

A real-time study of the phase-separation process during polymerization of rubber-modified epoxy

Jong-Pyng Chen and Yu-Der Lee*

Institute of Chemical Engineering, National Tsing Hua University, Hsinchu, Taiwan, Republic of China

(Received 5 October 1993; revised 5 April 1994)

The phase-separation process of a rubber-modified epoxy system during curing was described in terms of a nucleation–growth mechanism. It was derived from morphological observations that spherical domains were developed during polymerization in a continuous matrix. The morphological changes were recorded in real time by means of optical microscopy. We have applied a model to predict the amount and radius of the dispersed phase that segregated during a thermosetting polymerization. The model was based on the Flory–Huggins equation for the thermodynamic description as well as constitutive equations for the nucleation and growth rates. Using this model, we could semi-quantitatively interpret and describe the phase-separation process of the second phase from a curing mixture. During the initial polymerization period, the mixture remained homogeneous; at a certain reaction extent a thermodynamically stable rubber-rich phase with critical particle size r_c or larger grew spontaneously. The build-up of molecular weight in the matrix during polymerization resulted in the changing of the two-phase morphology and the fixation of the spherical domain structure. Nucleation was the controlling factor of the phase-separation process. We concluded that the nucleation and growth of spherical second phase was expected to be directly related to the interfacial tension, increase of molecular weight, thermodynamic properties and composition gradient.

(Keywords: phase separation; nucleation–growth mechanism; rubber-modified epoxy)

INTRODUCTION

Thermosetting resins in the glassy state are undesirably brittle. It has long been known that the fracture toughness of thermoplastics or thermosetting resins can be considerably improved with small rubber particles dispersed in polymer matrices¹. The fracture toughness of thermosetting epoxy resin, improved by the incorporation of liquid rubber, was demonstrated in the late 1960s by Sultan and McGarry². Since then, several investigations^{3–10} have shown that, when an elastomer, generally a low-molecular-weight carboxyl-terminated butadiene–acrylonitrile (CTBN) copolymer (Hycar), was copolymerized with the epoxy prepolymer, a uniformly dispersed phase of small rubber particles was formed *in situ* and prior to gelation.

A marked improvement of fracture toughness is observed when the mixture containing approximately 10% by weight of the CTBN rubber is allowed to have a rubber-rich phase finely dispersed in an epoxy-rich matrix. The two-phase morphology, which is formed upon curing at an elevated temperature, is accomplished by utilizing the partially miscible nature of the two components. Subsequently, it has been found^{3,4,6,11} that the degree of improvement depends critically on the size of the rubber-rich phase domains and reaches a maximum when the size distribution is in the range 1–5 μm .

A correlation between size and shape of the rubbery domains and mechanical properties of the cured material has been suggested^{4,12–14}. Understanding the phase-separation mechanism may therefore lead to better design of toughened materials. Since the morphology of the cured system depends on the competing effects between phase separation and polymerization, the various factors that influence the kinetics of both processes need to be understood to achieve an optimum heterogeneous structure.

Although evidently the phase-separation process in a CTBN-modified epoxy resin system is directly related to the miscibility between CTBN and the epoxy system for a given temperature, composition and reaction extent, nevertheless only a few experimental studies have been reported in the literature^{15–19}. Williams *et al.*^{16,17,20} developed a model to predict the fraction, composition and average radius of the dispersed phase segregated during a thermosetting polymerization, i.e. rubber-modified epoxy system, with qualitative agreement between nucleation model predictions and experimental observations. Yamanaka, Takagi and Inoue^{18,19} investigated the phase-separation mechanism of a CTBN–epoxy mixture in the curing process by light scattering. Their results suggested that phase separation proceeded through spinodal decomposition and co-continuous two-phase structure induced by the increase in the molecular weight of epoxy. In their case, the spherical domain of the phase-separation structure resulted from

* To whom correspondence should be addressed

the fixation at the late stage of spinodal decomposition by the formation of epoxy network.

In this paper the phase-separation behaviour and structure development of CTBN-modified epoxy before and during the curing process were studied. While the subject has been dealt with in several publications^{3,4,6,11,15-21}, no systematic real-time microscopy study has been carried out along with other techniques. We have therefore undertaken an investigation using thermal analysis, chromatography, rheology and microscopy, to arrive at a semi-quantitative model for the phase-separation process. The phase-separation behaviour in CTBN-modified epoxy resin during curing was monitored by optical microscopy, until the system was completely vitrified. Analysis results by differential scanning calorimetry (d.s.c.) provided the time-conversion curves. High-performance liquid chromatography (h.p.l.c.) and rheometry were carried out to monitor the growth of molecular weight of epoxy. From these results, we acquired a better understanding of the mechanism of structure development in terms of a nucleation-growth mechanism. Based on the Flory-Huggins equation for free energy calculation as well as constitutive equations for coalescence, nucleation and growth, we are able to predict the nucleation and growth of the dispersed phase segregated during a thermoset polymerization.

EXPERIMENTAL

Materials

The chemical structures of the components used in this work are shown in *Figure 1*. The epoxy oligomer used in this study was the diglycidyl ether of bisphenol A (DGEBA) made by Shell Chemical Co. (Epon 828). The rubber modifier was liquid copolymer of carboxyl-terminated butadiene-acrylonitrile (CTBN) containing 18 wt% acrylonitrile, which was available from B. F. Goodrich under the tradename of Hycar. It will be referred to as CTBNX8 in the subsequent discussion, and the dosage used in this study is the same as the commercially frequently used dosage of 2–10% by weight. The curing agent, dicyanodiamide (DICY), was obtained from Nippon Carbide Industries Co. Inc. All materials were bought from commercial sources and used without further purification (the purity of DICY is not less than 99.7%²²).

Analysis

The experimental determinations of cure kinetics were performed by differential scanning calorimetry (d.s.c.). Microcalorimetric measurements were recorded with a Mettler TA3000 thermal analysis system equipped with DSC-20 measuring cell. The mixtures of Epon 828/DICY were cured isothermally in the calorimeter cell for various times, then quenched in liquid nitrogen. These partially cured Epon 828/DICY were used for the kinetics study. The partially cured samples were then scanned in the calorimeter at a heating rate of 10°C min⁻¹. The residual heat of reaction (ΔH_{res}) was measured, during a temperature ramp from 40 to 300°C, from the area of the exothermic peak.

The experimental measurements of molecular weight were carried out by high-performance liquid chromatography (h.p.l.c.). The partially cured Epon 828/DICY sample was dissolved in tetrahydrofuran (THF) to produce a 2.4 wt% solution. The soluble fractions were characterized by h.p.l.c. on an HP-1090A apparatus with THF as the elution solvent. The first appearance of an insoluble fraction showed that gelation had been attained. Eluted macromolecules were characterized simultaneously by refractive index (*RI*) and by ultra-violet absorption ($\lambda = 254$ nm). Number- and weight-average molecular weights were calculated using a calibration with polystyrene standards.

Dynamic viscosity measurements of pure DGEBA epoxy prepolymer and of the reactive mixture, in the range of temperature of 50–180°C and cure temperature, were performed with a Rheometrics Mechanical Spectrometer (RMS-605) equipped with parallel plates of diameter 5 cm.

