Effects of Mixing Temperatures on the Morphology and Toughness of Epoxy/Polyamide Blends

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ABSTRACT: A new mixing process was explored to increase further the fracture toughness and to investigate the toughening mechanisms of epoxy/nylon blend. In this process, without mechanical mixing, the mixtures of epoxy and premade nylon 6 powder were heated without the curing agent to specific temperatures, referred to as the "mixing temperature." For epoxy/nylon blends, at sufficiently high temperatures, a semi-interpenetrating network-like structure can be developed at the interphase *via* the reaction between the amine end group and the epoxide group. The depth of interphase and the extent of reaction depends on the mixing temperature. The strong dependency of the fracture energy on mixing temperature reveals the positive effect of the newly developed structure at the interphase. The increase of fracture toughness is possibly due to the enhanced crack fingering bifurcation/deflection mechanism resulting from the lamellae developed in the interphase and the enhanced plastic deformation of epoxy as a result of preyielding of the interphase. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 1055–1063, 1999

Key words: epoxy/nylon blend; mixing temperature; fracture toughness; morphology; semi-IPN-like structure

INTRODUCTION

Epoxies are often used as the matrix in structural composites because of their high stiffness, high strength, chemical resistance, and excellent dimensional stability. However, their low toughness, especially in the presence of sharp cracks, detracts from this usage. Hence, an improvement in toughness of brittle epoxies is greatly desired. Toughness of epoxies has often been successfully enhanced by the incorporation of a second phase, such as rubber or thermoplastic polymers.[1–4] For the rubber-toughened epoxy, the improved toughness has been reported to be due mainly to the enhanced shear deformation of the matrix material.[5,6] The shear deformability of epoxies depends on intrinsic properties like crosslink density and the glass transition temperature. Thus, low crosslinked epoxies can be successfully toughened by the inclusion of rubber, but extremely brittle high crosslinked epoxies cannot be. Moreover, the desirable intrinsic properties of the matrix, such as high strength and high stiffness, are inevitably lowered due to the low stiffness and strength of the added elastomeric materials. This limits the number of high-performance applications such as aerospace. Thus, recently, rigid thermoplastics, such as polysulfone, polyester, and polyamide, have been used as a second phase,[7–15] because the good intrinsic mechanical

properties of the matrix have remained unaffected by the inclusion of the rigid thermoplastics. Moreover, for toughening of highly crosslinked epoxies, thermoplastic polymers have been found to be more effective than rubber. The enhanced toughness of rigid thermoplastic-toughened epoxies has been suggested to be caused by the rupture and the crack bifurcation of rigid polymers.[7,13–15]

For epoxy/thermoplastic blends, the resulting morphology after cure has been known to affect the fracture toughness and toughening mechanisms strongly.[16–18] Also, it has been found that the semi-interpenetrating network (IPN) structure is more effective than a simple dispersed structure.[16,18] However, until now, the exact causes for enhanced toughness due to the semi-IPN structure have not been clear. Thus, in an effort to investigate the effects of a semi-IPN structure on the thermal and mechanical properties of epoxy/thermoplastic blends, nylon 6 and a bifunctional epoxy were selected due to the expected reactivity between them. In this study, a new mixing process was explored for morphology control.

EXPERIMENTAL

Diglycidyl ether of bisphenol A (DGEBA) and 4,4′-diaminodiphenylmethane were used as the base epoxy resin and curing agent, respectively. The optimum concentration of curing agent, 20 phr, was used. For the modifier, nylon 6 (Jeil Co.) was used in a premade particulate form, as shown in Figure 1. The composition of nylon in blends was fixed at 5 wt %.

The nylon 6 particles were made as follows: (1) nylon beads were completely dissolved in glycerol or ethylene glycol above 200°C with mechanical agitation. (2) The solution was cooled down to room temperature without agitation. During this stage, the nylon was crystallized as isolated spherulites. (3) After complete crystallization and phase separation, the solution was washed with water more than three times to dissolve out the solvent. (4) The washed powders were filtered and dried at room temperature. The size of the powder used in the study was ~ 20 μm. The properties of the powders—such as melting temperature, glass transition temperature, and crystallinity—remained unchanged by the process.

