Polymerization-Induced Bimodal Phase Separation in a Rubber-Modified Epoxy System

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ABSTRACT: The bimodal phase separation process of a rubber-modified epoxy system, consisting of diglycidyl ether of bisphenol A (DGEBA), and a hydroxyl-terminated butadiene–acrylonitrile random copolymer (HTBN), during curing with tetrahydrophthalic anhydride was studied by time-resolved small-angle light scattering (TRSALS), differential scanning calorimetry (DSC), and digital image analysis (DIA). The HTBN/DGEBA mixture reveals an upper critical solution temperature (UCST). At higher curing temperatures, double-peak structure from the matrix was investigated by TRSALS and confirmed by DIA. The special two characteristic size distribution behavior was explained qualitatively by nucleation growth coupled with spinodal decomposition (NGCSD) and the competition between phase separation and polymerization. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 59–67, 1999

Key words: polymerization-induced phase separation; bimodal phase separation; double-peak structure; digital image analysis; nucleation growth coupled with spinodal decomposition

INTRODUCTION

Epoxy resins constitute one of the major classes of thermosetting polymers in use, including matrices for composites and structural adhesives.[1] In the last 2 decades, a large amount of research has been done on the relationship between structure and properties of epoxy resins owing to the potential of their industrial applications.[2–10] In recent years, polymerization-induced phase separation (PIPS) in thermoset rubber blends has received renewed interest because of its unusual equilibrium and nonequilibrium pattern formations.[11–14] Kinetics and mechanism of PIPS are

more complex to study than those of the common thermally induced phase separation (TIPS), while the latter has been extensively studied both theoretically[15,16] and experimentally[17,18] in polymer blends. There are limited studies in the problem of phase separation driven by polymerization where phase separation and polymerization occur simultaneously.[11,13,14]

When a polymer blend is brought from an initially homogeneous state into an unstable spinodal region, various modes of concentration fluctuation develop and are amplified in the mean time by virtue of thermal fluctuations. If thermal fluctuation is fully suppressed, a single selective mode grows predominantly so that the structure becomes more regular, and a spinodal ring may be observed by light scattering. But for the case of PIPS, the drive force of the system is the progressive increase of molecular weight of the polymerizing monomers. A nucleation growth (NG) mechanism may take place in PIPS simultaneously with spinodal decomposition (SD). Because PIPS

has now become an effective and practical method of producing some special binary or ternary composite materials, the understanding of its governing mechanisms is of much more importance in elucidating development of final morphology.

In the case of rubber-modified epoxy resin mixtures, after the temperature jumps to the curing temperature, the homogenous mixture starts to demix due to the increase in the molecular weight of epoxy, which resulted in the poor miscibility between the liquid rubber and the epoxy. According to the results of Yamanaka et al.,[19] the curing-induced phase separation proceeds mainly via spinodal decomposition. During the curing process, the system has to pass through the *meta*-stable region before it is thrust into the unstable region, and hence, phase decomposition by a nucleation growth mechanism is expected to take place. However, Yamanaka[19] thought that this is not conceivable because, first, nucleation growth is well recognized to be a very slow process and it may be skipped (i.e., nothing happens at the *meta*-stable region) and, second, nucleation occurs accidentally, and the subsequent growth results in a domain structure without a well-defined correlation length (it never results in the regular structure that gives a light-scattering peak). However, recent studies revealed that nucleation growth does happen in such a polymerization-induced phase separation.[20,21] The real beginning of the phase separation was found by SAXS to be much earlier than the cloud-point temperature determined by a light-scattering technique. Before the rapid formation of particles at the cloud point, phase separation has already occurred through a nucleation growth mechanism for a relatively long time period.

In a previous article,[14] the phase separation mechanism and structure development during curing of epoxy with a novel liquid rubber—ZR (made in Tsinghua University, Beijing, China) were investigated. Due to its good miscibility with epoxy, cocontinuous structure of the final morphology could be easily controlled and then obtained.

In the present article of the series, another liquid rubber, hydroxyl-terminated acrylonitrile–butadiene random copolymer, HTBN, which is a little poorer in compatibility with epoxy, was used to study its role on polymerization-induced phase separation in an epoxy system. The reaction-induced phase separation was observed *in situ* with methods of different observation techniques, that is, time-resolved small-angle light scattering (TRSALS), optical microscopy (OM), differential

Figure 1 Chemical structures of epoxy monomers, curing agent, accelerator, and rubber.

scanning calorimetry (DSC), digital image analysis (DIA), etc. Bimodal phase separation and a double-peak structure were observed by TRSALS and confirmed by DIA. Reasonable explanations were given to deduce the formation of such a special bimodal distribution morphology.

