

Single-phase and multiple-phase thermoplastic/thermoset polyblends:

1. Kinetics and mechanisms of phenoxy/epoxy blends

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The kinetics of the curing reaction for phenoxy/epoxy/diaminodiphenyl sulfone blends with and without an accelerator have been investigated through differential scanning calorimetry (d.s.c.), FTi.r. and viscosity measurements. Phenoxy is miscible with epoxy monomer and low-molecular-weight epoxy during the early stages of curing, but phase separation starts when the epoxy molecular weight is increased to a critical value. The viscosity and the crosslinking density increase with increasing epoxy molecular weight. The viscosity at the initiation of phase separation is the most important factor in determining the final morphological structure. Opaque, translucent and transparent products can be obtained by kinetic control of the curing rate. A model to describe the phase separation of any thermoplastic/thermoset blend system in terms of thermodynamics and kinetics is presented in this paper.

(Keywords: semi-IPN; epoxy; phenoxy; kinetics; miscibility; phase separation)

INTRODUCTION

Crosslinked epoxy resins are generally brittle and the incorporation of discrete rubber particles to increase their fracture toughness has been the subject of intensive investigation¹⁻¹¹. Alternatively, the toughening of the crosslinked epoxy resins can be achieved by the incorporation of a high-performance ductile thermoplastic that tends to change the energy dissipative processes more than simply from the resin matrix deformation¹²⁻²⁰. Bucknall and Partridge investigated the blends of poly(ether sulfone) (PES) in a high-performance trifunctional epoxy resin and found nodular morphological features with diameter between 0.2 and 6.0 μm and the improvement in fracture toughness was insignificant^{12,13}. Hedrick and McGrath reported that the thermoplastic polysulfone (PSF) was separated from the epoxy resin matrix as dispersed particles of diameter between 0.5 and 2.0 μm ^{15,16}. Levita⁷ was able to obtain a homogeneous blend of amine-terminated acrylonitrile-*co*-butadiene rubber (ATBN) and the liquid diglycidyl ether of bisphenol A (DGEBA) by slow curing at 15°C so that the diffusion of the liquid rubber to form a separated phase was limited due to high viscosity. Bucknall and Gilbert¹⁷ found poly(ether imide) (PEI) in a tetrafunctional epoxy resin as a separate phase and the fracture toughness was significantly improved while the modulus showed only a modest reduction. Iijima *et al.*¹⁹ studied the modification of epoxy resin with 10 parts per hundred parts of resin (phr) of various molecular weights of poly(phthaloyl diphenyl ether) (PPDE) and found

phase separation only in the blend with the highest molecular weight ($MW=56\,300$). Iijima *et al.*²⁰ also reported the use of epoxy-terminated poly(aryl ether sulfone)s as toughening modifiers for epoxy resins. Essentially all the studies on thermoplastic/thermoset blends previously reported involve a homogeneous, pre-cured mixture consisting of the thermoplastic, the epoxy monomer and the curing reagent. As the resin cures, the molecular weight increase causes a decrease in the configurational entropy of mixing. This is thermodynamically unfavourable for a miscible system owing to the increase in the free energy of mixing. Other than from a purely thermodynamic viewpoint, kinetic factors are also important in determining the final morphological properties of a cured resin. In the present study we report a thermoplastic/thermoset blend system (phenoxy/epoxy) that can exist as either a single-phase or multiple-phase morphology by kinetic control of the curing rate. We will explain this interesting phenomenon in terms of thermodynamics and kinetics. We will also focus on why some systems can exist only homogeneously, some systems only heterogeneously, and others either homogeneously or heterogeneously.

REACTION MECHANISMS AND KINETICS

The typical diamine/epoxy reaction can be represented by



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The reaction is known to be autocatalysed by OH^- and the kinetic equation of the reaction is well established²¹⁻²³ as

$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha^m)(1 + \alpha)^n \quad (1)$$

where α is the conversion of epoxide, and k_1 and k_2 are the specific rate constants. The quantities m and n are adjustable parameters and the sum $m + n = 2$ has been adopted in most literature. Golub and Lerner²⁴ studied the curing reaction of the diamine/epoxy system by FTi.r. and found a close match between the experimental results and the values predicted by theory when the curing conversion was less than 50%. Therefore, equation (1) can be simplified to give

$$\frac{d\alpha}{dt} = k_1(1 - \alpha) + k_2\alpha(1 - \alpha) \quad (2)$$

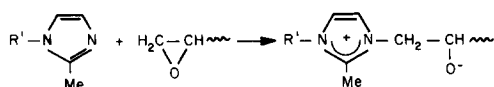
Integration of the above equation gives

$$\alpha = \frac{1 - \exp[-(k_1 + k_2)t]}{1 + (k_2/k_1)\exp[-(k_1 + k_2)t]} \quad (3)$$

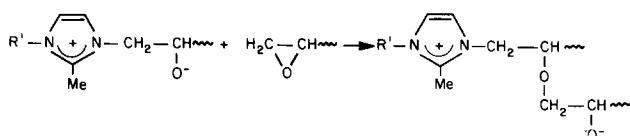
Equation (3) can be further rearranged to give

$$-(k_1 + k_2)t = \ln \frac{1 - \alpha}{1 + (k_2/k_1)\alpha} \quad (4)$$

The epoxy can also be cured by using imidazole as an accelerator through ring-opening addition of the epoxide groups²⁵⁻²⁹ as in



The alkoxide ion is an effective catalytic centre which is able to react readily with another epoxide



The rate equation of the anionic polymerization can be written as

$$-\frac{d[E]}{dt} = k_p[\text{anion}][E] \quad (5)$$

where $[E]$ is the epoxy concentration and $[\text{anion}]$ is the propagating species concentration. If the propagating species concentration is assumed to be constant during the curing reaction³⁰, then

$$[\text{anion}] = k'[\text{imidazole}]_0 \quad (6)$$

where $[\text{imidazole}]_0$ is the initial imidazole concentration. The kinetic equations can be expressed in terms of epoxy conversion as follows

$$\frac{d\alpha}{dt} = k(1 - \alpha) \quad (7)$$

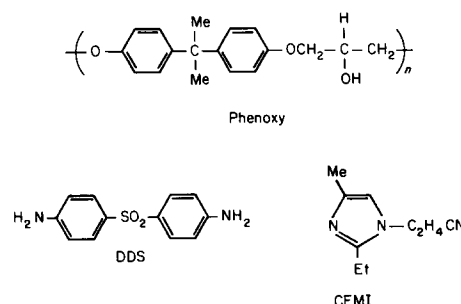
$$\ln \frac{1}{1 - \alpha} = kt \quad (8)$$

The rate constant k can be obtained from the slope of the straight line plotted for $\ln(1/1 - \alpha)$ versus time.