For the preparation of specimens, the mixtures of epoxy and premade nylon powder were heated
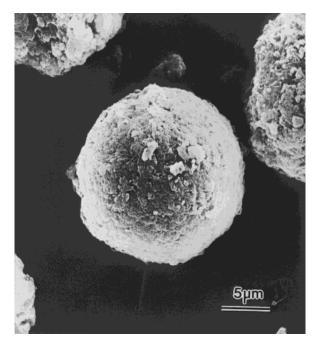

Figure 1   SEM micrographs of premade nylon 6 powder.

at the rate of 10°C min^{-1}, without stirring, to specific temperatures, referred to herein as the "mixing temperature" (T_{mix}). When T_{mix} was reached, the mixture was rapidly cooled to room temperature, again without stirring. At room temperature, the curing agent was added (with stirring), and the mixture was cured for 2 h at 80°C and postcured for another 2 h at 150°C.

In this study, the fracture toughness was measured by applying linear elastic fracture mechanics. The fracture energy, G_{Ic} was determined using a single-edge notched-type specimen (4 mm × 11 mm × 100 mm) in a 3-point bending geometry. These specimens were precracked by tapping a fresh razor blade chilled in liquid nitrogen into them. The specimens were tested on a screw-driven Instron machine at 0.01 mm s^{-1} crosshead speed. The following relationships were used to calculate G_{Ic} from each sample and crack dimension:

$$U = G_{Ic} \times B \times D \times \Phi,$$
$$\Phi = 0.5 \times (a/D) + (1/18\pi) \times (2L/D) \times (a/D)^{-1}$$

where U is the fracture energy, B is the sample thickness, D is the sample width, a is the initial crack length, and L is the span length.[19]

To examine the yielding behavior of the materials, specimens were deformed in uniaxial
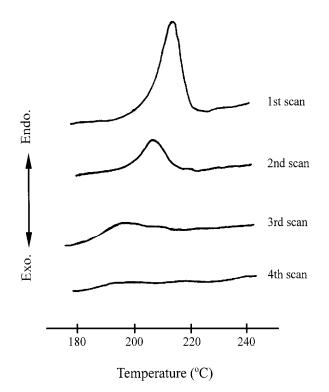
Figure 2 Effects of sequential scans on DSC thermograms of epoxy/nylon blends.

compression. Rectangular rod-shaped specimens were used with a height-to-width ratio of 2 : 1. The uniaxial compression tests were performed at a constant crosshead speed of 0.01 mm s^{-1}. The load from the measured load-displacement curve was converted to stress using the specimen's initial cross-sectional area. Then, the modulus and yield stress were determined.

Scanning electron microscopy (SEM) was used to study and record the fractured surfaces of the pure and modified epoxies. The fractured surfaces were coated with a thin layer of gold-palladium. Polarized transmission optical microscopy was used to investigate the crystal morphology of the blends. Thin sections of the specimens were made by using petrographic polishing techniques.[20]

Dynamic mechanical thermal analysis and Differential Scanning Calorimetry (DSC) were used to measure the glass transition temperatures and other thermal properties of modified epoxy, respectively. The frequency used for dynamic mechanical thermal analysis was 1 Hz, and the heating rate for both was 5°C min^{-1}.

RESULTS

Effects of Thermal Treatment on Thermal Properties of the Epoxy/Nylon Blends

Sequential scans of a mixture of nylon particles and uncured epoxy without the curing agent by DSC are shown in Figure 2. During the first scan, a sharp melting endotherm was observed with a maximum at 212°C (melting maximum of pure nylon: 225°C). During subsequent scans, the peak shifted to lower temperature and broadened. Also, the heat of fusion considerably decreased. After the third scan, the melting endotherm almost disappeared.