Real-time microscopy observation

To study the phase-separation behaviour prior to the addition of curing agent, the blends of DGEBA and CTBNX8 were prepared by thoroughly stir-mixing the two liquid resins in desired volume proportions for 10 min at a temperature of 150°C in a silicone oil bath. This temperature was chosen to ensure thorough mixing in the compatible state, as judged by the transparency of the mixture, and at a sufficiently low viscosity. After mixing, the blend was degassed in a vacuum chamber, maintained at about 1 Torr, for about 5 min. Then a drop of the mixture was quickly placed on a glass slide while

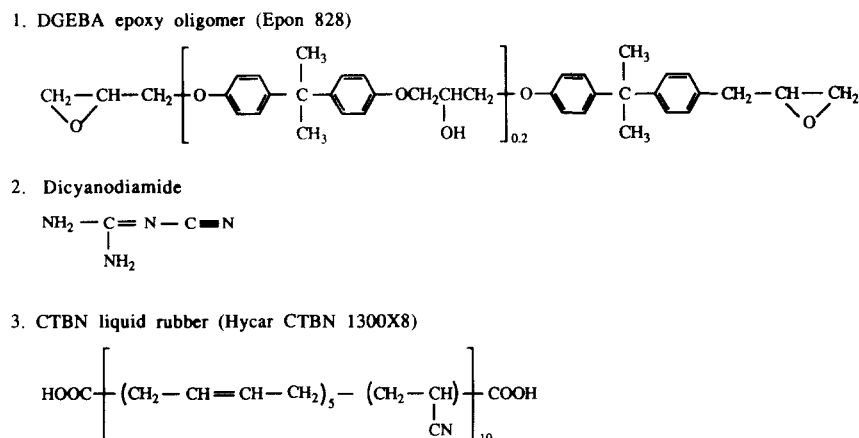


Figure 1 The chemical structures of the components used in this work

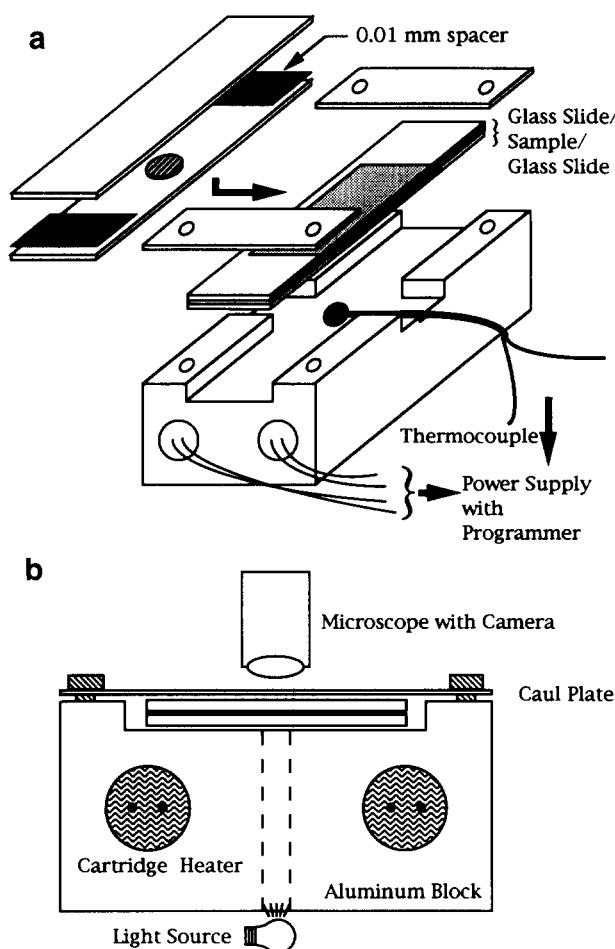


Figure 2 The optical microscope hot stage used to observe and record the real-time phase-separation process

it was still warm, and was covered with another glass slide. Both slides were then clamped together. Two pieces of 0.01 mm thick steel spacers were placed between top and bottom glass slides to control the sample thickness. This assembly was then transferred to a hot stage that can be programmed to provide a linear temperature rise and fall, as shown in Figure 2. The hot stage was mounted horizontally on a Zeiss Optical Microscope and conditioned at temperatures similar to those used in mixing to bring the sample to a compatible state. During the cooling mode, the onset of phase separation was observed under the light microscope.

Measurements of the phase-separation behaviour during the isothermal curing reaction were performed on the ternary mixture (epoxy oligomer/DICY/CTBNX8 liquid rubber). A DICY/epoxy premixture was made first by milling DICY thoroughly with Epon 828 in ratio of 1:1 using a three-roll mill. Samples used in these measurements were prepared by first stir-mixing the blend of Epon 828 and CTBNX8 in desired proportions at 80°C for 10 min; at this point the DICY/epoxy premixture was added to the blend (the proportions of Epon 828, DICY and CTBNX8 are shown in Table I), which were further thoroughly mixed for 1 min and degassed in a vacuum chamber (ca. 1 Torr) for 3 min. Upon degassing, samples for microscopy studies were prepared in the same manner as described earlier and transferred to the same hot stage. The hot stage was

Table 1 The composition and nomenclature of reactive mixture used in this study

Nomenclature	Epoxy (phr)	DICY (phr)	CTBNX8 (phr)
A-8-2	100	4	2
A-8-5	100	4	5
B-8-2	100	4.2	2.1
B-8-26	100	4.3	26.2
C-8-10	100	5	10

maintained at the cure temperature and used for observation of changes in morphology. Concurrent with this measurement, a portion (ca. 15 g) of each degassed sample was placed in a Rheometrics Mechanical Spectrometer (RMS-605) to monitor simultaneously the changes in shear viscosity at the same cure temperature. The RMS-605 was equipped with a pair of parallel plates. The cure time started from the moment the temperature of the thermocouple reached the curing temperature. Structure development with curing was observed under a light microscope, and the change in morphology profile was recorded at appropriate time intervals during isothermal curing.

RESULTS

During the curing process, the DGEBA/DICY/CTBNX8 mixture undergoes kinetic, physical and morphological changes as shown below.

Cure kinetics study of DGEBA/DICY/CTBNX8 mixture

Differential scanning calorimetry (d.s.c.) can be used to determine indirectly the advancement of the cure of thermosetting systems, with the assumption that the heat evolved is proportional to the extent of reaction²³⁻²⁵. The degree of conversion α can be derived from the experimental technique and calculated from:

$$\alpha = \frac{\Delta H_{\text{rxn}} - \Delta H_{\text{res}}}{\Delta H_{\text{rxn}}} = \frac{\Delta H_t}{\Delta H_{\text{rxn}}} \quad (1)$$

where ΔH_{rxn} is the exothermic heat per mole of reacting groups and ΔH_{res} is the residual heat of reaction. Ideally, ΔH_{rxn} is the total heat liberated when an uncured mixture is taken to complete cure. The reaction rates can be estimated from tangents to the α versus time curves. The thermokinetics model is usually expressed in the form:

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

and the temperature dependence is taken into account through the rate constant K_c given by:

$$K_c = A \exp(-E_c/RT) \quad (3)$$

Figure 3a shows DGEBA/DICY(4 phr) cure kinetics data at various cure temperatures measured by d.s.c. The slope of each plot represents the rate constant K_c . A plot of $\ln K_c$ versus $1/T$ is shown in Figure 3b and gives the activation energy $E_c = 39.2 \text{ kcal mol}^{-1}$. The energy E_c can be used to estimate the reaction extent from 140 to 190°C by equation (2) at various cure times.

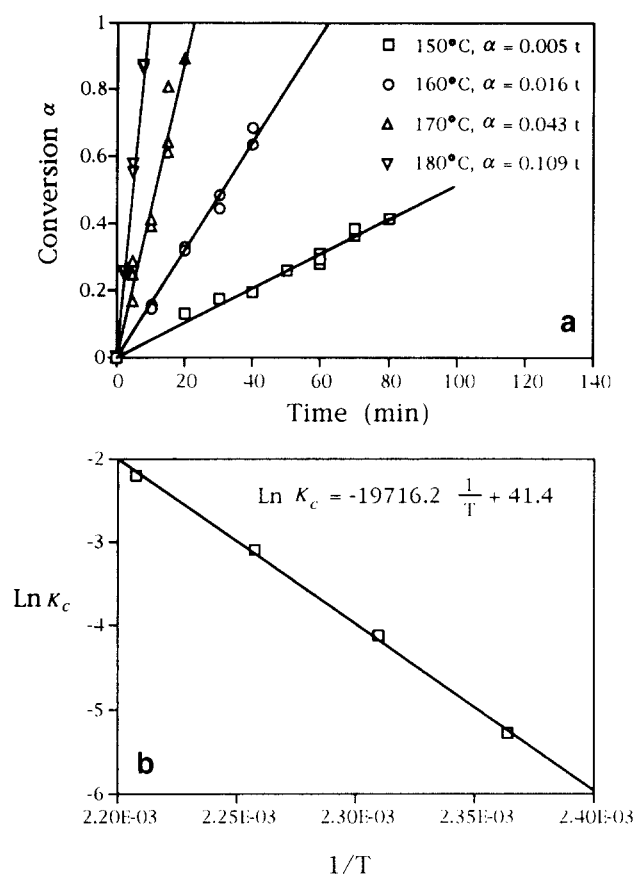


Figure 3 Isothermal cure kinetic data of DGEBA/DICY(4 phr). (a) The reaction extent of DGEBA/DICY at various cure temperatures, calculated by equation (1). (b) The temperature dependence of rate constant K_c , $E_c = 39.2 \text{ kcal mol}^{-1}$

Growth in molecular weight of epoxy

The reaction of DICY with a DGEBA epoxy prepolymer is very complicated^{26–28}. In order to determine the conditions for formation of an infinitely large branched structure, we introduce a convenient quantity, the branching coefficient β , as defined by Flory²⁹. In our case, if we denote α_a and α_e , respectively, the fractions of DICY and epoxy functional groups that have reacted, the branching coefficient is:

$$\beta = \alpha_a \alpha_e = r \alpha_a^2 = \alpha_e^2 / r$$

where r is the ratio of amine (m_a) to epoxy (m_e) functional groups initially present in the reactive mixture:

$$r = m_a / m_e = f_a n_a / f_e n_e$$

with f_e and f_a the functionalities of the n_e and n_a moles of DGEBA and DICY molecules.

