

In Situ Detection of the Onset of Phase Separation and Gelation in Epoxy/Anhydride/Thermoplastic Blends

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Abstract: The isothermal cure reactions of blends of epoxy (DGEBA, diglycidyl ether of bisphenol A)/anhydride resin with polyamide copolymer (poly(dimmer acid-co-alkyl polyamine)) or PEI were studied using differential scanning calorimetry (DSC). Rheological measurements have been made to investigate the viscosity and mechanical relaxation behavior of the blends. The reaction rate and the final cure conversion were decreased with increasing the amount of thermoplastics in the blends. Lower values of final cure conversions in the epoxy/thermoplastic blends indicate that thermoplastics hinder the cure reaction between the epoxy and the curing agent. Complete miscibility was observed in the uncured blends of epoxy/thermoplastics up to 120 °C but phase separations occurred in the early stages of the curing process at higher temperatures than 120 °C. According to the rheological measurement results, a rise of G' and G'' at the onset of phase separation is seen. A rise of G' and G'' is not observed for neat epoxy system since no phase separation is seen during cure reaction. At the onset of phase separation the rheological behavior was influenced by the amount of thermoplastics in the epoxy/thermoplastic blends, and the onset of phase separation can be detected by rheological measurements.

Keywords: cure reaction, epoxy/thermoplastic, phase separation, rheological measurement, rheological behavior.

Introduction

Polymer modification has been an important subject in recent years to improve the mechanical properties of engineering plastics and thermoset resins in order to meet highly qualified structural and mechanical component applications. A number of works on epoxy resin modification with both functionalized and non-functionalized thermoplastics have been undertaken till now.¹⁻⁵ Epoxy/polyetherimide (PEI: Ultem 1000) and epoxy/polyethersulfone (PES: Udel) blends have been investigated as typical examples of those modified epoxy resins, and the toughness of epoxy was significantly improved by adding PEI or PES, with retaining high glass transition temperature and high mechanical strength.¹⁻³ Most of the studies on thermoset/thermoplastic blends have dealt with thermoplastics-such as commercial grades of PEI, PES, polysulfone, nylon 610, polyimide etc.-as a modifier, which is incompatible with the epoxy resin in cured blends.⁶⁻¹⁷

Cure reactions of thermoset/thermoplastic blends can be examined by differential scanning calorimetry (DSC), although a fourier transform infrared spectroscopy - attenuated total reflectance (ATR-FTIR) has been also used to

estimate the reaction parameters.¹⁵ In DSC analysis, both the isothermal and the dynamic heating modes have been used extensively to determine the cure reaction parameters for the neat epoxy and epoxy/thermoplastic blends, which are mostly cured with an anhydride curing agent. In the epoxy system based on diglycidylether of bisphenol A (DGEBA), the cure reactions are typically characterized by an initial accelerated reaction, due to autocatalysis in the early stages of the reaction, while, in the latter stages, a decrease in the reaction rate is exhibited by the onset of gelation and vitrification due to the cure reactions becoming diffusion controlled. Dynamic mechanical measurements have been made using a Rheometrics RDA II to investigate the mechanical relaxation behavior of the epoxy/thermoplastic blends.^{18,19} As the thermoset precursor reacts the thermoset/thermoplastic blend separates into two phases since an average molecular weight is increased and reached where a homogeneous mixture no longer favored.

In the present study as a modifier, polyamide copolymer (poly(dimmer acid-co-alkyl polyamine)) is used for DSC and viscosity measurements and PEI for dynamic measurements. The polyamine-containing polyamide copolymer could be participated in cure reaction at the interface between epoxy and the copolymer. The cure reaction and phase separation of an epoxy system containing the DGEBA and anhydride

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curing agent, and their blends with PEI or polyamide were studied.