EXPERIMENTAL

Materials

Figure 1 shows the structural formulae of the epoxy monomers, the curing agent, the curing accelerator, and the rubber HTBN.

The DGEBA (Diglycidyl Ether of Bisphenol A) based epoxy monomers were E-51 (Shanghai Resin Factory, Shanghai, China), with an equivalent weight of epoxy groups of 190 g/equiv, average molecular weight $\overline{M_n} = 380$ ($\bar{n} = 0.03$) and E-39-D (Jiaxing Chemicals, Zhejiang Province, China), with an equivalent weight of epoxy groups of 248 g/equiv, average molecular weight $\overline{M_n} = 496$ ($\bar{n} = 0.50$). The curing agent was methyl tetrahydrophthalic anhydride (MeTHPA, Labora-

Figure 2   Time-resolved small-angle light-scattering apparatus.

tory Factory of Shanghai Jinshi Fine Chemicals, China). The corresponding curing accelerator was *N,N'*-dimethyl benzyl amine (BDMA, Shanghai No. 3 Chemical Reagent Factory, China).

HTBN was supplied by our department. Its hydroxyl group content was 0.62 wt %, acrylonitrile group content was 15.38 wt %, average molecular weight $\overline{M_n}$ was 1700, respectively. It was a viscous liquid rubber, which is light yellow and greenish.

Cloud-Point Curves Measurement (CPC)

Mixtures of HTBN with epoxy monomers, E-51 and E-39-D, were carefully prepared by stir mixing both components in desired weight fractions, for about 10 min, at convenient temperatures to attain the homogeneous region (as judged by the transparency of the mixture). Then, mixtures were transferred to the cover glass on the hot stage to start CPC measurement.

The time-resolved small-angle laser light-scattering device shown in Figure 2 was also used here to obtain CPC as well as to study the kinetics of phase separation in the following studies. The CPC measurement is based on the decrease in the fraction of transmitted light at the time of phase separation, due to the difference in the refractive indices of both.

Sample Preparation for SALS and Epoxy Conversion Measurement

The epoxy monomer E-51, liquid rubber HTBN, curing agent MeTHPA, and curing accelerator BDMA were thoroughly mixed in desired weight ratio, i.e., HTBN/E-51/MeTHPA/BDMA = 40/90/70/0.056 at room temperature and then degassed

in vacuum for 5–10 min. Two cover glasses were preheated for 5–10 min on the hot stage. The mixture was cast onto the glass and sandwiched by another one with a spacer of about 100 μm to get average thickness and keep from accidental oxidation. The scattering intensity was recorded by either video recorder and/or computer hard disk.

Time-Resolved Small-Angle Light Scattering

The principle of a time-resolved small-angle light-scattering apparatus was described in some earlier articles.[14,17,22–24] Figure 2 shows the laser light-scattering apparatus used in this study. Detailed description of this apparatus is available elsewhere in our articles[14,25] and will not be repeated here. A normal laser beam (He-Ne laser of 7.5 mW, λ_0 = 632.8 nm) was employed as a light source. A two-dimensional CCD (charge coupled device) camera was used to record the change of scattering profiles and scattering patterns with time during phase separation. The image intensity is corrected for refraction, double scattering, and geometric effects.[25,26] Contributions from parasitic light, thermal fluctuations, and dark current were collected together in a way immediately after transferring the sample as a background.

A temperature controller, which can control four channels at the same time, is interlinked by a RS232 communication port to the computer. The heating blocks made of brass were designed with screwal-shape grooves, where electric heating wire is fixed. It is a unique technique for a good heat transfer, which provides the possibility of heating or cooling at different rates. The accuracy of the temperature control is in the order of ±0.1°C. It took about 5–10 s for the system to reach thermal equilibrium, but it was negligibly short compared to the actual experimental times (several minutes to hours).

The induction time was determined between the initial curing time and the detectable light-scattering intensity change during curing.