The relationship derived by Stockmayer³⁰ for three-dimensional condensation polymers is adapted here for the computation of the weight-average molecular weight of the polymer, M_w :

$$M_w = \frac{n_e M_{we}^2 + n_a M_{wa}^2 + Z}{n_e M_{we} + n_a M_{wa}} \quad (4)$$

where M_{we} and M_{wa} are the initial molecular weights of the epoxy oligomer and DICY, and Z is given by:

$$Z = \frac{\alpha_e f_e n_e [\alpha_e (f_e - 1) M_{we}^2 + \alpha_a (f_a - 1) M_{wa}^2 + 2 M_{we} M_{wa}]}{1 - \alpha_e \alpha_a (f_e - 1)(f_a - 1)} \quad (5)$$

The weight-average molecular weight M_w of epoxy during polymerization is then calculated from kinetic data by equation (4) from d.s.c. results.

H.p.l.c. was used in this study as it is one of the most promising techniques for the identification of the molecular composition of epoxy systems³¹. The intensity of the peaks in the h.p.l.c. chromatograms is proportional to the concentration of each species present in the reactive mixture. The average molecular weight can then be calculated from the experimental values of each species fraction.

Figure 4 shows the build-up of molecular weight of epoxy calculated by equation (4) and measured by h.p.l.c. at various curing temperatures, respectively. A fairly good agreement between theoretical value and experimental observation was obtained.

Chemo-rheological study of DGEBA/DICY/CTBN mixture

The rheological behaviour of a reacting system is governed by two effects: the first is related to the molecular structural changes induced by the cure reactions, and the second is associated with variation of segmental mobility. In our chemo-rheological experiment conducted at a constant temperature, the increase in molecular weight because of the cure reaction caused an increase in the viscosity, which initially varied linearly with time. The curves with open circles and squares in Figure 5 show the chemo-rheological behaviour of

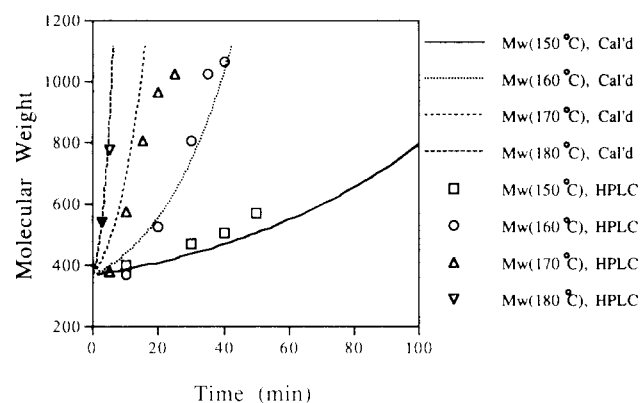


Figure 4 Molecular weights of DGEBA/DICY at different cure time, measured by h.p.l.c. and calculated by equation (4)

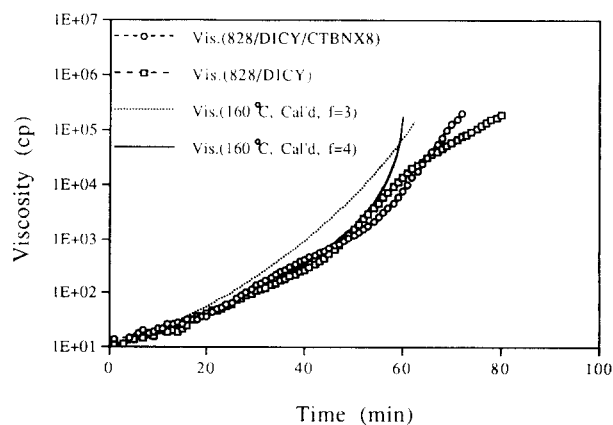


Figure 5 Typical chemo-rheological curves of DGEBA/DICY and DGEBA/DICY/CTBNX8 measured at 160°C by RMS and calculated by equation (9)

DGEBA/DICY/CTBNX8 and DGEBA/DICY measured at 160°C by RMS-605. The gelation of DGEBA/DICY/CTBNX8 mixture took place earlier than for DGEBA/DICY mixture. This was due to the fact that the existence of CTBNX8 might retard the mobility of cured DGEBA/DICY segments at high conversion.

The exposure of the DGEBA/DICY mixture to high temperature promoted the nucleophilic addition of primary amines to the epoxide rings. An upturn in viscosity, due to branching of the linear products, was then observed before the occurrence of gelation at which the viscosity reached an infinite value. The progressive increase in viscosity of the liquid reacting system, up to an infinite value as the gel point was approached, could be explained by its dependence on weight-average molecular weight.

Reviews on the chemo-rheology of thermosets are available in the literature^{32–35}. Here we attempt to apply the chemo-rheological behaviour of thermosetting matrices by relating the viscosity changes with the development of the molecular structure and the thermal history.

The relationship between viscosity and molecular weight proposed by Valles and Macosko³⁶ for a non-linear copolymerization is considered here:

$$\eta = K(gM_w)^{3.4} \quad (6)$$

where K is a constant, M_w is the weight-average molecular weight of the polymer and g is the ratio of the radius of gyration of a branched chain to that of a linear chain with the same molecular weight.

The value of g in equation (6) is related to the reagent functionality and branching coefficient^{37,38}. In particular, when $f_a = 4$:

$$g = \frac{1-3\beta}{2\beta} \ln\left(\frac{1-\beta}{1-3\beta}\right) \quad (7)$$

and when $f_a = 3$:

$$g = \frac{3(1-2\beta)}{\beta} \left[\frac{1}{2} \left(\frac{1-\beta}{\beta} \right)^{1/2} \ln\left(\frac{(1-\beta)^{1/2} + \beta^{1/2}}{(1-\beta)^{1/2} - \beta^{1/2}} \right) - 1 \right] \quad (8)$$

Normalizing the viscosity to its initial value at $\alpha_c = 0$, where the initial weight-average molecular weight M_{w0} is:

$$M_{w0} = \frac{n_e M_{we}^2 + n_a M_{wa}^2}{n_e M_{we} + n_a M_{wa}}$$

the dependence of the viscosity on the thermoset growing molecular weight can be given by:

$$\frac{\eta(\alpha)}{\eta_0} = \left(\frac{gM_w}{M_{w0}} \right)^{3.4} \quad (9)$$

The calculated chemo-rheological curves given by equation (9) are illustrated as full and broken curves in Figure 5. We found that the combination of equation (4) with equation (9), especially for $f_a = 4$, gave a good quantitative estimate of the chemo-rheological data, and hence molecular-weight change. It is reasonable to let $f_a = 4$ for calculating $\eta(\alpha)$ by equation (9) because the four -NH groups of DICY are all reactive for non-stoichiometric DGEBA/DICY system. For catalyst-added epoxy-DICY mixture, i.e. commercial formulation, chemists sometimes let $f_a = 3$ because only three of the

four -NH groups are effective in catalysed conditions. The larger deviation at the later stage of cure (e.g. cure time = 50 min or $\alpha_c > 0.95$) does not affect the study of phase separation, which takes place well before gelation. However, the result is useful quantitative information, combined with thermodynamic data, to predict the phase-separation process.