Experimental

Materials. The epoxy system was based on a commercial grade of DGEBA (KUKDO Chemicals Co., Korea) with an average epoxy equivalent weight of 187.5 g/eq. The epoxy blends with a polyamide copolymer, poly(dimmer acid-*co*-alkyl polyamine) (Aldrich, USA), and a PEI (Ultem 1000, Dupont, USA) were cured with an anhydride curing agent, nadic methyl anhydride (KUKDO Chemicals Co., Korea), in the presence of a catalyst, 2,4,6-tris(dimethylaminomethyl) phenol, (KUKDO Chemicals Co., Korea). The chemical structures of materials are shown in Figure 1.

Preparation of Blends. The polyamide copolymer solution or the PEI solution in methylene dichloride was mixed with the epoxy prepolymer under high-speed stirring for 2 hrs at room temperature. Then the solvent was removed in a rotary

vacuum evaporator at 80 °C for 24 hrs. A stoichiometrically balanced amount of a curing agent (or 120% excess to investigate the effect of the partitioning of the curing agent in both of the separated phases in the blends) with a catalyst (5-10 phr) were blended with the epoxy/thermoplastic mixture in a three-roll mill at room temperature for 1 hr.

Differential Scanning Calorimetry. The cure kinetics and the degree of conversion as a function of time can be obtained using differential scanning calorimetry (DSC), which is operated isothermally at 110, 120 and 130 °C to find the parameters of the cure kinetics for the reactive epoxy/thermoplastic blends. The calculated parameters were the reaction order (n) and the rate constant (k).

The degree of cure, α (i.e., cure conversion), was determined based on the following equation:

$$\alpha = \frac{\Delta H_t}{\Delta H_\infty} \quad (1)$$

where ΔH_t is the partial heat of reaction at time t and ΔH_∞

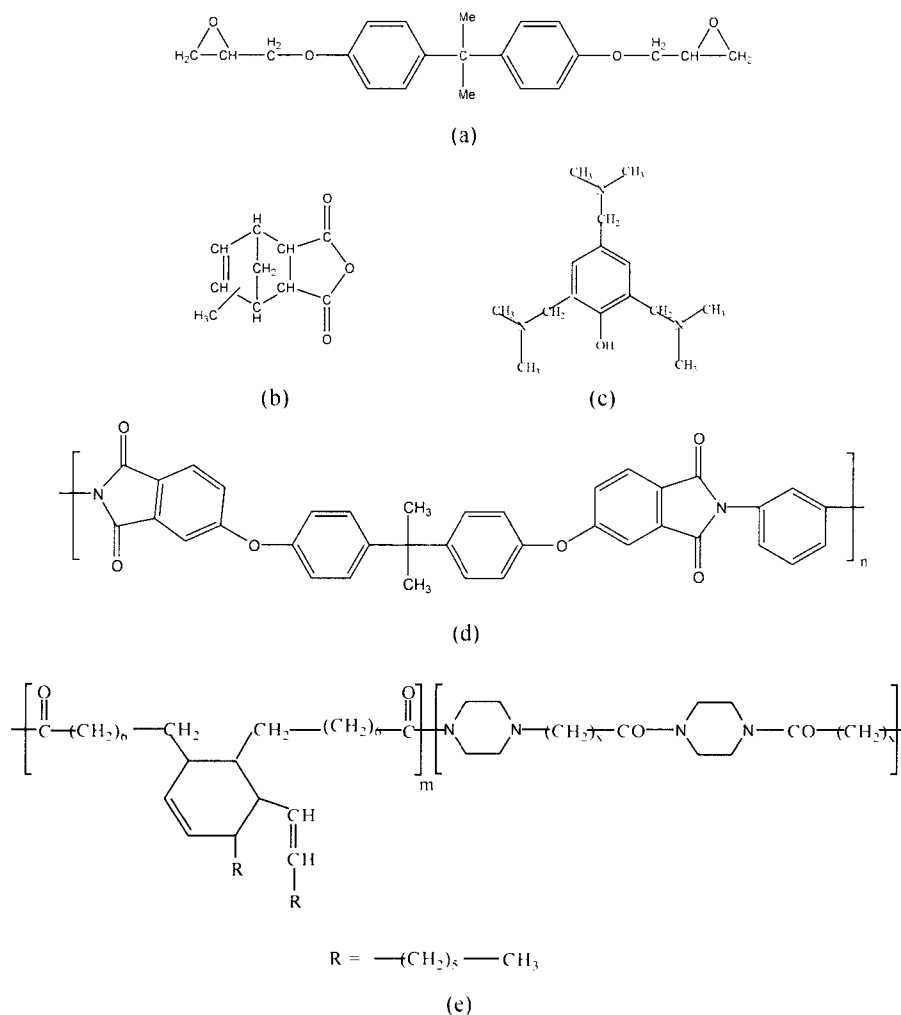


Figure 1. Chemical structures of diglycidyl ether of bisphenol A (a), nadic methyl anhydride (b), 2,4,6-tris(dimethylaminomethyl) phenol (c), PEI(d), and poly(dimmer acid-*co*-alkyl polyamide)(e).

is the total heat of the reaction. The cure reaction rate, r , was obtained from the cure conversion data as a function of time by taking the derivative of α with respect to time:

$$r = \frac{d\alpha}{dt} \quad (2)$$

Dynamic Mechanical Measurements. Dynamic mechanical measurements were made using a Rheometrics RDA II in this work. Measurements using 25 mm parallel plates at 50 rad/s in a temperature-controlled chamber were taken continuously throughout the entire cure processes to detect the change in dynamic mechanical properties before and after phase separation in the epoxy/thermoplastic blends.

Results and Discussion

Miscibility of Epoxy/Thermoplastic Blends. Most binary blends of engineering thermoplastics, PEI, PES, and polyamide, with a DGEBA-based epoxy resin, exhibited a single glass transition, indicating complete miscibility over a given or an entire composition range.²⁰⁻²² The glass transition temperature of the neat epoxy resin used in this experiment was -25°C . As expected, in this study, a single glass transition temperature of the epoxy/polyamide copolymer blends has been shown (i.e., approximately -9°C for 10 phr of polyamide composition), which indicates that the epoxy/polyamide copolymer blend is miscible and the same is the epoxy/PEI blend.

As an alternative way to investigate miscibility of multi-component blends, simple optical tests of clarity have been widely employed. A visual observation indicated that the epoxy/polyamide copolymer blend and epoxy/PEI blend without anhydride, up to 120°C , were to be homogeneous and optically clear. In comparison, with anhydride, the blends became gradually turbid as cure reaction proceeded at elevated temperatures of about 120°C or higher.

Cure Reaction. The typical cure conversion and the conversion rate vs. time are shown in Figures 2 and 3, respectively. The conversion drastically increased as time increased, as was also seen in some works on cure kinetics of epoxy/thermoplastics blends.^{7,12,20-25} After a drastic increase in conversion in the early stages of the cure reaction, a retardation of the conversion gradually occurred as the blends matrix became vitrified and the cure reaction rapidly became diffusion controlled, as shown in Figure 3. On increasing the curing temperature, the position of the maximum rate of conversion was shifted to the shorter time. As thermoplastic content increased, the final conversion decreased at the same cure temperature. As cure temperature increased, the final conversion increased for all compositions of thermoplastic in the blends.

