 1.9 MPa.m^{1/2}. In 30 wt% PEI networks, there was a slight drop in K_{Ic} value to 1.7 MPa.m^{1/2}. According to SEM, there was no phase separation in the 10 wt% PEI networks, resulting in no increase in K_{Ic} . As PEI contents increased to 20 wt%, the particulate morphology

with PEI spheres in epoxy matrix was observed. It was thought that the ductile PEI spheres provided the particle bridging toughening mechanism. However, as the PEI contents in the networks increased to 30 wt%, the phase inversion took place and formed PEI-based materials, resulting in decreasing in K_{Ic} . More interestingly, in the PEI-modified networks, high glass transition temperature (T_g) was retained and modulus was increased compared with the unmodified networks.

The effect of the PEI toughener composition on the mechanical properties of epoxy networks was investigated by Hourston and associates (Hourston et al., 1997). The mixture of difunctional epoxy resins (DGEBA) and/or trifunctional epoxy resins (triglycidyl-p-aminophenol, TGPAP) and/or tetrafunctional epoxy resins (tetraglycidyl-diaminodiphenylmethane, TGDDM) was blended with PEI toughening agents (Mn 18,000 g/mol) and using DDS as curing agents (Figure 5). The blends were cured at 180°C for 2 hours and postcured at 190°C for 10 hours. K_{Ic} and G_{Ic} were determined as a function of PEI contents in the networks using various weight ratios of di, tri or tetrafunctional epoxy resins. In most cases, K_{Ic} and G_{Ic} values increased as increasing PEI contents (up to 20 wt%) in the networks. The mixtures of di- and trifunctional epoxies, which have the lowest crosslink density and thus the highest ductility, were more toughenable than those containing the tetrafunctional epoxy (TGDDM). The possible toughening mechanism was not discussed because the phase separation of this system was not investigated.

Conclusions

Incorporation of thermoplastic materials into the epoxy networks is a promising alternative to improve their mechanical properties without sacrificing thermal properties and strength. Phase separation of thermoplastic and epoxy phases occurred as increasing the contents of the thermoplastic toughening agents. At low contents of the toughening agents, e.g., 5-10 wt%, the particulate morphology (thermoplastic domains in the epoxy matrix) took place. As the toughening agent loadings increased, e.g., 15-30 wt%, the phase inversion occurred. K_{Ic} and G_{Ic} values, indicating toughness properties of the networks, generally increased as increasing the contents of toughening agents. In the other word, the toughness properties improved when the morphology of the networks changed from homogeneity of the epoxy phase to the particulate and to the phase-inverted morphology eventually. Many possible toughening mechanisms have been proposed to explain this behavior although they are still not fully understood.

References

- Bucknall, C. B., & Gilbert, A. H. (1989). Toughening tetrafunctional epoxy resins using polyetherimid. *Polymer*, 30, 213-219.
- Bucknall, C. B., & Partridge, I. K. (1986). Phase-separation in cross-linked resins containing polymeric modifiers. *Polymer Engineering & Science*, 26, 54.
- Chikhi, N., Fellahi, S., & Bakar, M. (2002). Modification of epoxy resin using reactive liquid (ATBN) rubber. *European Polymer Journal*, 3, 251-264.
- de Nograra, F. F., Llano-Ponte, R., & Mondragon, I. (1996). Dynamic and mechanical properties of epoxy networks obtained with PPO based amines/mPDA mixed curing agents. *Polymer*, 37, 1589-1600.
- Gilbert, A. H., & Bucknall, C. B. (1991). Epoxy-resin toughened with thermoplastic. *Makromolecular Chemie, Macromolecular Symposium*, 45, 289-298.
- Girard-Reydet, E., Sautereau, H., & Pascault, J. P. (1999). Use of block copolymers to control the morphologies and properties of thermoplastic/thermoset blends. *Polymer*, 40, 1677-1687.