EXPERIMENTAL

Materials

Liquid epoxy resin Epon 826 ($EEW=182$) was obtained from Shell Chemical Company. Phenoxy resin PHKK, a high-molecular-weight, solid epoxy resin ($M_n=20\,000-25\,000$), was obtained from Union Carbide. Diaminodiphenyl sulfone (DDS) and 1-cyanoethyl-2-ethyl-4-methylimidazole (CEMI) were respectively the curing agent and accelerator employed in this study. The chemical structures of phenoxy, DDS and CEMI are



Curing procedure

Powdered phenoxy resin (10 phr) was dissolved in the epoxy resin at 110°C and a stoichiometric amount of the curing agent (DDS) was added. The mixture was then degassed at 100°C in a vacuum oven for 15 min and the mixture remained clear at this stage. The resultant solution was then cooled to 70°C , the desired quantity of accelerator was added and the resultant mixture was cast immediately in a teflon die. For the compact tension specimen, a fresh razor was placed in the die in such a position that a sharp notch was formed later. The same curing cycle was used throughout this study, keeping the mixture at 135°C for 1.5 h, at 160°C for 1.5 h, and at 190°C for an additional 2.5 h.

Kinetic measurements

The curing reaction was followed by infra-red spectroscopy on a Nicolet 520 FTIR spectrometer equipped with a temperature-controlled cell. A series of spectra was taken on the pre-cured mixture sandwiched between two KBr pellets and maintained at 135°C . The kinetics were determined by a method previously reported³¹ which uses the absorbance ratio A_{915}/A_{2968} . The 2968 cm^{-1} band is characteristic of the epoxy methyl group and was used as the internal standard; the 915 cm^{-1} band is the characteristic band of the epoxide group. The conversion of epoxide is calculated from

$$\alpha = (C_0 - C)/(C_0 - C_f) \quad (9)$$

where α is the epoxide conversion, C_0 is the absorbance ratio of the pre-cured mixture, C is the absorbance ratio at reaction time t and C_f is the post-curing absorbance ratio.

Viscosity measurements

Measurements of viscosity versus time at 135°C were performed using a Brookfield RVT viscosimeter. Each experiment was carried out on 200 g of the pre-mixed blend in a 250 ml beaker placed in a constant-temperature oil bath.

D.s.c. analyses

Dynamical differential scanning calorimetry was carried out on a Seiko DSC 220. Typically, a reaction mixture sample (10–20 mg) was sealed in an aluminium pan and the curing was allowed to proceed under a nitrogen atmosphere at a heating rate of $10^{\circ}\text{C min}^{-1}$. Integration of the exothermic peak gave the enthalpy of the curing reaction. For static measurements the calorimeter was initially maintained at 135°C , then the pre-heated sample (10–20 mg) was added to an aluminium sample cell. Data acquisition began after 1 min to allow equilibration of the system.

RESULTS AND DISCUSSION

Opaque, translucent and transparent products

Figure 1 shows the photograph of the cured specimens of the phenoxy/epoxy/DDS blends containing various amounts of CEMI accelerator. The specimens with less than 0.1 phr, 0.15 phr, and greater than 0.3 phr of CEMI are opaque, translucent, and transparent, respectively. At 0.15 phr the specimen is translucent. This is at the transition from opaque to transparent. Figure 2 shows the transmittance at 650 nm versus CEMI content, which gives a quantitative measure of the transparency of these blends. The scanning electron microscopy (SEM) micrographs (not shown here) provide direct evidence for the single-phase and multiple-phase morphologies of these blends³². The SEM micrographs will be presented in our next paper³³.

D.s.c. analyses

D.s.c. has been used previously to study the curing behaviour of epoxy systems³⁴. Dynamic d.s.c. curing plots from this study are illustrated in Figure 3. The curing reaction of epoxy and DDS is shown in the curve for sample A in Figure 3, where only a broad single exothermic peak between 135°C and 320°C (peak at 225°C) is present. The presence of CEMI accelerator adds a small exothermic peak at 117°C and the size of the peak increases with increasing CEMI content. The enthalpy of the main peak decreases only slightly with increasing amounts of accelerator and the peak maximum temperature remains essentially unchanged, as shown in Figure 3. Figure 4 illustrates the

d.s.c. thermograms of the epoxy-curing experiments carried out isothermally at 135°C using the stoichiometric amount of DDS and 0.5 phr CEMI separately. The anionic chain polymerization between epoxy and CEMI is significantly faster than that between epoxy and DDS. Therefore, under dynamic curing conditions, CEMI initiates the epoxy reaction at a lower temperature and affects, to certain degrees, the later epoxy/DDS curing reaction. CEMI in this study can be considered as a co-curing agent with a greater reactivity than DDS.

Viscosity measurements

The plots of viscosity versus isothermal curing time at 135°C are shown in Figure 5. The gel time of the mixture decreases with increasing CEMI content. When the mixture contains 0.3 or 0.5 phr CEMI, the final cured product is transparent and morphologically homogeneous^{32,33}. When the mixture contains 0.15 phr CEMI or less, the corresponding gel time is significantly increased while the resultant product is translucent to opaque because of different degrees of phase separation. When the curing rate is relatively high, the dissolved phenoxy molecules are completely locked within the epoxy network even though the thermodynamics favour phase separation of the phenoxy. When the curing rate

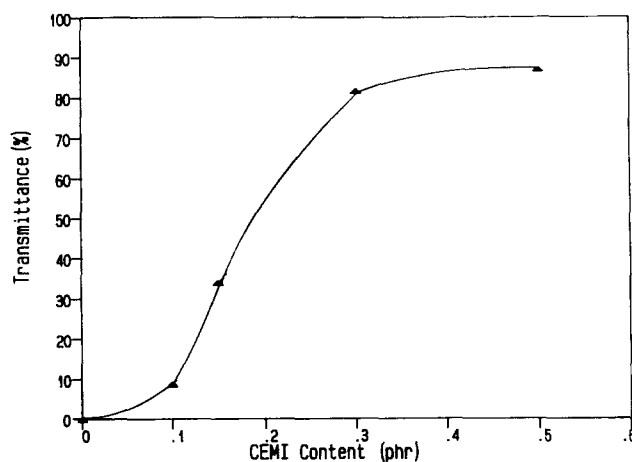


Figure 2 Plot of transmittance at 650 nm versus CEMI content in phenoxy/epoxy/DDS blends