Morphology changes as observed via optical microscopy

Optical micrographs show that a binary mixture of the epoxy oligomer and CTBNX8 liquid rubber was heterogeneous at room temperature. The well dispersed spherical CTBNX8 domains gave the epoxy-CTBNX8 systems (without DICY) a turbid or 'snowy' appearance. When the temperature was elevated, e.g. to 80°C, the mixture changed to a homogeneous system. When the homogeneous mixture was cooled down slowly, the clear solution became cloudy, at which point, depending on cooling rate, rubber particles formed. The rubber droplets appeared as tiny dots at the beginning, and then the diameter of the droplets grew gradually to around 10 μm . Owing to the low viscosity of DGEBA, some smaller spherical domains migrated into larger domains and coalesced.

Both the epoxy-rubber mixture and the epoxy-DICY mixture gave clear solutions above 130°C. Combinations of these two mixtures produced clear solutions, also.

Figure 6 shows representative optical micrographs observed at various stages for the curing B-8-2 system at 150°C. Immediately after the temperature jumped from room temperature to the curing temperature, the epoxy-rubber mixture was homogeneous (Figure 6a). The DICY powder (melt temperature 209–212°C) was dispersed as islands in the epoxy-rubber mixture. At the early stage, the spherical CTBNX8 domains dissolved, shrank and disappeared. In the meantime, the DICY powder dissolved gradually as the cure continued. After a certain time elapsed, many tiny spots appeared, resulting in a fairly regular microscopic texture, i.e. phase separation (Figure 6b). Then the image contrast of the texture became strong and the average diameter of the spots grew gradually with cure time (Figure 6c). Finally, the diameter of the spherical second phase was fixed around 3 μm . The final morphology was arrested well before gelation. For CTBNX8 concentrations less than 20%, spherical rubber inclusions about 1–4 μm in size were found by optical micrography. When it was beyond 25% (e.g. B-8-26), epoxide domains of about the same size were present (Figure 7), indicating an inversion of the phases.

Table 2 and Figure 8 give a summary of the optical microscope observations. The time to nucleation t_{nucl} represents the cure time at which the tiny dots were first observed under transmission optical microscope at 200 times magnification. For 2 and 5 phr CTBNX8 system, i.e. A-8-2, A-8-5 and B-8-2, the trend of t_{nucl} versus cure temperature is almost the same. For higher rubber content, i.e. C-8-10, the reacting mixture has lower t_{nucl} for the same cure temperature.

The variation in particle size may be due to the competing actions of two complementary separation processes, aggregation of particles and chain extension processes, since rubber precipitation induced by curing agent and the build-up of molecular weight of epoxy-resin

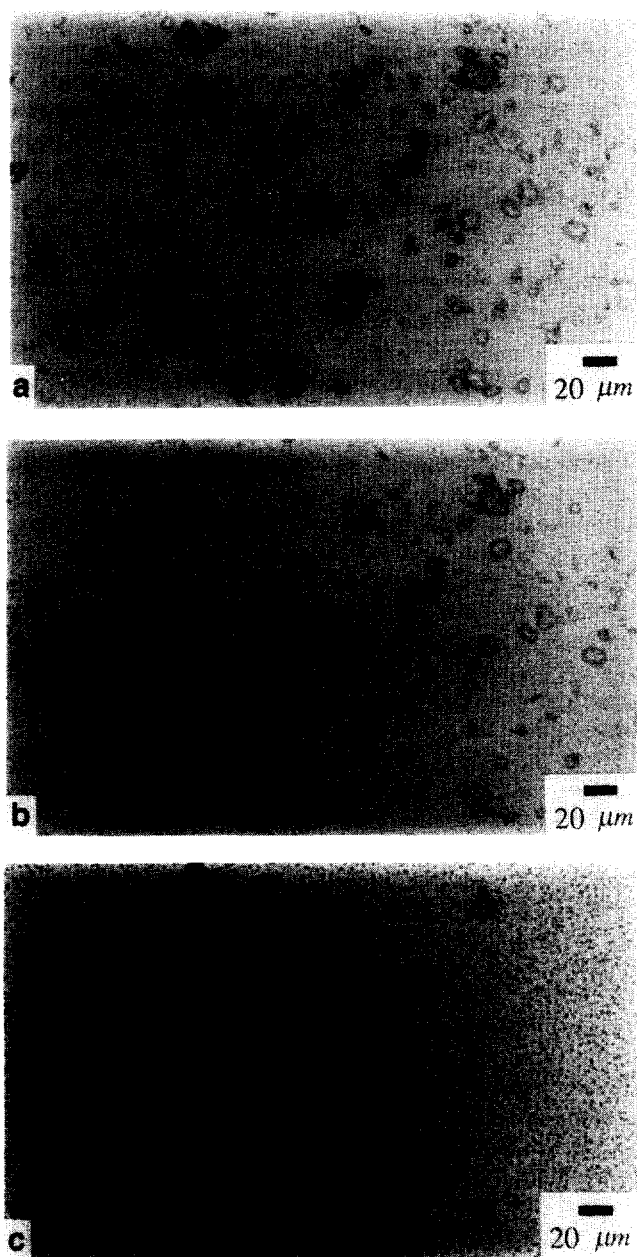


Figure 6 Transmission light micrographs of B-8-2 sample cured at 150°C: (a) 35 min, (b) 74 min, (c) 101 min

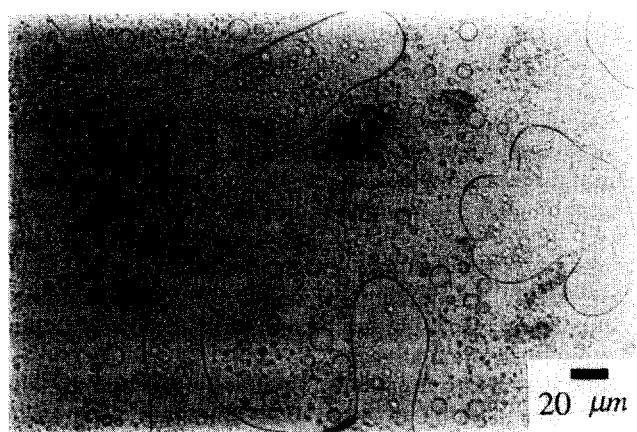


Figure 7 Phase inversion of B-8-26 reactive mixture, at 28 min of 160°C cure

Table 2 Summary of *in situ* phase separation

Nomenclature	Epoxy (phr)	DICY (phr)	CTBNX8 (phr)	T_{cure} (°C)	t_{nuc} (min)
A-8-2-150	100	4	2	150	50
A-8-2-160	100	4	2	160	20
A-8-2-170	100	4	2	170	7
A-8-2-180	100	4	2	180	2.5
A-8-5-140	100	4	5	140	120
A-8-5-150	100	4	5	150	55
A-8-5-160	100	4	5	160	23
A-8-5-170	100	4	5	170	8
A-8-5-180	100	4	5	180	2.5
B-8-2-150	100	4.2	2.1	150	60
B-8-2-160	100	4.2	2.1	160	20
B-8-2-170	100	4.2	2.1	170	7
C-8-2-150	100	5	10	150	39
C-8-2-160	100	5	10	160	9
C-8-2-180	100	5	10	180	1

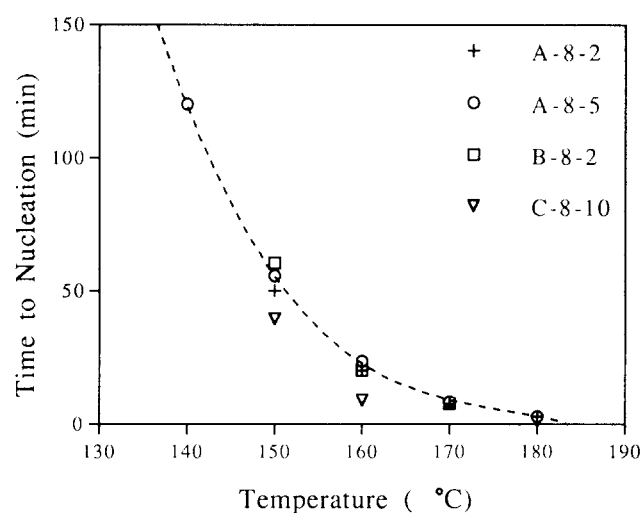


Figure 8 Time to nucleation (t_{nuc}) for isothermal curing of DGEBA/DICY/CTBNX8 reactive mixture with different compositions

molecules have previously been identified as the two factors that cause phase separation during the cure of CTBN rubber-modified DGEBA epoxy systems³⁹⁻⁴¹.

DISCUSSION

The phase-separation model described below is used to provide an explanation for the ensemble of experimental results.