- Hendrick, J. L., Yilkor, I., Jurek, M., Hedrick, J. C., Wilkes, G. L., & McGrath, J. E. (1991). Chemical modification of matrix resin networks with engineering thermoplastics: 1. Synthesis, morphology, physical behaviour and toughening mechanisms of poly(arylene ether sulphone) modified epoxy networks. *Polymer*, 32, 2020-2032.
- Hourston, D. J., Lane, J. M., & Zhang, H. X. (1997). Toughening of epoxy resins with thermoplastics: 3. An investigation into the effects of composition on the properties of epoxy resin blends. *Polymer International*, 42, 349-355.
- Huang, P., Zheng, S., Huang, J., & Guo, Q. (1997). Miscibility and mechanical properties of epoxy resin/polysulfone blends. *Polymer*, 38, 5565-5571.
- Kinloch, A. J., Maxwell, D., & Young, R. J. (1985). Micromechanisms of crack-propagation in hybrid-particulate composites. *Journal of Material Science Letter*, 4, 1276.
- Li, L., Liu, M., & Li, S. (2004). Morphology effect on water sorption behavior in a thermoplastic modified epoxy resin system. *Polymer*, 45, 2837-2842.
- Li, S., Hsu, B. L., Li, F., Li, C. Y., Harris, F. W., & Cheng, S. Z. D. (1999). A study of polyimide thermoplastics used as tougheners in epoxy resins-structure, property and solubility relationships. *Thermochimica Acta*, 340, 221-229.
- McGrath, J. E., Pak, S. J., Lyle, G. D., & Mercier, M. (1993). Synthesis and characterization of novel toughened thermosets derived from pendent amines on the backbone of poly(arylene ether sulphone)s. *Polymer*, 34, 885-895.
- Mimura, K., Ito, H., & Fujioka, H. (2001). Toughening of epoxy resin modified with *in situ* polymerized thermoplastic polymers. *Polymer*, 49, 9223-9233.
- Min, B. G., Hodgkin, J. H., & Stachurski, Z. H. (1993). Reaction mechanisms, microstructure, and fracture properties of thermoplastic polysulfone-modified epoxy resin. *Journal of Applied Polymer Science*, 50, 1065-1073.
- Min, B. G., Stachurski, Z. H., & Hodgkin, J. H. (1993). Microstructural effects and the toughening of thermoplastic modified epoxy resins. *Journal of Applied Polymer Science*, 50, 1511-1518.
- Murakami, A., Saunders, D., Ooishi K., & Yoshiki, T. (1992). Fracture-behavior of thermoplastic modified epoxy resins. *Journal of Adhesion*, 39, 227-242.
- Pearson, R. A., & Yee, A. F. (1993). The preparation and morphology of PPO-epoxy blends. *Journal of Applied Polymer Science*, 48, 1051-1060.
- Pearson, R. A., & Yee, A. F. (1993). Toughening mechanisms in thermoplastic-modified epoxies: 1. Modification using poly(phenylene oxide). *Polymer*, 34, 3658-3670.
- Poncet, S., Boiteux, G., Pascault, J. P., Sautereau, H., Seytre, G., Rogozinski, J., et al. (1999). Monitoring phase separation and reaction advancement in situ in thermoplastic/epoxy blends. *Polymer*, 40, 6811-6820.
- Rajagopalan, G., Gillespie, J. W., Jr. & McKnight, S. H. (2000). Diffusion of reacting epoxy and amine monomers in polysulfone: A diffusivity model. *Polymer*, 41, 7723-7733.
- Riffle, J. S., Yilgor, T. I. C., Wilkes, G. L., McGrath, J. E., & Banthia, A. K. (1983). Elastomeric polysiloxane modifiers for epoxy networks: Synthesis of functional oligomers and network formation studies. In R. S. Bauer (Series Ed.), *ACS Symposium Series: Vol. 221. Epoxy resin chemistry II* (pp.21-54). Washington, DC: American Chemical Society.
- Siddhamalli, S. K. (2000). Phase-separation behavior in poly(ether imide)-modified epoxy blends. *Polymer- Plastic Technology & Engineering*, 39, 699-710.
- Srinivasan, S. A., & McGrath, J. E. (1998). Amorphous phenolphthalein-based poly(arylene ether) modified cyanate ester networks: 1. Effect of molecular weight and backbone chemistry on morphology and toughenability. *Polymer*, 39, 2415-2427.

- Sue, H. J., Garcia-Meitin, E. I., & Pickelman, D. M. (1996). Fracture behavior of rubber-modified high performance epoxies. In C. B. Arends (Ed.), *Polymer toughening* (pp.136-174). New York: Marcel Dekker.
- Sue, H. J., Puckett, P. M., Bertram, J. L., & Walker, L. L. (2000). The network structure of epoxy systems and its relationship to toughness and toughenability. In R. A. Pearson, H. J. Sue, & A. F. Yee (Series Eds.), *ACS Symposium Series: Vol. 759. Toughening of Plastics* (pp.171-197). Washington, DC: American Chemical Society.
- van Overbeke, E., Carlier, V., Devaux, J., Carter, J. T., McGrail, P. T., & Legras, R. (2000). The use of Raman spectroscopy to study the reaction between an amine-terminated thermoplastic and epoxy resins. *Polymer*, *41*, 8241-8245.
- van Overbeke, E., Devaux, J., Legras, R., Carter, J. T., McGrail, P. T., & Carlier, V. (2003). Phase separation in epoxy-copolyethersulphone blends: Morphologies and local characterisation by micro-Raman spectroscopy. *Polymer*, *44*, 4899-4908.
- Varley, R. J., Hodgkin, J. H., Hawthorne, D. G., Simon, G. P., & McCulloch, D. (2000). Toughening of a trifunctional epoxy system: Part III. Kinetic and morphological study of the thermoplastic modified cure process. *Polymer*, *41*, 3425-3436.
- Varley, R. J., Hodgkin, J. H., & Simon, G. P. (2001). Toughening of a trifunctional epoxy system: Part VI. Structure property relationships of the thermoplastic toughened system. *Polymer*, *42*, 3847-3858.
- Wu, S. J., Lin, T. K., & Shyu, S. S. (2000). Cure behavior, morphology, and mechanical properties of the melt blends of epoxy with polyphenylene oxide. *Journal of Applied Polymer Sciences*, *75*, 26-34.
- Yoon, T. H., Priddy, D. H., Lyle, G. D., Jr., & McGrath, J. E. (1995). Hydrolytically stable thermo plastic and thermosetting poly(arylene phosphine oxide) material systems. *Macromolecular Symposium*, *98*, 673-686.