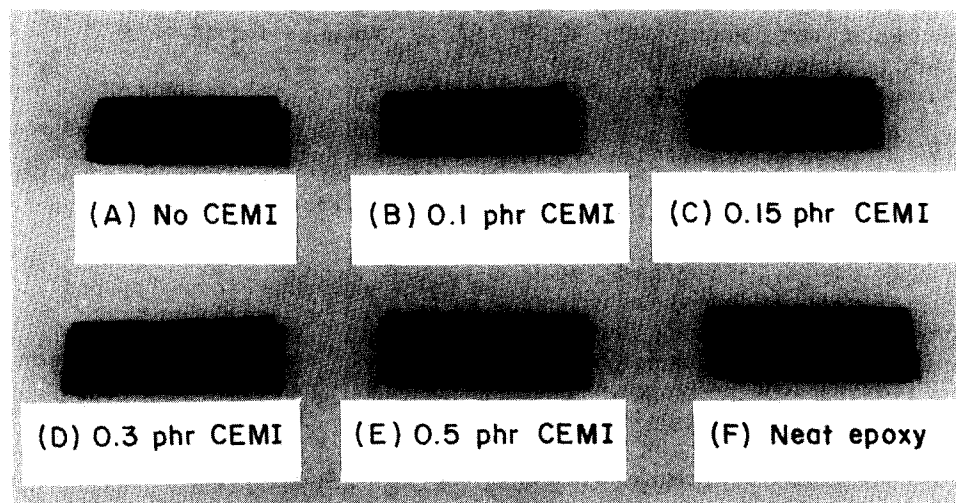


Figure 1 Specimens with different degrees of transparency from phenoxy/epoxy blends containing various amounts of CEMI

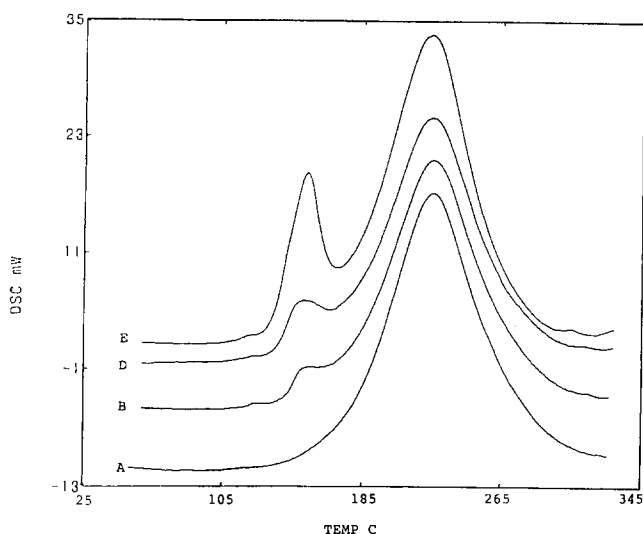


Figure 3 Dynamic d.s.c. thermograms of epoxy/DDS blends containing various amounts of CEMI accelerator: (A) no CEMI; (B) 0.1 phr CEMI; (D) 0.3 phr CEMI; (E) 0.5 phr CEMI

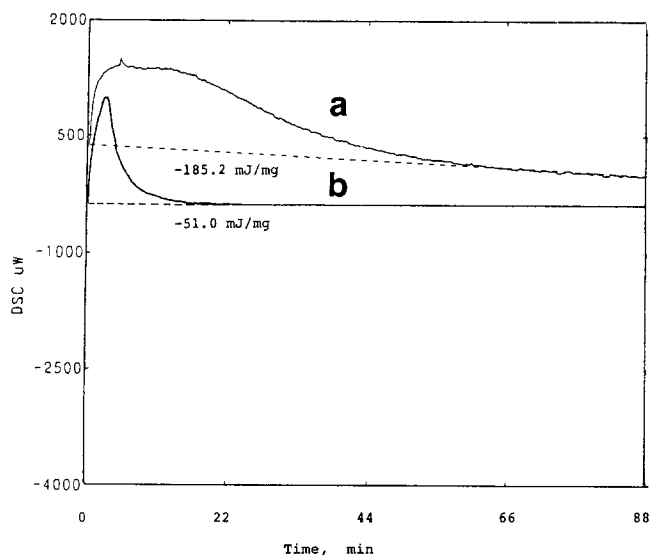


Figure 4 Isothermal d.s.c. thermograms at 135°C: (a) epoxy/DDS; (b) epoxy/0.5 phr CEMI

is relatively low, the resultant immiscibility owing to the epoxy molecular weight increase still allows the phenoxy resin to diffuse and coalesce to form a separate phase.

FTi.r. characterization and kinetics by FTi.r.

The characteristic i.r. bands assigned in this study are listed in Table 1. Figure 6a shows the FTi.r. spectra with time at 135°C for the phenoxy/epoxy/DDS blend in the range 2975–3680 cm⁻¹. The characteristic band at 3430–3581 cm⁻¹ corresponding to the hydroxy stretching vibration increases with curing time. The reversed trend observed for the N–H stretching vibration (3310–3480 cm⁻¹) is expected with the progress of the curing reaction. Figure 6b shows that the epoxide band (915 cm⁻¹) decreases with increasing reaction time. The epoxide band does not completely disappear, even after curing, which is not unexpected in any crosslinking reaction involving gelation and vitrification. Figure 7 shows the FTi.r. spectra of the epoxy curing with 0.5 phr

CEMI accelerator. The characteristic band for the hydroxy stretching vibration (3430–3581 cm⁻¹) remains essentially unchanged (Figure 7a) because this type of reaction neither generates nor consumes hydroxy groups. The absorption intensity of the epoxide (915 cm⁻¹) decreases only slightly and about 70% of the initial epoxide groups remain unreacted even after 1 h of post-curing heating at 190°C (Figure 7b).