As mentioned by Varley *et al.*,¹² this decrease in the final epoxy conversion with increasing thermoplastic content can be explained by the partitioning of epoxy resin in both the

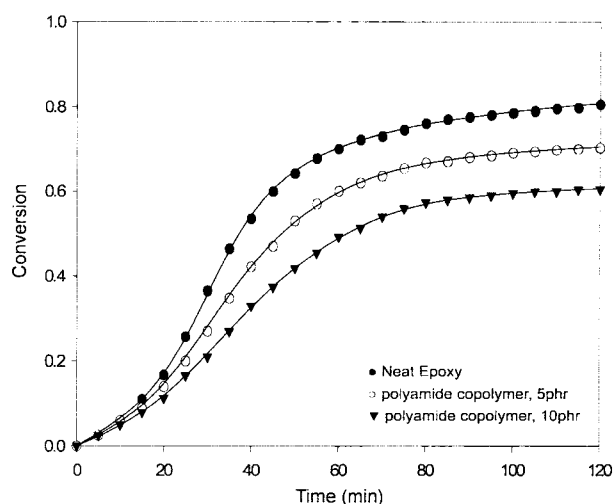


Figure 2. Typical cure conversions for the epoxy/anhydride/polyamide copolymer system at 110°C .

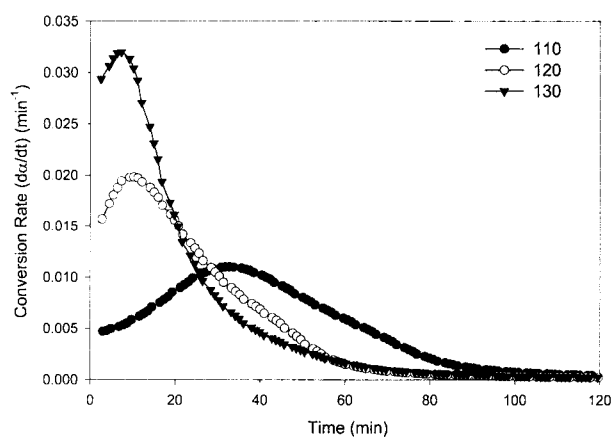


Figure 3. Plot of conversion rate vs. reaction time for the epoxy/anhydride/polyamide copolymer system (polyamide copolymer: 10 phr).

epoxy-rich phase and the thermoplastic-rich phase in the blends. As another possible way to explain the low final epoxy conversion, the partitioning of the curing agent in both of the separated phases in the blends may cause this decrease in the final epoxy conversion. Preliminary studies to investigate the effect of the partitioning of the curing agent in both of the separated phases in the blends showed that when the 20% excess of curing agent was added to the blends, evidently 10 to 15% increase in the final conversion was observed.

Viscosity Measurement. A polyamide copolymer as a thermoplastic is used to observe the viscosity behavior and monitor the onset of phase separation during the cure reaction. As the cure reaction occurs, the molecular weight increases and an average molecular weight is reached where

a homogeneous mixture is no longer favored and consequently the thermoplastic-reacting thermoset blend system begins to separate into two phases. At this point, as a result of both phase separation and advancement of the epoxy-anhydride reaction, the viscosity increases because the epoxy-anhydride cure reaction rate is readily increased in the polyamide-free phase. At the onset of phase separation, therefore, the viscosity begins to increase. This advancement of the epoxy-anhydride reaction can be detected by the viscosity measurements. The time-temperature history of both the onset of phase separation and reaction advancement is important in knowing and controlling the morphology. In some works,^{18,19} dynamic mechanical measurements were used as another way to describe the onset of phase separation in the thermoplastic/thermoset blends. A rheological detection of the onset of phase separation in the epoxy/polyamide copolymer blend is shown in Figure 4. In the figure, at the onset of phase separation, the increase in viscosity was observed, which is an evidence for the advancement of the epoxy-anhydride reaction. An approximate onset time was 20 min at 110°C in Figure 4 and the onset times of 5 and 4 min were observed at 120 and 130°C, respectively. After the onset of phase separation, the viscosity decreased slightly and then rapidly increased. The transmitted and polarized light microscope equipped with a heating stage was used to confirm optically the onset of phase separation and monitor phase separation through the cure reaction.