Nucleation-growth mechanism

According to our microscopy observations, the morphology of the phase-separated mixture in our system is not associated with a co-continuous structure that is characteristic of spinodal decomposition^{18,19}. Yamanaka, Takagi and Inoue suggested that phase separation continued through spinodal decomposition induced by the increase in the molecular weight of epoxy, that structure fixation at the early stage of spinodal decomposition yielded the co-continuous two-phase structure, and that the formation of spherical domain structure was the result of the fixation of the phase-separation structure at a late stage of spinodal decomposition by the formation of epoxy network. In our study,

the spherical domain structure started as dispersed dots, then conjugated with gradually growing diameters, as revealed by stronger and stronger image contrast (i.e. narrower interface region). Thus we conclude that the fixation of the phase-separation structure is determined at an early stage of polymerization, and the domain size is dependent on the progress of reaction. Obviously then the nucleation and growth mechanism dominates the phase-separation process during the polymerization of CTBNX8-modified DICY cured epoxy system.

The nucleation-growth mechanism of this study is interpreted in terms of the system's thermodynamic properties and interfacial energy. Based on these data as well as data obtained for molecular weight and viscosity through h.p.l.c. and rheometry, constitutive equations for prediction of coalescence, nucleation and growth rate are established as shown below.

Thermodynamic properties and nucleation

In the early stages of reaction before phase separation, we assume that mixing rules that are applicable for small molecules are also applicable here, and rubber is an inert component⁴²⁻⁴⁴ dissolving in a monodispersed epoxy resin that is undergoing polymerization. The rubber segments are treated as one type of material and all the other components as a second type. The Gibbs free energy of mixing per unit volume is described by the Flory-Huggins equation:

$$\Delta G^V = \frac{RT}{V_{E0}} \left(\frac{\phi_E}{z_E} \ln \phi_E + \frac{\phi_R}{z_R} \ln \phi_R + \chi_{ER} \phi_E \phi_R \right) \quad (10)$$

Here χ_{ER} is the interaction parameter between epoxy and rubber, ϕ_E and ϕ_R are the volume fraction of both components, and z_E and z_R are the ratios of molar volumes of both components with respect to the virgin epoxy-amine combination taken as the reference:

$$z_R = \bar{V}_R / \bar{V}_{E0}$$

$$z_E = \bar{V}_E / \bar{V}_{E0} = \bar{M}_n / \bar{M}_{n0} = 1 / \left(1 - \frac{2\alpha}{n_e / (n_e + n_a)} \right)$$

\bar{M}_{n0} and \bar{M}_n are the number-average molecular weight of virgin and curing epoxy-amine mixture respectively:

$$\bar{M}_{n0} = \frac{n_e M_{we} + n_a M_{wa}}{n_e + n_a}$$

$$\bar{M}_n = \frac{n_e M_{we} + n_a M_{wa}}{n_e + n_a - 2\alpha n_e}$$

where M_{wa} and M_{we} are the molecular weights of amine and epoxy prepolymer. Equation (10) can also be written as:

$$\Delta G^V = \frac{RT}{V_{E0}} \left[\left(1 - \frac{2\alpha}{n_e / (n_e + n_a)} \right) (1 - \phi_R) \ln(1 - \phi_R) + \frac{\phi_R}{z_R} \ln \phi_R + \chi_{ER} \phi_R (1 - \phi_R) \right] \quad (11)$$

\bar{V}_{E0} is the initial molar volume of the epoxy-amine copolymer, defined as:

$$\bar{V}_{E0} = \left(\frac{n_e M_{we} + n_a M_{wa}}{n_e + n_a} \right) / \rho_e \quad (12)$$

where $\rho_e = 1.18773 - 7.229 \times 10^{-4} T(^{\circ}\text{C})^{45}$ is the density of the epoxy-amine copolymer. While z_R remains constant, by definition, during polymerization, z_E increases with the molecular weight of the growing molecule. Then we can calculate the free energy of mixing by equation (11) after knowing the extent of curing (by equation (2)).

Then as reaction progresses, polymorphic transformations occurred. These involved simple decomposition into two-phase regions, in which the nuclei of a new phase were first formed at a particular rate, followed by the propagation of the new phase at a faster rate. The formation of a new phase in the parent system is assumed to be caused primarily by chemical and molecular-weight effects. We assume that the chemical effect, through the interaction parameter term, does not change significantly at low conversion and that the major factor controlling the free energy of mixing is the molecular weight of the polymerizing epoxy matrix. As polymerization continues, the increase in molecular weight causes the configurational entropy (the first two terms on the right-hand side of the Flory-Huggins equation) to decrease and hence the free energy of mixing to increase. Since the molecular weight of the system has been experimentally monitored during the reaction by h.p.l.c. (i.e. α), it is possible to calculate ΔG^V from equation (11) providing that a suitable value can be assigned to χ_{ER} . It turns out that the exact value of χ_{ER} is not critical to the shape of the free-energy curve. Accordingly, we have used the usual temperature dependence of interaction parameter $\chi_{ER} = 0.35 + 90/T(\text{K})^{46}$ in our calculation. When a certain reaction extent (α) is reached, the free-energy curve could predict phase-separation behaviour leading to two coexisting phases.

Using equation (11), we generate the typical binodal and spinodal curves of curing DGEBA/DICY/CTBNX8 (A-8 series mixtures at 160°C), which represent binodal and spinodal compositions related to various conversions, and are shown in Figure 9. On the basis of current understanding of polymer-polymer miscibility and phase diagram, if the curing proceeds at point P, the mixture is initially a homogeneous mixture and it will be thrust into a two-phase region after a certain curing time, e.g. P'. Hence, the nucleation is expected to take place in the curing process as the molecular weight of epoxy increases with curing.

In order for phase separation to occur in a homogeneous system, it is necessary for it to enter the metastable region

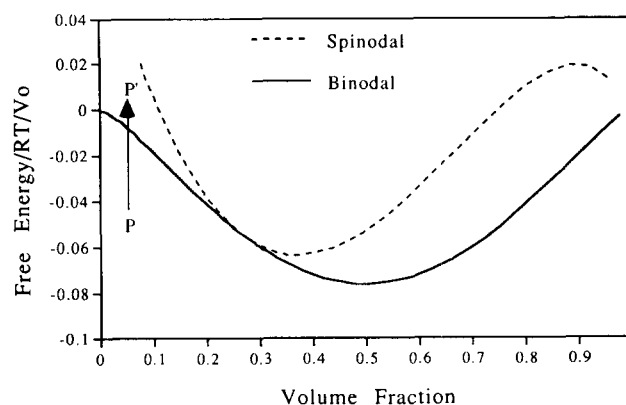


Figure 9 Spinodal and binodal curve of A-8-5 mixture at 160°C, derived and calculated from Flory-Huggins equation (equation (11))

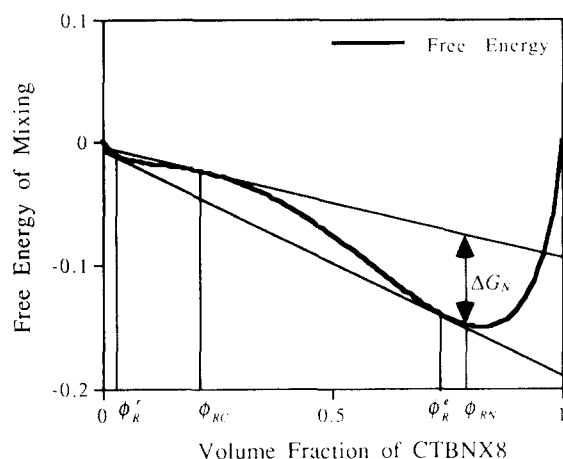


Figure 10 Free energy of mixing (ΔG^V) of A-8-5-160 when reaction extent reaches 0.3

(i.e. P' position of Figure 9), which can be calculated from a typical plot of the free energy at the selected reaction extent. Figure 10 shows such a plot, with ϕ_{RC} being the actual rubber concentration in the continuous phase at a certain reaction extent, ϕ_R^r and ϕ_R^e being the conjugated equilibrium compositions (rubber volume fraction) located on the binodal curve. The fact that $\phi_{RC} > \phi_R^r$ implies that the system is entering into the metastable region. The vertical distance between the tangent line at ϕ_{RC} and the free-energy curve represents the free-energy change per unit volume for the separation of a new phase with any arbitrary composition. The maximum value, ΔG_N , represents the free-energy change per unit volume of nucleation, and ϕ_{RN} is the actual composition of the segregated phase.