A small amount of CEMI in the epoxy matrix is unable to cure the epoxy to a high degree of conversion, and it only accelerates the initial reaction. Figure 8 shows the plots of epoxide conversion versus reaction time at 135°C according to equation (9). The conversion in the phenoxy/epoxy/DDS system (curve a, Figure 8) increases almost linearly with time and reaches 67% conversion in 1.5 h. If DDS is absent from the system and replaced by 0.5 phr CEMI, the initial conversion rate is significantly increased in the first 10 min and within the initial 25% conversion, as shown in curve b of Figure 8. After 10 min, the conversion rate of the system decreases rapidly and the epoxide conversion almost levels out after 25% conversion (curve b, Figure 8). When the epoxy is cured simultaneously by DDS and 0.5 phr CEMI (curve c, Figure 8), the initial conversion rate is as high as curve b in the early stages of the reaction and approaches the same rate as curve a after about 50% conversion. Comparing curves a and c of Figure 8, we see that the presence of CEMI in the system accelerates the initial conversion rate and is the major contributor to the initial conversion in the system.

Figure 9 shows the linear plot according to equation (4). This result confirms the Golub assumption²⁴ that

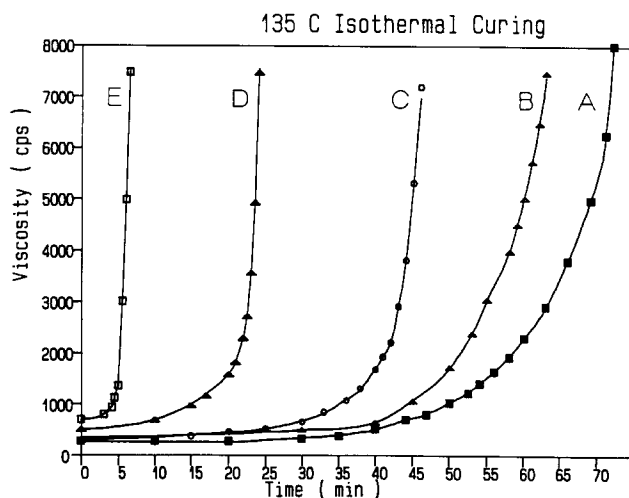


Figure 5 Plots of viscosity versus time for isothermal curing at 135°C of the phenoxy/epoxy/DDS blends containing various amounts of CEMI accelerator: (A) no CEMI; (B) 0.1 phr CEMI; (C) 0.15 phr CEMI; (D) 0.3 phr CEMI; (E) 0.5 phr CEMI

Table 1 Characteristic i.r. bands and peaks

Peak/band (cm ⁻¹)	Assignment
3581–3430	O–H stretch
3480–3310	N–H stretch
2962	Methyl C–H asymmetric stretch
1626	N–H deformation
1593	Substituted aromatic ring
1036	Aromatic deformation
915	Epoxide ring deformation

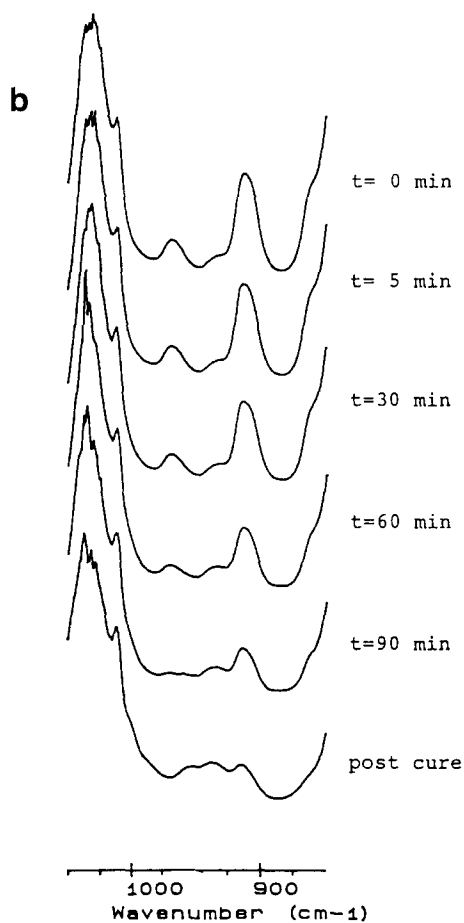
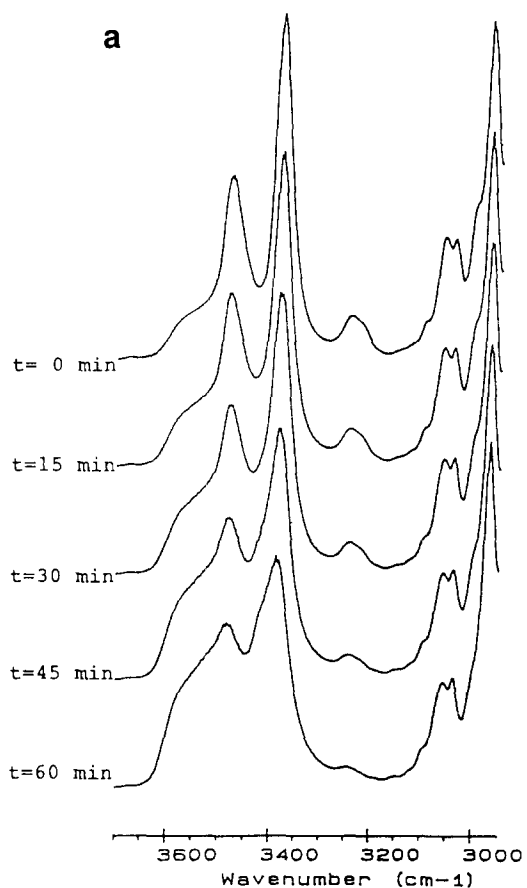


Figure 6 FTir. spectra for different curing times at 135°C of the phenoxy/epoxy/DDS blend: (a) 2975–3680 cm^{-1} ; (b) 860–1040 cm^{-1}

$m=n=1$ in the early stages of the epoxy-curing reaction, even with phenoxy in the system. The rate constants k_1 and k_2 obtained from the slope and intercept of Figure 9 are 8.68×10^{-3} and $1.21 \times 10^{-2} \text{min}^{-1}$, respectively.

Figure 10 shows the linear relationship established according to equation (8) and demonstrates the first-order reaction between epoxide and CEMI. The rate constant obtained from the slope of Figure 10 is $k=3.61 \times 10^{-2} \text{min}^{-1}$.