Dynamic Mechanical Measurement. Dynamic mechanical measurements were made for a PEI as a thermoplastic to monitor the onset of phase separation during cure reaction. As the thermoset precursor reacts the thermoset/thermoplastic blend separates into two phases since an average molecular weight is increased and reached where a homogeneous mix-

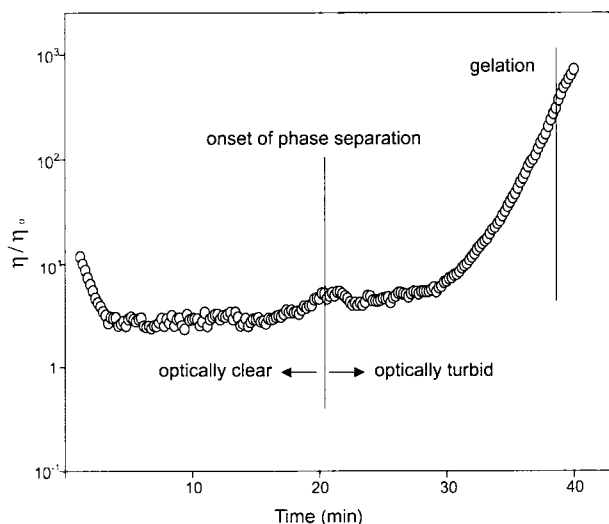


Figure 4. Typical onset of phase separation (η_0 : reference viscosity) and gelation time for epoxy/anhydride/polyamide copolymer (10 phr) system at 110°C.

ture no longer favored. With a viscometric detection of the onset of phase separation in the epoxy/thermoplastic blend, the dynamic mechanical measurements can be also used to monitor the onset of phase separation by detecting the rheological change of the blends which occurs during phase separation. The dynamic mechanical measurements could be sensitive to the change of rheological behavior at the onset of phase separation in the thermoset/thermoplastic blend system. At the onset of phase separation charge polarization is also observed at approximately the same time as in the mechanical properties, typically in viscosity.^{18,19} From the macroscopic measurement the morphology change from a homogeneous system to a heterogeneous two-phase material is to be seen as well.

The dynamic mechanical measurement results and the SEM images of fracture surfaces, taken after exposure to liquid nitrogen to identify phase-separated interfaces during cure reaction, are shown in Figures 5 and 6 for a neat epoxy and a epoxy/PEI system, respectively. The values of G' and G'' show distinct changes with time, which indicates that the changes in the values of G' and G'' is attributed to the onset

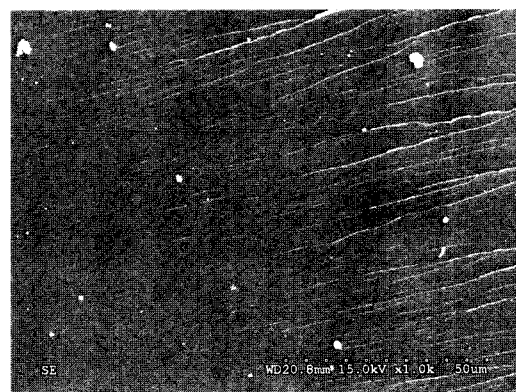
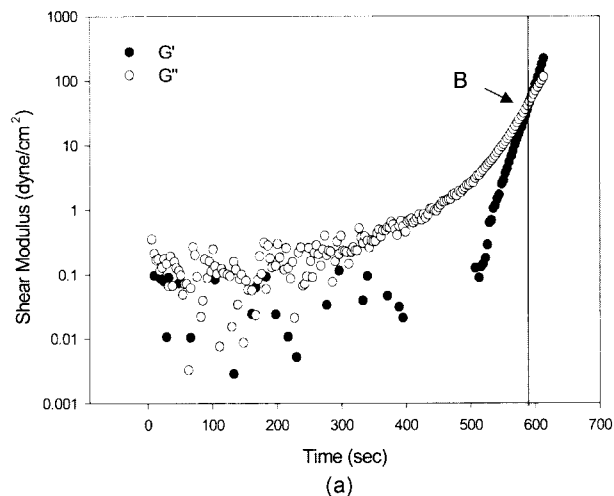