Interfacial energy and time to nucleation

Another factor affecting the nucleation-growth mechanism is the interfacial energy (σ_{12}). Since the molecular weight of the epoxy increases with the progress of the curing process, this interfacial energy cannot be treated as a constant. Instead, it is assumed to be influenced by the molecular-weight change of the system. Thus equations (13) and (14) by LeGrand and Gaines^{47,48}, giving the relationship between interfacial energy (σ_{12}) and molecular weight, are applied to the system of this study as well:

$$\sigma_{12} = k_0 - \frac{k_1}{M_w^{2/3}} - \frac{k_2}{M_R^{2/3}} \quad (13)$$

$$k_0 = \gamma_E + \gamma_R - 2\phi \left(\gamma_E - \frac{k_1}{M_w^{2/3}} \right)^{1/2} \left(\gamma_R - \frac{k_2}{M_R^{2/3}} \right)^{1/2} \quad (14)$$

where k_1 and k_2 are constants, and γ_E and γ_R are the surface tension of epoxy resin and CTBN rubber respectively.

The functional property of k_0 is such that it is practically independent of molecular weight⁴⁸, however. In this paper, the molecular weight of CTBNX8 rubber phase (M_R) is kept constant and that of epoxy phase (M_w) is varied; a plot of σ_{12} versus $M_w^{-2/3}$ will be linear with slope ψ . Then, equations (15) and (16) can be used to estimate σ_{12} of DGEBA/DICY/CTBNX8 mixture at a

certain reaction extent:

$$\sigma_{12}(T_{\text{cure}}, \text{ before cure}) = \sigma_{12}(55^\circ\text{C}, \text{ before cure}) - (d\sigma_{12}/dT)(T_{\text{cure}} - 55) \quad (15)$$

$$\sigma_{12}(T_{\text{cure}}, \text{ during cure}) = \sigma_{12}(T_{\text{cure}}, \text{ before cure}) - \psi M_{w0}^{-2/3} [(M_w/M_{w0})^{-2/3} - 1] \quad (16)$$

Sohn, Emerson and Koberstein⁴⁵ have recently reported the value of σ_{12} at 55°C to be 0.58 mN m^{-1} , and the temperature-dependent coefficient of interfacial tension $d\sigma_{12}/dT = -(0.01-0.02) \text{ mN m}^{-1} \text{ } ^\circ\text{C}^{-1}$ (typically $-0.0198 \text{ mN m}^{-1} \text{ } ^\circ\text{C}^{-1}$) between CTBN copolymers and epoxy prepolymer.

$\sigma_{12}(T_{\text{cure}}, \text{ before cure})$ is negative in the beginning of curing reaction and the mixture is miscible. $\sigma_{12}(T_{\text{cure}}, \text{ during cure})$ will increase with cure time, due to the build-up of molecular weight of epoxy, till $\sigma_{12} = 0$. The cure time at which $\sigma_{12} = 0$ can be defined as the time to nucleation t_{nuc} . Then σ_{12} becomes positive and the nucleation and phase-separation process will take place. The ψ value, which has the available experimental data ranging from 160 to 320 and was determined in LeGrand and Gaines' study⁴⁸, can be defined as a molecular weight parameter.

Nucleus size

The changes in free energy and interfacial energy can have a profound effect on the nucleus size, assuming that there is no difference between the specific volumes of the parent and the second phases and hence no strain at the interface. The change in free energy, ΔG , due to the formation of spherical nuclei consists of two terms: (a) the bulk free-energy decrease per unit volume, ΔG_N , and (b) the surface free-energy increase per unit area of the surface, i.e. σ_{12} . If the radius of a spherical domain of the second phase is r , then ΔG may be written as^{49,50}:

$$\Delta G = \frac{4}{3}\pi r^3 \Delta G_N + 4\pi r^2 \sigma_{12} \quad (17)$$

Clearly, for small r , the second term will dominate (it is positive while the first term is negative) and the second phase will therefore be thermodynamically unstable. However, if the second phase attains a critical size of radius r_c , the change in free energy ΔG will begin to decrease and further growth will be thermodynamically favourable.

If we let $(\partial \Delta G / \partial r)$ equal zero, then the critical radius (known as the critical nucleus size) r_c and the critical excess free energy ΔG_c can be expressed as follows:

$$r_c = 2\sigma_{12} / |\Delta G_N| \quad (18)$$

$$\Delta G_c = 16\pi \sigma_{12}^3 / (3|\Delta G_N|^2) \quad (19)$$

Nucleation rate and viscosity

In the derivation of equation (17), the elastic strain energy, if any, arising from the formation of the new phase is considered negligible. With this assumption, the rate of nucleation, that is, the number of nuclei that appear per unit volume of the parent mixture per unit time from a homogeneous system^{49,50}, may be written as¹⁷:

$$\frac{dP(r_c)}{dt} = N_0 D \exp\left(\frac{-\Delta G_c}{kT}\right) \quad (20)$$

where $P(r_c)$ is the volumetric concentration of particles (nuclei) with critical radius r_c , D is the diffusion coefficient of the rubber in the thermosetting resin, N_0 is an adjustable factor^{16,17} and k is the Boltzmann constant. ΔG_c is calculated from equation (19).

The diffusion coefficient may be expressed by the Stokes–Einstein equation:

$$D = D_0 T / \eta(\alpha, T) \quad (21)$$

where η is the viscosity of the epoxy–DICY copolymer at certain conversion and temperature.

The D_0 in equation (21) can be obtained by making a comparison between DGEBA/DICY/CTBNX8 mixture and water solution. As the initial viscosity of the DGEBA/DICY/CTBNX8 system at 140–180°C is close to 30 mPa s, i.e. 30 times that of water at room temperature, and the order of magnitude of the diffusion coefficient in liquid with viscosity close to water is $10^{-5} \text{ cm}^2 \text{ s}^{-1}$, then the diffusion coefficient of a small molecule in DGEBA/DICY at the cure temperature can be reasonably assumed as 10^{-6} – $10^{-7} \text{ cm}^2 \text{ s}^{-1}$. The order of magnitude of the diffusion coefficient may be estimated as 10^{-7} – $10^{-8} \text{ cm}^2 \text{ s}^{-1}$ because CTBN is a relatively large molecule. Then, we let D_0 be $10^{-8} \text{ cm}^2 \text{ s}^{-1} \text{ mPa s K}^{-1}$ for the following calculation.

Equation (22) is obtained, combining equations (20) and (21), and introducing equation (9), for the calculation of nucleation rate:

$$\frac{dP(r_c)}{dt} = N_0 D_0 T \eta_0^{-1} \left(\frac{gM_w}{M_{w0}} \right)^{-3.4} \exp\left(\frac{-\Delta G_c}{kT} \right) \quad (22)$$

where the molecular-weight factor (M_w/M_{w0}) was obtained from either h.p.l.c. and d.s.c. measurements or equations (4) and (9).

Then, equation (22) was solved numerically by the Euler method, combined with equations (4) and (7). The correlated transformation of α versus t was made using the experimental curve determined at 150–180°C as shown in Figure 3. The M_w/M_{w0} values were estimated by equation (4). A typical nucleation rate plot is shown in Figure 11. Correlating with the volumetric fraction of the second phase, which was estimated by the morphology micrography, the order of magnitude of N_0 could be determined as 10^{16} .

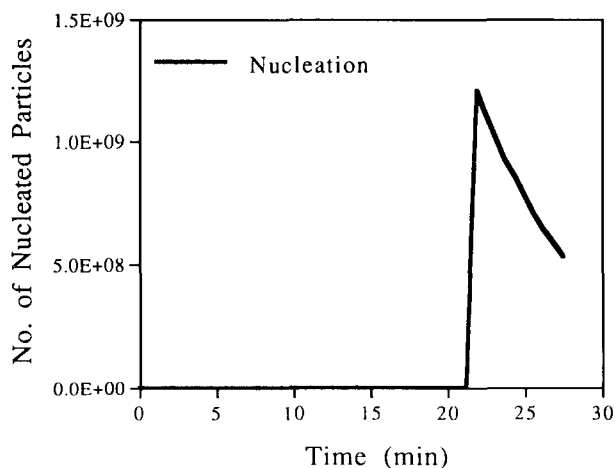


Figure 11 Nucleation rate of A-8-5-160, calculated by equation (22). N_0 was determined from micrograph analysis

Growth rate of nuclei and rubber concentration

The difference in rubber composition in the continuous phase (ϕ_{RC}) from the equilibrium value (binodal, ϕ_R^r) is the driving force for phase separation when the system enters the metastable region (see Figures 9 and 10). The growth of the second phase occurs, as shown in Figure 6, when the driving force ($\phi_{RC} - \phi_R^r$) is trying to restore the system to equilibrium conditions. Let $dP(R_i)$ be the particles with radius R_i per unit volume that were born at reaction extents between α_i and $\alpha_i + d\alpha$, then at $\alpha = \alpha_i$, this set of particles has a radius $R_i = r_c(\alpha_i)$. For $\alpha > \alpha_i$, the radius of the particle grows to a certain value $R_i > r_c(\alpha_i)$. However, $dP(R_i)$ is not a function of time.