The thermal properties of epoxy/nylon blends after cure are considerably affected by the mixing temperature. The dependency of the thermal properties of the blends on T_{mix} can be seen in Table I and in Figure 3. With an increase of T_{mix}, above 185°C, the glass transition temperature of the epoxy matrix increased almost linearly. Both the melting temperature (T_m) and the heat of fusion (ΔH) of nylon remained unaffected up to 210°C; but, at higher T_{mix}, they rapidly decreased. Complete dissolution of the nylon particles in epoxy can be obtained above 230°C. Thus, epoxy/nylon blends mixed at temperatures ranging from 220° to 230°C exhibited a pair of endotherm maxima due to partial dissolution of nylon particles, as shown in Table I.

The viscosity of the mixture after cooling was also affected by T_{mix}. The viscosity of the blends mixed at temperatures ranging from 210° to 230°C became too high to mix the curing agent uniformly, even at 5 wt % nylon composition. Thus, for higher composition, further processing could not be done.

Table I   Thermal Properties of Epoxy/Nylon Blends Mixed at Various Temperatures

T_{mix} (°C)	T_g (°C)[a]	T_m (°C)[b]	ΔH (cal g^{-1})
25	157.0	224.5	1.63
200	159.5	222.7	1.64
210	161.1	222.3	1.66
215	163.6	220.1	1.23
220	164.7	212.3, 222.8	1.11
230	166.0	207.7, 222.0	0.87

[a] T_g, glass transition temperature.
[b] Temperatures of the pair of endotherm maxima that resulted from partial reaction of nylon and epoxy.
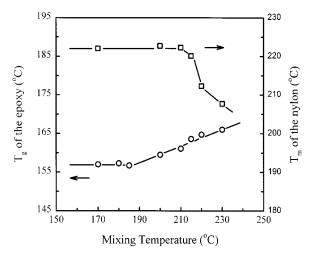
Figure 3 Effects of the mixing temperature on the glass transition temperature of epoxy matrix (○) and the melting temperature of nylon (□).

Effects of Thermal Treatment on the Mechanical Properties of the Blends

The modulus and yield stress of the modified epoxies remained unaffected by T_{mix} (as seen in Figure 4). However, the fracture toughness was highly affected. The effects of T_{mix} on the fracture energy of modified epoxy (5 wt % nylon) is shown in Figure 5. The fracture energy increases rather slowly with T_{mix} for temperatures up to 210°C, and then, at higher T_{mix}, ranging from 210° to 220°C, the fracture energy increased at a much highly rate. After that, the fracture energy decreased. Thus, the fracture energy of thermal treated epoxy/nylon
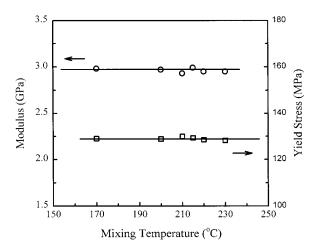

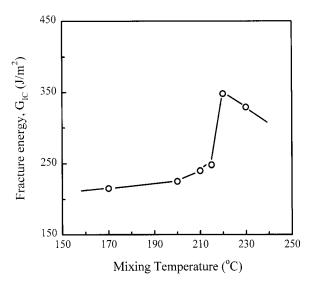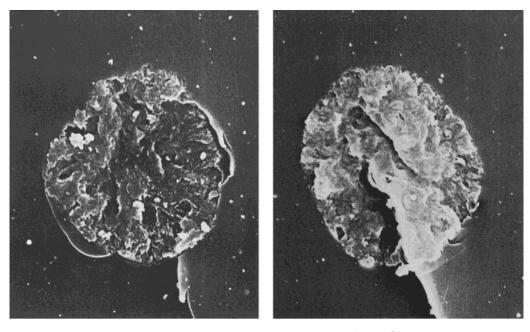**Figure 4** Effects of the mixing temperature on the modulus (○) and yield stress (□).