Figure 5. Dynamic mechanical values of modulus G' and G'' versus time for neat epoxy system cured at 130°C (a) and a SEM photograph (b).

of phase separation (marked "A" in Figures) as well as gelation (marked "B" in Figures with the remarkable increase in viscosity or modulus before vitrification time and confirmed by a manually-estimated gel time test on the hot plate and coincidentally appeared near the crossing point of G' and G''). The change in rheological behavior is expected to arise from the onset at the phase-separated interface to be optically observed. At the onset of the phase separation, the change in rheological behavior in terms of shear modulus is seen at approximately the same time as in the change in viscosity or in the mechanical properties. The change from a homogeneous phase to a heterogeneous phase is rapid and may depend on the amount of thermoplastic involved. It was observed that the degree of changes in rheological behavior in terms of shear modulus is too low to be detected for epoxy/thermoplastic blends with less than a 5 phr thermoplastic content. As the amount of thermoplastic increases in the blends, the change in rheological behavior at the phase-separated interface increases and eventually a rise of G' and G'' at the onset of phase separation is observed as shown in Figure 6. In Figure 5, no phase separation is observed for neat epoxy and obviously no stepwise rise of

G' and G'' is seen at the onset of phase separation, either.

Conclusions

The cure reactions of anhydride-cured epoxy/polyamide copolymer, poly(dimmer acid-co-alkyl polyamine), and epoxy/PEI blends were investigated over a range of composition, and the onset of phase separation was observed by means of viscometric and dynamic mechanical measurements. By increasing the contents of thermoplastics in the epoxy system, a decrease in the total heat of the reaction and final cure conversion were observed and the diffusion-controlled reaction took place in the much earlier stages of the reaction at the same cure temperature.

A viscometric detection of the onset of phase separation in the epoxy/thermoplastic blend was accomplished. At the onset of phase separation, the viscosity increases because of an increase in the cure reaction rate in the thermoplastic-free phase in the blends. Similarly, the dynamic mechanical measurement was used to monitor the onset of phase separation by detecting the change of rheological behavior which occurs during phase separation. According to the dynamic mechanical measurement results, a rise of G' and G'' at the onset of phase separation as well as gelation was observed. For neat epoxy, no phase separation was observed and no stepwise rise of G' and G'' was seen since there is no phase separation. It could be concluded that at the onset of phase separation the rheological behavior is influenced by the amount of thermoplastics in the epoxy/thermoplastic blends. The changes in rheological behavior at the onset of phase separation could be detected by viscometric means and dynamic mechanical measurements *in-situ* during cure reaction.

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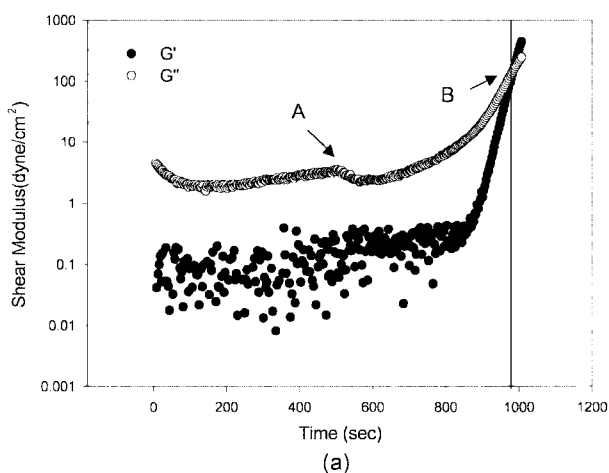


Figure 6. Dynamic mechanical values of modulus G' and G'' versus time for epoxy/PEI(10 phr) system cured at 130°C (a) and a SEM photograph (b).

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