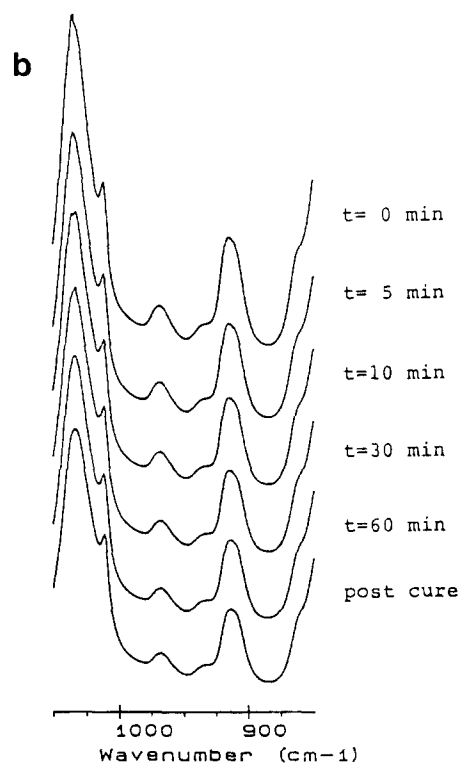
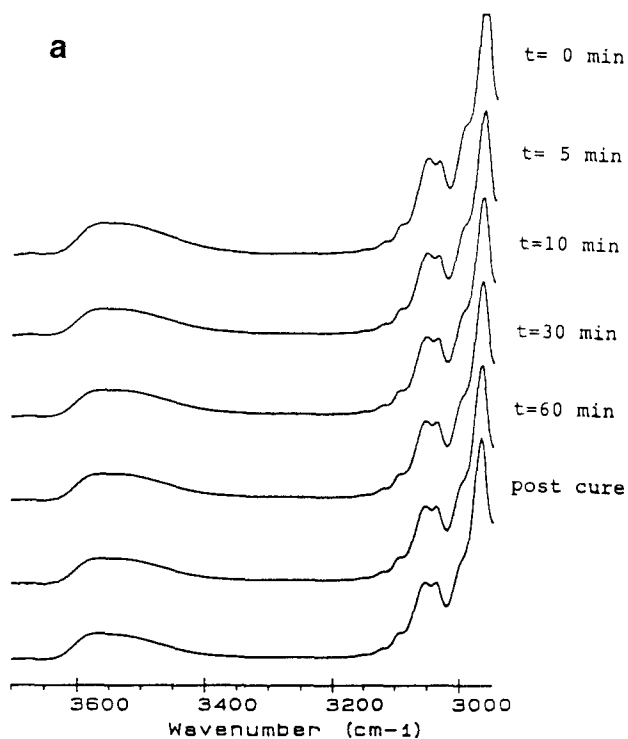


Figure 7 FTir. spectra for different curing times at 135°C of the phenoxy/epoxy/0.5 phr CEMI blend: (a) 2975–3680 cm^{-1} ; (b) 860–1040 cm^{-1}

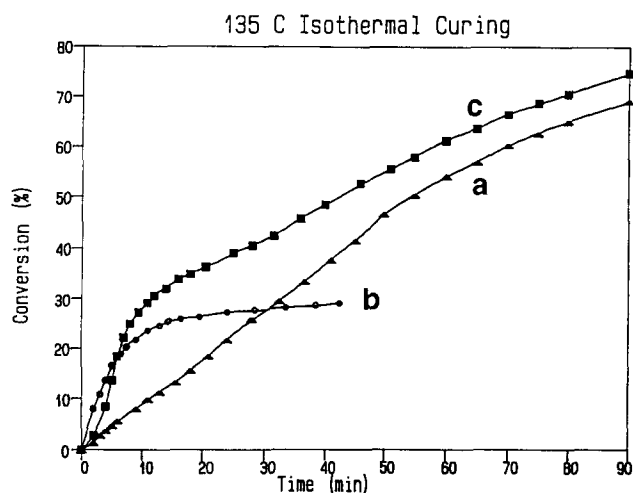


Figure 8 Epoxide conversion versus time at 135°C for isothermal curing of blends: (a) phenoxo/epoxy/DDS; (b) phenoxo/epoxy/0.5 phr CEMI; (c) phenoxo/epoxy/DDS/0.5 phr CEMI

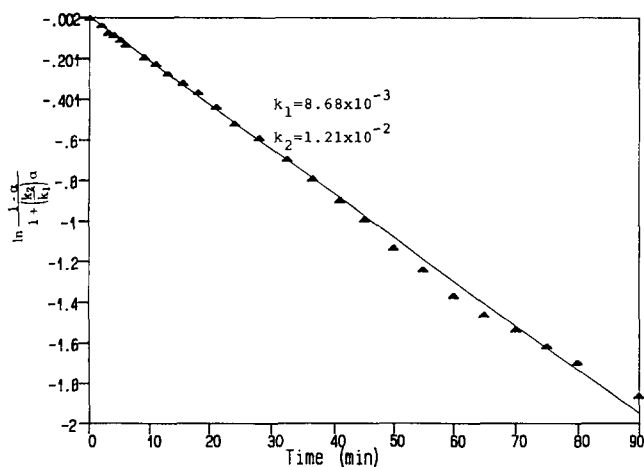


Figure 9 Kinetic plot for phenoxo/epoxy/DDS at 135°C

bicontinuous structure. Near the boundary between the binodal and spinodal regions, phase separation can occur either by an NG or an SD mechanism³⁶. For a non-crosslinkable polymer system, the morphology is mainly controlled by a thermodynamically reversible process which has a miscibility limit (structure freeze-in) near T_g or near a critical viscosity. In a dynamic and crosslinkable system such as the curing of a thermoset containing a thermoplastic, as in this study, the situation becomes more complicated. The morphology of the finally cured product is dependent on several factors: miscibility, critical viscosity, vitrification and gelation.