Figure 5 Effects of the mixing temperature on the fracture energy.

blends exhibited a maximum when T_{mix} was 220°C.
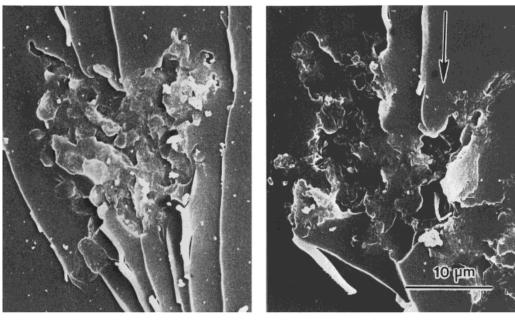
Fractographic Study

The fracture morphology of the epoxy/nylon blends after cure revealed the mixing and phase separation behavior of the blends. The SEM micrographs of fracture surfaces of the blends mixed with the different T_{mix} are shown in Figure 6. For T_{mix} below 210°C, the morphology of the blends was essentially the same as that mixed at room temperature. Behind each nylon particle, there occurred only one tail or crack bifurcation line that indicates the crack path altering and bridging mechanism. Each tail consists of a step and an associated welt. Steps and welts form as the pairs of cracks moving on the different planes interact with each other and recombine. Welts are plastically deformed as they are stretched between the surfaces of the opened crack. The ductile behavior of the nylon phase, as indicated by the fibrous nature, can also be seen on the fracture surfaces. With an increase of T_{mix}, the interphase becomes unclear, the size of the nylon phase decreases, and the fracture surface becomes rough and complex. Also, the number of secondary cracks behind each nylon phase increases.

The optical micrographs of the blends under cross polars also reveal the morphology of interphase after mixing process. Figure 7 shows optical micrographs of thin sections of the blends
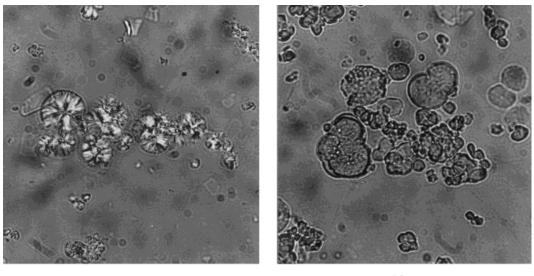
Figure 6 SEM micrographs of the fracture surfaces of epoxy/nylon blends made by mixing at: (a) 30°C, (b) 210°C, (c) 220°C, and (d) 230°C. (Arrow indicates the crack propagation direction.)
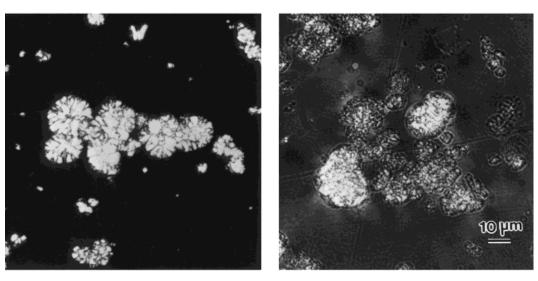
mixed at 200°C and 220°C, taken with 45° and 90° polars. As seen in the figure, after mixing above 215°C, the interphase also became unclear, and the birefringence became hazy. Gross plastic deformation of the epoxy matrix by the formation of shear bands or other plastic deformation is hard to see due to the birefringence of nylon crystals. The hazy birefringence around the inter-

Figure 7   Optical micrographs of epoxy/nylon blends made by mixing at: (a) 200°C, (b) 200°C, (c) 220°C, (d) 220°C. [(a) and (c) 45° polars; (b) and (d) 90° polars.]

phase may arise from tiny lamellae developed inside the interphase.