Epoxy Conversion

Epoxy conversion α(degree of reaction) was estimated by DSC (SETARAM DSC92, France), deduced from DSC thermograms by calculating the residual heat of reaction ΔH_{res} (the area of the exothermic peak, temperature range 100–250°C) involved from the reaction during the DSC heating run at 10°C/min,[19–21]

Figure 3 Determination of T_{cp} by light transmission. (HTBN/E-51 = 30/70, cooling rate = 1°C/min).

$$\alpha = \frac{\Delta H_{\text{tot}} - \Delta H_{\text{res}}}{\Delta H_{\text{tot}}} \times 100\%$$

where ΔH_{tot} is the total heat involved by the epoxy–anhydride reaction. Runs were carried out under nitrogen atmosphere. Samples were first cured at isothermal temperature, i.e., 130 or 160°C for certain time, then were quenched to 0°C immediately for dynamic DSC runs, from room temperature to 300°C at 10°C/min.

Optical Microscopy and Digital Image Analysis

Optical micrographs were taken by a Leitz microscope and were recorded with the same CCD camera (without objective) as used for the SALS experiments.[25] Sample preparation is the same as for SALS analysis. The phase separation pictures were digitized and saved on a hard disk at desired intervals. Digital image analysis was performed with self-programmed software.[30] Detailed description of this technique and its applications are available elsewhere.[31–33] Here, a two-dimensional Fourier transform (2DFT) of an original image was made to extract the power spectrum in q space, which corresponds to the light-scattering pattern in real space.

RESULTS AND DISCUSSION

Cloud-Point Curves

Determination of a particular cloud point (CP) was made by heating a sample to a temperature of about 50°C higher than the CP, keeping it constant for 5–10 min, and then decreasing it at a cooling rate of 1°C/min. The CP was determined from the resulting intensity vs. time, as shown in

Figure 3. Typically, each point was measured no less than three times.

CPC for mixtures of HTBN with epoxy monomers of different molecular weights, i.e., E-51 and E-39-D, are shown in Figure 4. An UCST (upper critical solution temperature) is observed for both samples. The most significant feature is the high sensitivity of the location of miscibility gaps as a function of the molecular weight of the epoxy monomer. Increasing $\overline{M}_n$ from 380 of E-51 to 496 of E-39-D leads to an increase in the precipitation threshold temperature (maximum of CPC) of ~45°C. It is interesting to realize that increasing $\overline{M}_n$ also leads to a change in the chemical composition of the epoxy molecule, i.e., an increase in the concentration of secondary OH groups. In turn, this leads to a negligible change in the solubility.[34,35] But the change in molecular weight has a pronounced effect on the miscibility gap locations.

This experimental fact supports the hypothesis used in theoretical models of phase separation in a rubber-modified thermoset,[36] where it was assumed that the very origin of the demixing of rubber from the epoxy matrix was the increase in the average molecular weight of the thermoset during polymerization.[11]

Time-Resolved Small-Angle Light Scattering

Figure 5 illustrates the evolution of light-scattering patterns during polymerization-induced phase separation of the epoxy system (HTBN/E-51/MeTHPA/BDMA = 40/90/70/0.056 by weight) at 160°C, much higher than the cloud-point curve (Fig. 4).

From Figure 5 it is seen, qualitatively but clearly, that after several minutes (about 9 min)

Figure 4 Cloud point vs. weight fraction for HTBN/E-51 and HTBN/E-39-D.

Figure 5 Evolution of light-scattering pattern for the epoxy system cured at 160°C. HTBN/E-51/MeTHPA/ BDMA = 40/90/70/0.056; (a) 9 min, (b) 10 min, (c) 11 min, (d) 12 min, (e) 15 min, (f) 18 min.

tion at about 11 min. Digital-image analysis (DIA) showed even clearer results than that of the light scattering (Fig. 8). At 11 min, a second scattering ring appears, which corresponds to the second scattering peak in Figure 6. DIA is a rather sensitive method when real image is available

(A) Intermediate stage

(B) Late stage

Figure 6 Evolution of light-scattering profile for the epoxy system cured at 160°C. HTBN/E-51/MeTHPA/ BDMA = 40/90/70/0.056; (A) intermediate stage, (B) late stage.

the scattering maximum appears in the detectable region; soon the maximum intensity increases and becomes broader with time. At about 11 min, a second maximum appears distinctively, and finally gets closer to the first and then turns into a broader one.