Hsich³⁵ and Yamanaka and Inoue¹⁸ have reported the morphological control of epoxy/CTBN systems by phase separation kinetics. The phase diagram in Figure 11 will be used to interpret our blend system in a qualitative manner. Since the temperature, composition and phenoxo molecular weight are kept constant in this study, the location of P_1 will be fixed. The increase in epoxy

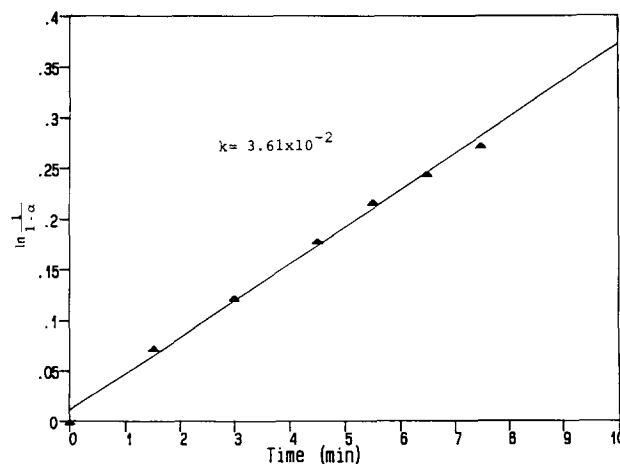


Figure 10 Kinetic plot for phenoxo/epoxy/0.5 phr CEMI at 135°C

Phase separation in terms of thermodynamics, kinetics and rheology

Polymer phase separation phenomena have recently been reviewed by Hsich³⁵ and Utracki³⁶. The phase separation mechanisms in the two regions, metastable (binodal) and unstable (spinodal), are quite different. Phase separation in the metastable region takes place by localized fluctuations of concentration (or density), and the mechanism is known as nucleation and growth (NG). The new phase starts from small nuclei which then proceed to grow and extend. In the spinodal region the concentration fluctuations are delocalized and no thermodynamic barrier exists towards phase transformation, leading to long-range, spontaneous phase separation. There is no sharp interfacial boundary between phases in the initial stage of phase separation. This process is called spinodal decomposition (SD). The phase separation process, either NG or SD, is a diffusion-controlled process. The natural form of the phase separation via the NG mechanism is the droplet/matrix type and the composition in the droplet is constant with only its size changing with time. In the SD mechanism, decomposition starts with a bicontinuous structure and gradually shifts to a droplet morphology of the minor component owing to the breakdown of the

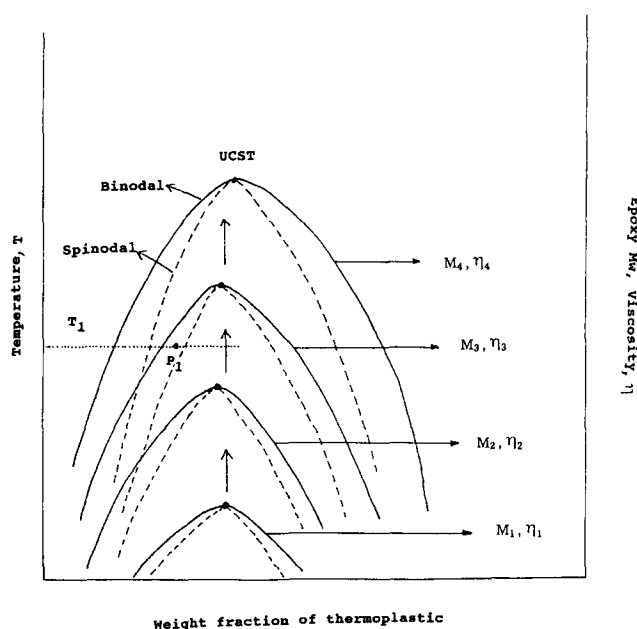


Figure 11 Phase diagram illustrating the phase separation mechanisms of thermoplastic/thermoset blends at constant temperature (T_1) and fixed thermoplastic fraction in terms of epoxy molecular weight and viscosity of the mixture

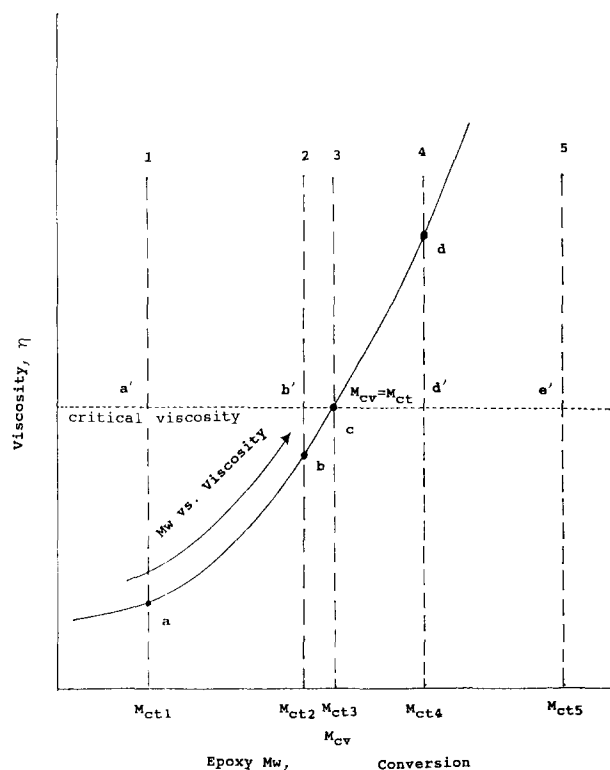


Figure 12 Diagram illustrating the conditions required for phase separation of thermoplastic/thermoset blends in terms of the critical epoxy molecular weight M_{ct} and the critical viscosity η_{cr} .

molecular weight shifts upward the binodal and spinodal curves while the T_g and crosslinking density of epoxy and the viscosity of the mixture are also increased. At the beginning of the curing reaction, P_1 is located above the binodal curve in a state where the system is miscible with the initial epoxy molecular weight M_1 and the mixture viscosity η_1 , as shown in *Figure 11*. As the reaction proceeds and the epoxy molecular weight is progressively increased to M_3 , phase separation starts by the NG mechanism when the binodal curve moves upward and passes point P_1 . In this metastable region (or in the unstable region), any further phase separation will be halted if the mixture viscosity is greater than a critical value. In such a case, phase separation by the NG mechanism will start and finish only in this metastable region. It is also quite possible that P_1 will fall into the unstable region by passing the spinodal curve at the time of structural freeze-in by vitrification or structural lock-in by gelation. In such a situation, the phase separation actually takes place by two mechanisms in sequence, first NG and then SD. Therefore, phase separation is considered to be very complex in a thermoplastic/thermoset curing system, involving time-dependent thermodynamics, kinetics and the viscosity of the system.