DISCUSSION

Effects of Thermal Treatment on the Interphase Structure of Epoxy/Nylon Blends

An understanding of the phase separation behavior in thermoset/thermoplastic blends is highly desirable, because the resulting mor-

phology is known to affect the physical and mechanical properties of the blends.[16–18] Moreover, it has been found that the interphasal morphology often affects the properties of the blends considerably. For example, in epoxy/poly(butylene terephthalate) (PBT) blends, the semi-IPN structure at the interphase gives a positive effect on fracture toughness.[16,18] In this system, the semi-IPN structure can be introduced by control of the mobility of PBT molecules during phase separation.

For the epoxy/nylon blends investigated, at sufficiently high mixing temperatures >200°C, a new structure can be developed at the interphase due to a reaction between the primary amine end group of nylon and the epoxide group.[21–23] The occurrence of the reaction can be clearly confirmed by the considerable decrease of crystallinity and the lowering/broadening of the melting peak on sequential scans of epoxy/nylon mixtures by DSC (see Figures 2 and 3). The amine end group of nylon can act as a curing agent and initiate the reaction between the components during the scan. Thus, on sequential scans, the mobility of the nylon molecules is highly restricted due to the formation of a network structure during the previous scan and, as a result, crystallization and phase separation are highly suppressed. Thus, finally, the mobility is so restricted as to prevent crystallization. The structure developed at the interphase by the reaction is not exactly a semi-IPN structure. But, due to its similarity, it can be called a semi-IPN-like structure. During crystallization after mixing, the relatively free nylon molecules can be crystallized as a form of isolated lamellae, instead of forming spherulite. Thus, finally, a large number of tiny lamellar crystals are developed inside the semi-IPN-like interphase. The depth of interphase and the amount of reaction depend on T_{mix}.

For $T_{mix} > 220$°C, the observed double melting endotherms in DSC scans are due to partial dissolution of nylon particles in the epoxy. The peak at 224°C corresponds to the melting of undissolved nylon, whereas the low peak corresponds to the nylon in the newly developed interphase. The rapid decrease of the low melting peak temperature when T_{mix} is >210°C also indicates the occurrence of a reaction between nylon and epoxy. The exact causes of the lowering of T_m are still unclear, but are possibly related to a reduction of lamellar thickness as a result of the reduction of molecular mobility of nylon due to network structure formation. The lowering of crystallinity with increase of T_{mix} is, as previously described, also due to the suppression of crystallization by network structure formation.

The increase of the glass transition temperature of the epoxy with T_{mix} can be another indication for the development of semi-IPN-like structure. Usually, for miscible or partially miscible blend systems, the glass transition temperature of the rigid component is lowered due to its miscibility with the soft segment. Thus, the increase of glass transition temperature in epoxy/nylon blends is thought to be due to the formation of a higher network structure by the prereaction of nylon and epoxy before cure.

Effects of Semi-IPN-like Structure on Fracture Toughness of Epoxy/Nylon Blends

The fracture energy of the epoxy has been reported to be successfully enhanced by the inclusion of premade nylon particles without loss of mechanical properties of epoxy.[13] From the fractographic study, the toughness enhancement of nylon particle-toughened epoxy is suggested to arise from a combination of (1) crack path altering, (2) primary crack bridging, (3) initiation of secondary cracks, (4) formation of multiple secondary cracks, and (5) ductile fracture of the nylon phase.

The strong dependency of the fracture energy on T_{mix} reveals the positive effect of the newly formed semi-IPN-like structure on fracture toughness. The morphology change with T_{mix} is well exhibited in the fracture surface of blends. When the premade nylon particles are mixed with epoxy below the onset temperature of melting and dissolution, the fracture morphology has remained unchanged. Sudden morphology change at T_{mix} >215°C is due to the partial dissolution of the nylon particles and a development of a new semi-IPN-like structure. These morphology changes by T_{mix} are well correlated with the change of thermal properties. The hazy birefringence under crosspolars may be due to the development of a large number of tiny lamellar crystals as a result of mobility restriction by the formation of a semi-IPN-like structure (see Figure 7).