The growth rate, defined as the increase in volume fraction per unit time, is assumed to be proportional to the interfacial area per unit volume and the driving force can be expressed as:

$$\frac{4\pi}{3} dP(R_i) \frac{dR_i^3}{dt} = k_m 4\pi R_i^2 dP(R_i) (\phi_{RC} - \phi_R^r) \quad (23)$$

where k_m is the mass-transfer coefficient; taken from stagnant medium to a sphere, it can be written as⁵¹:

$$k_m = D/R_i \quad (24)$$

Combining equations (23), (24) and (21), then introducing equation (9), we obtain:

$$R_i \frac{dR_i}{dt} = D_0 T \eta_0^{-1} \left(\frac{gM_w}{M_{w0}} \right)^{-3.4} (\phi_{RC} - \phi_R^r) \quad (25)$$

Thus, the growth rate of second phase (nuclei) can be estimated by solving equation (25) numerically by the Euler method, combined with equations (4) and (7).

Verification

There are several possibilities for the trajectory line of phase separation, corresponding to the progress of the curing reaction, which depend on the thermodynamic equilibrium and the rate of polymerization. The trajectory line should follow the rule of thumb that the free-energy change from α_i to $\alpha_i + d\alpha$ must be positive and $\phi_{RC}(\alpha_i + d\alpha) < \phi_{RC}(\alpha_i)$, as shown in Figure 12. Figure 13 shows the typical growth track of second phase, observed by microscopy and calculated by equation (25) for different reaction progress. The calculated track is in good agreement with experimental results for reaction progress 2 shown in Figure 12. Figure 13 also illustrates that the growth rate and final domain size of second phase are strongly dependent on the trajectory of ϕ_{RC} . For different conversion, when the nucleus size reaches stable r_c , it starts to grow, causing the domain growth to have different track and time to nucleation t_{nucl} .

The time lag, the time interval from the time the system enters into the metastable region to nucleation, indicates the miscibility and interfacial tension between CTBNX8 and reacting DGEBA/DICY mixture. Figure 14 demonstrates that the interfacial tension has a strong influence on the time to nucleation, t_{nucl} .

The above discussions, a combination of experimental observation in real time on the morphology that evolved in a reacting mixture with calculated results from equations (22) and (25), provide an insight into the fact that nucleation–growth is the prevailing mechanism of phase separation. Williams *et al.* concluded that growth

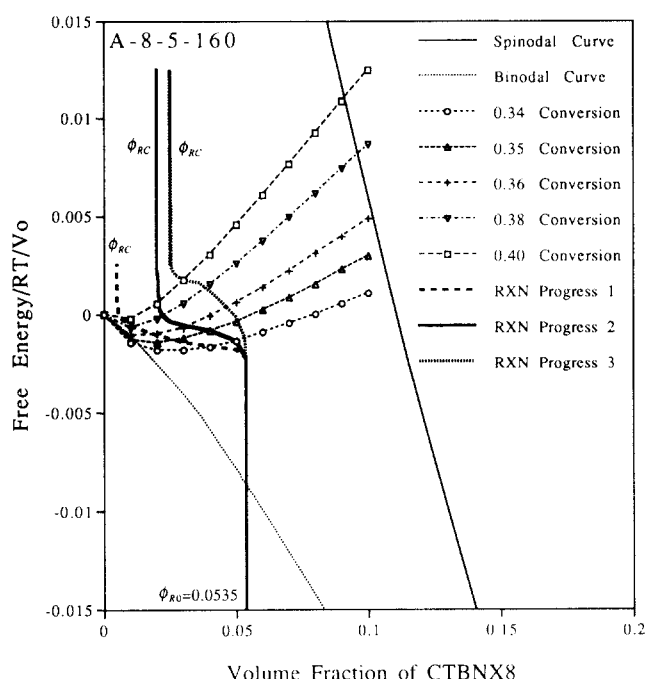


Figure 12 Diagram of reaction progress trajectories in the metastable region for polymerizations starting from the same initial CTBNX8 concentration ($\phi_{R0}=0.0535$)

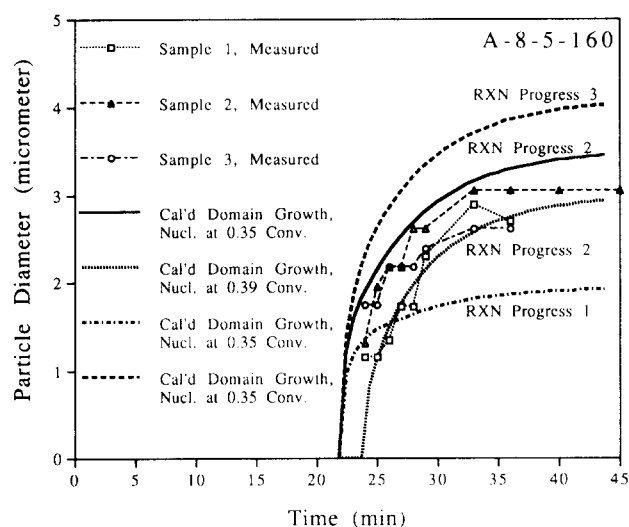


Figure 13 Comparison between experimental data and calculated growth rates of phase domain. The calculated curves are based on equation (25) and reaction progress trajectories (ϕ_{RC}) as shown in Figure 12

was the controlling process, and that interfacial tension had practically no effect on the final particle size^{16,45}. In this study, the phase-separation process is strongly dependent on the interfacial strength and the concentration of rubber-rich phase in the continuous phase.

CONCLUSION

We have applied a model to predict the nucleation and growth of the dispersed phase segregated during a thermoset polymerization (i.e. a rubber-modified epoxy system). The model was based on a thermodynamic description through the Flory-Huggins equation as well as constitutive equations for coalescence, nucleation and

growth rates. The phase-separation process of rubber-modified epoxy during curing was described in terms of a nucleation-growth mechanism. We obtained a semi-quantitative agreement between model predictions and experimental observations in this paper.

The morphological changes occurring during polymerization were followed continuously by means of transmission optical microscopy and were reproducible. It was found that phase separation takes place well before the gelation point, at a time when mobility is still possible.

During an initial polymerization period the mixture remained homogeneous; at a certain reaction extent a thermodynamically stable rubber-rich phase with particles of size r_c or larger grows spontaneously. The time to nucleation and the growth rate of the spherical second phase were expected to be directly related to the interfacial tension, increase of molecular weight, thermodynamic properties and composition gradient. The changing and fixation of the two-phase morphology during polymerization were shown to be the result of molecular-weight build-up in the matrix of epoxy-rich phase. Since curing reactions precede phase separation, the increased viscosity could be expected to retard significantly the long-range migration of molecules in the subsequent phase separation.

The microstructure formation is governed by the competitive progress of the phase separation ($\phi_{RC}-\phi_R^L$) and the chemical reaction (η/η_0 or M_w/M_{w0}). Under conventional curing conditions, the phase separation is allowed to proceed to control morphology.

A variety of different morphologies, and therefore material properties, can be obtained from a single rubber-modified epoxy formulation. The volume fraction, domain size and number of particles of phase-separated rubber-rich phase are determined by the competing effects of incompatibility, rate of nucleation and domain growth, and the quenching of morphological development by gelation.