Only a few workers have reported previously^{14,32,35,37} that thermoplastic/thermoset blends with similar compositions are able to exist either as single-phase or multiple-phase structures through kinetic control of the curing rate. We can consider the final cured product in any thermoplastic/thermoset blend system to be in one of four classes: (1) miscible and single phase; (2) immiscible and multiple phase; (3) miscible and multiple phase; and (4) immiscible and single phase. Classes 1 and 2 are well recognized in polymer blends as a generally accepted rule in terms of thermodynamics. A well mixed blend of a

miscible pair such as polystyrene and poly(phenylene oxide) can be considered as an example of class 1. If kinetic factors are taken into consideration, class 3 can occur. We will take our system (phenoxy/epoxy) as an example and use *Figure 12* (see later) to explain the existence of either class 2 or class 4 in terms of thermodynamics and kinetics.

If we neglect the contribution from kinetic factors and maintain constant temperature and identical phenoxy fractions in the mixture, the epoxy molecular weight alone will be enough to dictate the miscibility or the free energy of mixing according to the relationships derived from Flory-Huggins theory³⁸

$$\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T\Delta S_{\text{mix}} \quad (10)$$

$$\frac{\Delta G_{\text{mix}}}{(V_A + V_B)} = RT \left(\frac{\rho_A \phi_A}{M_A} \ln \phi_A + \frac{\rho_B \phi_B}{M_B} \ln \phi_B \right) + B \phi_A \phi_B \quad (11)$$

Here ϕ , ρ , M , and B are the component volume fraction, mass density, molecular weight and binary interaction energy density, respectively. The entropy part of equation (11) is always negative, thus favouring miscibility, while the enthalpy part can be either positive or negative depending on the sign of B . If B is negative, an indication of exothermic mixing, the system will be miscible regardless of temperature and/or the component molecular weight. When B in equation (11) is positive (endothermic mixing), it is possible to switch the sign of ΔG_{mix} or the miscibility of the system by varying the component molecular weight and/or the temperature. As the curing proceeds, the epoxy molecular weight will increase and reach a critical value to change the sign of ΔG_{mix} from negative to positive. We define this thermodynamically critical epoxy molecular weight at $\Delta G_{\text{mix}} = 0$ as M_{ct} . Theoretically we should be able to calculate M_{ct} from equation (11) if B is known.

The viscosity of the mixture is directly related to temperature, epoxy conversion, T_g and crosslinking density. The mixture viscosity during curing is another important factor that determines the status of the final phase besides the thermodynamics. When the mixture viscosity is greater than a critical level η_{cr} , the phenoxy suffers either structural freeze-in by vitrification or lock-in by gelation and further diffusion of phenoxy becomes totally impossible. The relation between the viscosity and molecular weight of a thermoplastic can be expressed as

$$\eta = K(MW)^n \quad (12)$$

where $n = 1$ if MW is below the critical entanglement MW and $n = 3.4$ if MW is greater than the critical entanglement MW . The above relation may not be perfectly applicable in our system, especially during the later stages of high crosslinking, but certainly it is suitable in the earlier stages of the curing reaction.

Figure 5 shows the plots of viscosity versus time where all the initial slopes are relatively low but jump to extremely high at later stages of the reaction. This sudden viscosity increase can be interpreted as the order change from 1 to 3.4 in equation (12). Vitrification and gelation owing to the increase in epoxy molecular weight during curing are other reasons for the observed gelling. Higher crosslinking provides the irreversible structure lock-in and prevents phenoxy diffusion and coalescence even at a temperature above the T_g of phenoxy or even above the T_g of the cured epoxy.

Crosslinking density is a statistical function of the epoxy molecular weight in a typical curing reaction and can be calculated theoretically. We define the epoxy molecular weight at the critical viscosity (η_{cr}) as M_{cv} when the phenoxy suffers complete freeze-in or lock-in within the epoxy matrix. For convenience, we intend to use the critical viscosity as the demix limit in the following interpretation. The critical viscosity can result from the reversible structural freeze-in or the irreversible structural lock-in or both. M_{ct} based on thermodynamics and M_{cv} based on viscosity (kinetics) are two independent variables in a dynamic curing process in this study. Now we will begin to explain why the critical epoxy molecular weight based on thermodynamics (M_{ct}) is the single most important factor in dictating the final phase morphology. M_{ct} is a function of phenoxy molecular weight, volume fraction and temperature. A higher epoxy M_{ct} means a greater miscibility between phenoxy and epoxy. If the temperature and phenoxy volume fraction are fixed, M_{ct} will also be fixed in the system. Ideally, M_{ct} can be estimated experimentally by locating the cloud point with time at constant temperature. We will use *Figure 12* to show that a homogeneous but immiscible blend can exist through kinetic control in any thermoplastic/thermoset blend system.

Case 1: $M_{ct} = M_{cv}$ (line 3, Figure 12)

As mentioned earlier, both M_{ct} and M_{cv} are already fixed in this particular case although the values are unknown. Therefore, this is an imaginary blend having identical critical molecular weights both thermodynamically and kinetically, i.e. $M_{ct} = M_{cv}$. Phase separation becomes feasible thermodynamically but such a demixing process is completely halted after this point (M_{ct3} , *Figure 12*) owing to high viscosity. The final cured product will be homogeneous morphologically but inherently immiscible from a thermodynamic viewpoint.

Case 2: $M_{ct} \ll M_{cv}$ (line 1, Figure 12)

This is the case where the M_{ct} of epoxy is significantly smaller than M_{cv} . Phenoxy is miscible only with epoxy monomer or low MW epoxy during the early stages of the reaction, as shown by line 1 in *Figure 12*. This system is favourable for phase separation because the viscosity of the mixture is still relatively low at the initiation of phase separation. When the epoxy MW is increased to M_{ct1} (point a), the barrier towards diffusion and coalescence of phenoxy into spherical particles is still relatively low. In this case, the final cured product with single-phase morphology is very difficult to achieve or almost impossible to achieve by kinetic control of the curing rate.

Case 3: $M_{ct} > M_{cv}$ (line 4, Figure 12)

Thermodynamic immiscibility occurs when the viscosity of the mixture is already higher than the critical viscosity (η_{cr}) and the corresponding epoxy MW (M_{ct4} , *Figure 12*) is also higher than M_{cv} . Therefore, the phenoxy molecules at this time have already been frozen or locked within the epoxy matrix and any migration of phenoxy is completely halted. The final cured product in this case is expected to be morphologically homogeneous but thermodynamically immiscible. It is possible that a phenoxy resin with a lower molecular weight than the one employed in this study can be classified as case 3.