The exact causes for the toughness enhancement in the presence of semi-IPN-like structure are still unclear. However, a semi-IPN-like structure developed in the epoxy/nylon blends is possibly able to enhance toughness due to: (1) enhanced crack bifurcation/deflection by the tiny crystals in the semi-IPN-like structure and (2) enhanced plastic deformation of the epoxy in the interphase by stress concentrations around the large number of tiny crystals as a result of preyielding of the semi-IPN-like structure.

When a crack propagates through the materials, the front of the crack tip has been suggested to proceed as a series of fingers,[24,25] as seen in Figure 8. This is thought to occur by a meniscus instability mechanism. The remnants of this process in a crosslinked glass are referred to as the basic longitudinal texture. The width of the fin-
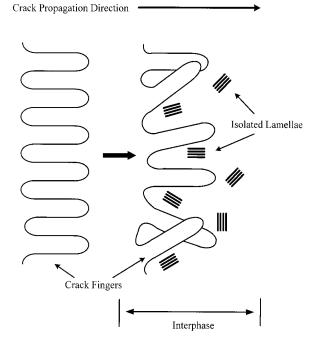
Crack Propagation Direction

Isolated Lamellae

Crack Fingers

Interphase

Figure 8 Schematic drawing of crack fingering bifurcation/deflection mechanism.

gers ahead of the crack front is thought to be on the order of 100 nm. Thus, the dimension of the fingers would be the same order as the crystal lamellae, but much smaller than the size of individual spherulite. During the fracture of epoxy blends with large crystalline thermoplastic domains, the crack mainly proceeds through the relative homogeneous matrix phase, and the fingers ahead of the crack tip are rarely redirected. However, for the fracture of epoxy blends with large numbers of tiny lamellae in semi-IPN-like regions, the fingers bifurcate and deflect many times, which can increase the fracture toughness of the blends. A part of the toughening provided by bifurcation is through the energy required to create new surface. Additionally, there is the energy absorbed, because the welt, which has been subsequently formed from each bifurcation, is plastically deformed when it is stretched between the surfaces of the opened crack.

For thermoplastic modified epoxies, it has been suggested that the thermoplastic phase induces a stress concentration by yielding before the epoxy does, which causes the epoxy to undergo shear yielding. So, in epoxy/thermoplastic blends with a semi-IPN-like structure, if the semi-IPN-like structure ahead of crack tip is deformed at a stress lower than the yield stress of the epoxy, the tiny crystalline domains would like to change

their shape. Thus, the change of shape causes the stress concentration around the domains, which could induce shear yielding in the surrounding epoxy matrix.

CONCLUSIONS

In an effort to investigate the effects of an interphase on the thermal and mechanical properties of epoxy/thermoplastic blends, nylon 6 and DGEBA epoxy were selected due to the expected reactivity between them. In this study, a new mixing process was explored for morphology control.

For epoxy/nylon blends at sufficiently high mixing temperatures, a semi-IPN-like structure can be developed at the interphase due to the reaction between the amine end group of nylon and the epoxide. The occurrence of the reaction can be clearly confirmed by the considerable decrease of crystallinity and the lowering/broadening of the melting peak on sequential scans of epoxy/nylon mixtures. The depth of the interphase and the amount of reaction depend on T_{mix}.

In this system, the lowering of crystallinity and the melting temperature of the nylon phase with T_{mix} are also due to the suppression of crystallization by network structure formation. The increase of the glass transition temperature of the epoxy with T_{mix} can be another indication for the development of a semi-IPN-like structure by the reaction.

The strong dependency of fracture energy on T_{mix} reveals the positive effect of the semi-IPN-like structure on the toughness. The increase of fracture toughness is possibly due to enhanced crack fingering bifurcation/deflection by the tiny lamellae developed in the interphase and enhanced plastic deformation of the epoxy as a result of preyielding of semi-IPN-like structure.

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