The result in this study is particularly interesting since microscopic examination of the samples during the crosslinking reaction revealed that the growth of second-phase domains depended on the competing effects

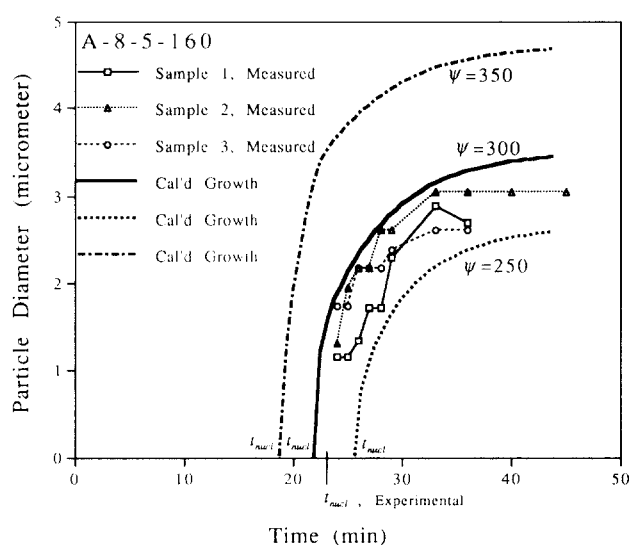


Figure 14 The effect of the interfacial tension value (related ψ value) on the calculated domain growth track of phase-separation process

between phase separation and polymerization during the curing treatment. Therefore, understanding the phase-separation mechanism will lead to a better design of toughened materials through controlling optimum heterogeneous structural morphology.

ACKNOWLEDGEMENTS

J.P.C. wishes to thank Professor T. K. Kwei of the Department of Chemistry, Polytechnic University, Brooklyn, for his insightful discussions.

REFERENCES

- Bucknall, C. B. 'Toughened Plastics', Applied Science, London, 1977
- Sultan, J. N. and McGarry, F. J., MIT Research Report No. R69-59, 1969
- Rowe, E. H., Siebert, A. R. and Drake, R. S. *Mod. Plast.* 1970, **47**, 110
- Sultan, J. N. and McGarry, F. J. *Polym. Eng. Sci.* 1973, **13**, 29
- Kunz, S. C. J., Sayre, A. and Assink, R. A. *Polymer* 1982, **23**, 1897
- Riew, C. K., Rowe, E. M. and Siebert, A. R. 'Toughness and Brittleness of Plastics' (Eds. R. D. Deanin and A. H. Grignola), Adv. Chem. Ser. No. 154, American Chemical Society, Washington, DC, 1976, p. 326
- Manzione, L. T., Gillham, J. K. and McPherson, C. A. *J. Appl. Polym. Sci.* 1981, **26**, 2391
- Bascom, W. D., Cottingham, R. L., Jones, R. L. and Peyser, P. *J. Appl. Polym. Sci.* 1975, **19**, 2545
- Morgan, R. J., Mones, E. T. and Steele, W. J. *Polymer* 1982, **23**, 295
- Meeks, A. C. *Polymer* 1974, **15**, 675
- McGarry, F. J. *Proc. R. Soc. Lond. A* 1970, **319**, 59
- Manzione, L. T., Gillham, J. K. and McPherson, C. A. *J. Appl. Polym. Sci.* 1981, **26**, 889
- Manzione, L. T., Gillham, J. K. and McPherson, C. A. *J. Appl. Polym. Sci.* 1981, **26**, 907
- Chan, L. C., Gillham, J. K., Kinloch, A. J. and Shaw, S. J. in 'Rubber-Modified Thermoset Resins' (Eds. C. K. Riew and J. K. Gillham), Adv. Chem. Ser. No. 208, American Chemical Society, Washington, DC, 1984, p. 235
- Wang, T. T. and Zupko, H. M. *J. Appl. Polym. Sci.* 1981, **26**, 2391
- Vázquez, A., Rojas, A. J., Adabbo, H. E., Borrajo, J. and Williams, R. J. *Polymer* 1987, **28**, 1156
- Moschiar, S. M., Riccardi, C. C., Williams, R. J. J., Verchère, D., Sautereau, H. and Pascault, J. P. *J. Appl. Polym. Sci.* 1991, **42**, 717
- Yamanaka, K., Takagi, Y. and Inoue, T. *Polymer* 1989, **30**, 1839
- Yamanaka, K. and Inoue, T. *J. Mater. Sci.* 1990, **25**, 241
- Williams, R. J. J., Borrajo, J., Adabbo, H. E. and Rojas, A. J. in 'Rubber-Modified Thermoset Resins' (Eds. C. K. Riew and J. K. Gillham), Adv. Chem. Ser. No. 208, American Chemical Society, Washington, DC, 1984, p. 195
- Naé, H. N. *J. Appl. Polym. Sci.* 1986, **31**, 15
- Product brochure of Nippon Carbide Industries Co. Inc.
- Prime, R. B. in 'Thermal Characterization of Polymeric Materials' (Ed. E. A. Turi), Academic Press, New York, 1981, Ch. 5
- Apicella, A., Nicolais, L., Iannone, M. and Passerini, P. *J. Appl. Polym. Sci.* 1984, **29** (6), 2083
- Barton, J. M. in 'Epoxy Resins and Composites' (Ed. K. Dušek), Adv. Polym. Sci., Vol. 72, Springer-Verlag, Berlin, 1985, p. 110
- Sacher, E. *Polymer* 1973, **14**, 91
- Zahir, S. A., Int. Conf. in Org. Coat. Sci. Tech., Athens, 1980
- Lin, Y. G., Sautereau, H. and Pascault, J. P. *J. Appl. Polym. Sci.* 1986, **32** (4), 4595
- Flory, P. J. 'Principles of Polymer Chemistry', Cornell University Press, Ithaca, NY, 1953
- Stockmayer, W. H. *J. Polym. Sci.* 1952, **9**, 69
- Halpin, J. C., Apicella, A. and Nicolais, L. 'Polymer Processing and Properties' (Eds. G. Astarita and L. Nicolais), Plenum, New York, 1984, p. 143
- Roller, M. B. *Polym. Eng. Sci.* 1986, **26**, 432
- Apicella, A. 'Developments in Reinforced Plastics-5' (Ed. G. Pritchard), Elsevier, New York, 1986, p. 151
- Schmitt, G., Wiley, J. and Gotro, J. *SPE ANTEC Tech. Papers* 1987, **33**, 977
- Paithankar, D., Sangani, A. and Martin, G. *SPE ANTEC Tech. Papers* 1988, **34**, 1146
- Valles, E. M. and Macosko, C. W. *Macromolecules* 1979, **22**, 521
- Zimm, B. H. and Stockmayer, W. H. *J. Chem. Phys.* 1949, **17** (12), 1301
- Kinloch, A. J., Shaw, S. J., Tod, D. A. and Hunston, D. L. *Polymer* 1983, **24**, 1341
- Siebert, A. R. and Riew, C. K. *Org. Coat. Plast.* 1971, **31**, 552
- Sayre, J. A., Assink, R. A. and Lagasse, R. R. *Polymer* 1981, **22**, 87
- Lee, W. H., Hodd, K. A. and Wright, W. W. in 'Rubber-Modified Thermoset Resins' (Eds. C. K. Riew and J. K. Gillham), Adv. Chem. Ser. No. 222, American Chemical Society, Washington, DC, 1989, p. 263
- Hycar RLP Product Brochure RLP-2, 'Toughen Epoxy Resins with Hycar RLP', B. F. Goodrich Co., p. 6
- Krause, S. J. *Macromol. Sci. (C)* 1972, **7**, 251
- Paul, D. R. and Barlow, J. W. *Polymer* 1984, **25**, 487
- Sohn, J. E., Emerson, J. A. and Koberstein, J. T. *J. Appl. Polym. Sci.* 1989, **37**, 2627
- Champetier, G. and Monnerie, L. 'Introduction à la Chimie Macromoléculaire', Masson, Paris, 1969, p. 135
- Wu, S. 'Polymer Interface and Adhesion', Marcel Dekker, New York, 1982, pp. 112-115
- LeGrand, D. G. and Gaines, G. L., Jr. *J. Colloid Interface Sci.* 1975, **50**, 272
- Doremus, R. H. 'Rates of Phase Transformations', Academic Press, Orlando, FL, 1985, p. 65
- Rao, C. N. R. and Rao, K. J. 'Phase Transitions in Solids', McGraw-Hill, New York, 1977, p. 81
- Sherwood, T. K., Pigford, R. L. and Wilke, C. R. 'Mass Transfer', McGraw-Hill, New York, 1975, p. 215