Figure 6 gives more detailed and quantitative analysis of the structural development and the wave-vector of scattered light measured in the medium ($q = 4\pi/\lambda \sin(\theta/2)$, where θ is the scattering angle, and λ is the wavelength of light). During the time interval 0–8.75 min, no obvious scattering peak could be detected by the TRSALS device, even though we tried increasing the power output of the light source, removing the attenuator, and shortening the distance between the sample and screen, etc. Microscopic pictures shown in Figure 7 that no obvious phase separation could be observed before 9 min also supported the result. The morphology of the separated phase at 9 min is something like a cocontinuos structure, then it grows into droplets in a bimodal distribu-

Figure 7 Time change of optical microscopic pictures for the epoxy system cured at 160°C. HTBN/E-51/MeTHPA/BDMA = 40/90/70/0.056; (a) 9 min, (b) 10 min, (c) 11 min, (d) 12 min, (e) 15 min, (f) 18 min.

Figure 8 Plot of power spectrum of the 2DFT of Figure 7. HTBN/E-51/MeTHPA/BDMA = 40/90/70/0.056; (a) 9 min, (b) 10 min, (c) 11 min, (d) 12 min, (e) 15 min, (f) 18 min.

because 2DFT does not have the defect of incident beam influence. Both the peaks change their positions to smaller q over a relatively wide time range, i.e., turn into a big structure in real space with time. But the peak $q_{m,1}$ at smaller q dominates the whole procedure and grows more rapidly than the other for longer times. The peak $q_{m,2}$ at bigger q grows with peak $q_{m,1}$, and remains as the shoulder of peak $q_{m,1}$.

It is well known that spinodal decomposition is a faster process, so what happened during such a long time from 0–9 min compared to the whole reaction period (~18 min). From epoxy conversion obtained by DSC, the conversion is only about 47% at 9 min of cure at 160°C (Fig. 9). Epoxy curing evolves chain extension, branching, and perhaps crosslinking. This double-peak structure in Figures 5 and 6 with developing maximal does not meet the Cahn-Hilliard analysis. If it is a spinodal decomposition process, should only one maximum be detected, what was going on inside the mixtures during curing?

As a matter of fact, many researchers have observed the development of multiple peaks dur-

ing phase separation. Yamanaka et al.[19, 37] maybe the first one who found such phenomenon in a rubber-modified epoxy system. Liu et al.[38] once found such a phenomenon in a system of

Figure 9 Epoxy conversion vs. time at 130 and 160°C. HTBN/E-51/MeTHPA/BDMA = 40/90/70/0.056; (a) 9 min, (b) 10 min, (c) 11 min, (d) 12 min, (e) 15 min, (f) 18 min.

PS(OH) and PBMA. They said it could not explain this phenomenon simply in a nonlinear theory, and it must exist in another phase separation mechanism—maybe contributed from the hydrogen bond. He et al.[39] observed such a phenomenon in a system of poly(styrene-*stat*-*p*-(1,1,1,3,3,3-hexafluoro-2-hedroxyisopropyl)-α-styrene) and poly(butyl methacrylate). They explained their data with rather broad polydispersities of the polymer components as well as heterogeneities in the sequence statistics of the copolymer, which may lead to a simultaneous phase separation into multiple systems; another explanation is the possible existence of small local inhomogeneities induced by the preparation of the blends by solution casting. Edel[24] also found a system of polystyrene and poly(methyl methacrylate-*stat*-cyclohexyl methacrylate). He explained that it might be that the high intensity of the anomalous scattering during the early stage covers one of the double peaks because double peaks occur only on gold and carbon substrates not on the glass substrate.

Recently, Chen et al.[20] found in a system of epoxy-terminated butadiene–acrylonitrile random copolymers with epoxy that the appearance of a precipitated phase is much earlier than the cloud-point time. Nucleation growth was believed to take place far before the so-called spinodal decomposition.

Our system is similar to that of Chen's, and their explanation fits well for the initial stage of our system. From time 0 to about 9 min, the system is going on a nucleation growth mechanism, which takes a long time; although the phase morphology would be heterogeneous, the size is so small (the precipitated phase size is smaller than 1000 Å according to Chen) that it goes beyond the visual observation range; it is still transparent in a He-Ne light source ($\lambda_0 = 632.8$ nm) or usual white light (optical microscope). A rapid change of the phase transition occurs at t_{cp} (beginning of the cloud-point temperature in light scattering) indicating fast spinodal decomposition (without energy barrier) started.