Case 4: $M_{ct} \gg M_{cv}$ (line 5, Figure 12)

This is an entirely miscible system, regardless of epoxy molecular weight, because the critical MW line (M_{ct5} , line 5) will never intercept the viscosity *versus* MW curve. The final cured product is morphologically homogeneous and thermodynamically miscible. However, to identify whether it is a truly thermodynamically miscible blend as distinct from these single-phase blends of cases 1, 3, 4, and 5 is very difficult experimentally.

If the final cured product is morphologically homogeneous but thermodynamically immiscible, both d.s.c. and rheometric dynamic spectrometry (r.d.s.) analyses will show only a single T_g , an indication of a miscible blend. End-group-capped phenoxy with extremely low molecular weight probably belongs to this case. The emphasis on end-group capping is necessary, otherwise these low MW phenoxy with epoxide end-groups will behave like the epoxy monomer.

Case 5: $M_{ct} < M_{cv}$ (line 2, Figure 12)

This case best describes the situation in this study. M_{ct2} is only slightly lower than the critical viscosity molecular weight M_{cv} . When the epoxy molecular weight is increased beyond the critical M_{ct2} (point b, *Figure 12*), the viscosity of the mixture is already approaching the critical viscosity η_{cr} . The time-dependent diffusion and coalescence processes for phenoxy phase separation from the epoxy matrix are relatively difficult but still possible. Therefore, the phase separations of the final cured products will be incomplete to different degrees depending on the rate of reaction in this critical range (point b to point c). The SEM fracture surface morphology of the most slowly cured phenoxy/epoxy/DDS blend (curve A, *Figure 5*) indicates that about two-thirds of the phenoxy spherical particles are within the circular intermediate zone of incomplete phase separation; clean interfaces are apparent for only one-third of the particles^{32,33}.

The degree of phase separation is progressively decreased with increasing CEMI accelerator content in the system. This means that if M_{ct} is only slightly lower than M_{cv} , the morphological structure of the final cured product can be manipulated by kinetic control of the curing rate. The kinetic approach for the NG and SD phase separation mechanisms has been recently reviewed by Hsieh³⁵.

In order to address this subject in a semi-quantitative manner, the kinetic information from the viscosity *versus* time curves shown in *Figure 5* and line 2 in *Figure 12* will be used. For convenience, we will arbitrarily assume that the critical viscosity η_{cr} is 5000 cps (critical viscosity line, *Figure 12*) and that the viscosity required to initiate phase separation η_i is 3000 cps (point b, *Figure 12*, corresponding to $MW = M_{ct2}$) in this system. The time interval between point b and point c is a very important factor in determining the final phase morphology and certainly it is not a linear relation. *Table 2* lists the viscosity increase rates and time intervals required to increase the viscosity from 3000 to 5000 cps (representing an increase in epoxy MW from M_{ct2} to M_{cv} , *Figure 12*) for the various blends shown in *Figure 5*. As mentioned earlier, the blend containing 0.15 phr CEMI occurs exactly at the transition from single-phase to multiple-phase morphology. The critical time and critical viscosity increase rate calculated from the curve for sample C in *Figure 5* and from *Table 2* are 1.87 min and

Table 2 Summarized data^a on time intervals and viscosity increase rates between initiation^b and termination^c of phase separation

Blend	CEMI content (phr)	Time	Time	$\Delta\eta/\text{time}$	$\Delta\eta/\text{time}$
		(min) 3000–5000 cps	(min) 2000–5000 cps	3000–5000 cps	2000–5000 cps
A	0	5.50	10.63	364	282
B	0.1	5.10	8.78	392	342
C ^d	0.15	1.87	3.77	1110	796
D	0.3	0.94	2.18	2127	1376
E	0.5	0.53	0.85	3774	3529

^aData in this table are extracted from Figure 5

^bThe viscosity of the mixture when the epoxy molecular weight is at M_{ci} and immiscibility or phase separation starts

^cThe viscosity of the mixture when the epoxy molecular weight is at M_{cv} and phenoxy diffusion is terminated due to structural freeze-in or lock-in

^dThis blend is at the transition from morphological homogeneity to inhomogeneity

1110 cps min⁻¹, respectively. The curing rate in terms of either the viscosity increase rate or the time interval between points b and c (Figure 12) has to exceed the above critical values in order to give a single-phase product. These single-phase blends (with CEMI contents greater than 0.3 phr) are considered to be thermodynamically immiscible. However, these transparent products show only single T_g values by d.s.c. and r.d.s. analyses, indicating miscible blends. Therefore, a miscible blend by the single- T_g approach might not be a truly thermodynamically miscible blend.

The experimental results used in proposing this model are not without deficiency. The chemical structures of the CEMI-cured and DDS-cured epoxies are not identical and we have neglected that difference. The proposed model can properly explain the observed phenomena in this study and others^{19,32,33,37} and the concept of this model can also be extended to other thermoplastic/thermoset systems used in coatings, paints, reaction injection moulding and special composites. A similar study using variations in the molecular weight of the thermoplastic in the thermoplastic/thermoset blend to provide additional evidence to support this model is in progress and will be published at a later date.

The phenoxy resin employed in this study is not an inert thermoplastic; it has epoxy end-groups unless it is specifically end-capped. A typical curing reaction should also involve the epoxy end-groups from the phenoxy. The presence or absence of epoxy end-groups in the phenoxy must have a great influence on the final morphology of the blend and this area has not been explored in this study. One important question we hesitate to answer at this time is what mechanism, NG, SD, or both, really takes place in this system. However, the morphological evidence we will present in our next paper strongly suggests that the SD mechanism is the major or only mechanism involved.

CONCLUSIONS

The kinetics of the curing reaction for phenoxy/epoxy/DDS blends with and without CEMI accelerator were investigated by d.s.c., FTi.r. and viscosity measurements. Opaque, translucent and transparent products could be obtained through kinetic control of the curing rate by varying the amount of accelerator in the system. A model to describe the phase separation mechanism in terms of thermodynamics and kinetics was proposed which can explain the phase morphological phenomena observed in any thermodynamic/thermoset polyblend.

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