Concerning the double-peak structure phenomenon occurring in our system and in Yamanaka's,[19, 37] a plausible explanation may arise from the following scenario (Fig. 10). If the curing proceeds at point P (time = t_0), at the very beginning of the polymerization-induced phase separation, the mixture is initially homogenous and it will be thrust into a two-phase region after a certain time of curing (time = t_1). That is, the molecular weight of epoxy increases, which causes the UCST curve to shift to higher temperature. At

Figure 10 Schematic diagram of temporal change of UCST curves. Dotted curve: spinodal curve, solid curve: binodal curve.

this time the mixture falls into the *meta*-stable region and starts to decompose via a nucleation growth mechanism. It is plausible that all polymerization-induced phase separation will pass through the *meta*-stable region; however, it is not conceivable that all the PIPS will have a fairly long induction time. Because it is a rather slow process and very small in size, its light-scattering pattern and microscopic morphology are difficult to be found. In the mean time, the molecular weight of epoxy continues to increase, and the mixture falls into an unstable region and then starts to decompose via a spinodal mechanism (time = t_2), because if it is a fully NG process, no light-scattering peak can be detected experimentally. Because spinodal decomposition is a spontaneous and fast process, there will be a lot of change in the light-scattering ring-like pattern and microscopic morphology. The phase structure grows quickly, and a major spinodal pattern is observed.

Anyhow, when the nuclei formed during nucleation growth goes into the spinodal decomposition region, it may produce a secondary characteristic wavelength (structural length). Because it is a NG-initialized spinodal decomposition, let us call the secondary characteristic wave length "nucleation growth coupled with spinodal decomposition wave length" as λ_2, which corresponds to the scattering vector q_2 in Figure 6. According to the classical theory of spinodal decomposition mechanism,[40] when the characteristic wave vector q is bigger than critical wave vector, i.e., scattering vector $q > q_c$ (as shown in Fig. 11), this fluctuation will be eliminated. On the other hand, when $q > q_c$, this fluctuation will grow via the spinodal mechanism. It im-

Figure 11 The plot of $R(q)$ (amplification factor) vs. scattering vector q.

plies that if the nuclei formed during the induction period have grown to the size larger than the critical size $\lambda_C \sim 1/q_c$, this structure will grow further when the system is thrust into the unstable region. At higher curing temperature, the nucleation growth phase separation rate increases much faster than polymerization rate. When the system enters the spinodal region, the characteristic wavelength λ_2 may be larger than the critical wavelength, $\lambda_C \sim 1/q_c$, and can grow with the main spinodal decomposition wavelength λ_1 (λ_1 corresponds to scattering vector q_1).

In our system, the higher the curing temperature, the faster nucleation growth rate. Thus, we expect that lowering the curing temperature will slow down the nucleation growth rate during the induction period, and the nuclei formed have not grown to the size larger than λ_c. In that case, when the system is thrust into the unstable region, the structure formed during the induction period will be eliminated as it processes the wave vector $q > q_c$. The corresponding experimental results shown in Figures 12 and 13 are the system cured at lower temperature 130°C, it is clear that no double-peak structure can be observed. This confirms the argument given above. In addition, it is imaginable that some part of the mixture is still at the *meta*-stable region and undergoing growth of the nuclei formed while the system is mainly undergoing spinodal decomposition. That is why there are droplets among the cocontinuous network at 9 min and so on (Fig. 7).

In conclusion, polymerization-induced double-peak structure phenomenon arises from phase equilibrium shifting from *meta*-stable region to unstable region when phase separation rate is faster enough than reaction rate (Fig. 14). Double-peak structure would probably occur between

Figure 12 Evolution of light-scattering pattern for the epoxy system cured at 130°C. HTBN/E-51/MeTHPA/BDMA = 40/90/70/0.056; (a) 35 min, (b) 45 min, (c) 55 min, (d) 65 min, (e) 75 min, (f) 85 min.

temperature 160° and 180°C. Otherwise, only the major spinodal decomposition can be observed and no double peaks will occur. The double-peak structure phenomenon in our system may be mainly due to "nucleation growth coupled with spinodal decomposition."

Figure 13 Evolution of light-scattering profile for the epoxy system cured at 130°C. HTBN/E-51/MeTHPA/BDMA = 40/90/70/0.056.

Figure 14 Influence of curing temperature on induction time measured by TRSALS. HTBN/E-51/MeTHPA/BDMA = 40/90/70/0.056.

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