

Effects of the Molecular Weight of Poly(ether imide) on the Viscoelastic Phase Separation of Poly(ether imide)/Epoxy Blends

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ABSTRACT: The phase separation of diglycidyl ether of bisphenol A/methyl tetrahydrophthalic anhydride blends modified with three poly(ether imide)s (PEIs) of different molecular weights was investigated with scanning electron microscopy (SEM) and time-resolved light scattering (TRLS). The morphologies observed by SEM for the three blends were all close to a cocontinuous structure with different periodic distances. The results of TRLS indicated that the phase separation for the PEI-modified epoxy blends took place according to the spinodal decomposition mechanism and the onset time of phase separation, with the periodicity of the phase structure depending on the PEI molecular weight and cure temperature. The time-de-

pendent peak scattering vector was simulated with a Maxwell-type viscoelastic relaxation equation, indicating that the coarsening process of epoxy droplets was mainly controlled by the viscoelastic flow. Relaxation times obtained at different temperatures for the three blends could be described by the Williams–Landel–Ferry equation. The effects of the PEI molecular weight on the processes of viscoelastic phase separation were investigated, and the observed trends could be explained qualitatively through thermodynamic analysis. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 3158–3167, 2009

Key words: blends; phase separation; viscoelastic properties

INTRODUCTION

Epoxy resins are widely used in casting, adhesive, and composite applications. They have many attractive properties: they are easy to cure and process, are resistant to moisture, solvents and chemicals, and have good mechanical and electrical properties. Because of their brittleness, attempts have been made to modify epoxy resins with a high-performance engineering thermoplastic that has a high glass-transition temperature (T_g) and toughness, such as polysulfone (PSF),¹ poly(ether sulfone),² poly(ether ether ketone),³ or poly(ether imide) (PEI).^{4,5} In the cure process of thermoset resins, the entropy of mixing decreases as the molecular weight increases, whereas the Flory–

Huggins interaction parameter (χ) changes little; that is, the enthalpy remains almost constant.

According to the Flory–Huggins mean-field theory, increasing the molecular weight of the thermoset component beyond that at which a homogeneous mixture is no longer favored initiates phase separation, generating various heterogeneous two-phase morphologies.^{2,6} Different phase morphologies can be obtained, depending on the competition between the thermodynamics, the kinetics of phase separation, and the crosslinking chemical reaction, which are all governed by the curing conditions and composition as well as the molecular weights and molecular weight distribution. It is well-known that a cocontinuous two-phase system will exhibit unique mechanical properties, a high initial modulus, large extension, and complete strain recovery.

The polymer molecular weight is one of the most important factors influencing the thermodynamic and kinetic properties and thus the final morphology of materials. Nonetheless, the effect of the thermoplastic molecular weight on phase separation has not been as extensively studied as the phase-separation process in polymer diluent or thermoplastic/thermoplastic systems as well as thermoplastic/thermoset systems. Moreover, no publication thus far has reported the effect of the molecular weight on

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viscoelastic phase separation. Matsuyama et al.⁷ investigated the effect of the polymer molecular weight on the initial phase-separation rate and droplet growth rate in the latter stage in a polypropylene/diphenyl ether system via thermally induced phase separation. Gelles and Frank⁸ studied the effect of the molecular weight on the kinetics of phase separation in polystyrene (PS) and poly(vinyl methyl ether) blends by using the technique of excimer fluorescence. The growth rate of the dominant concentration fluctuation during the initial stages of spinodal decomposition was found to decrease with increasing PS molecular weight. The effects of the molecular weight and its distribution on the early stage of the spinodal decomposition of polybutadiene (PB) and styrene-butadiene random copolymers were studied by Hashimoto et al.⁹ The apparent or mutual diffusivity and the wave number of the dominant mode of the fluctuations decreased with the molecular weight of PB increasing.⁹ The characteristic parameters for the four mixtures turned out to be identical; thus, the dynamics were found to be insensitive to the molecular weight distribution, depending only on the weight-average molecular weight.¹⁰

For thermoplastic/thermoset systems, the effect of varying the rubber molecular weight on reaction-induced phase separation in rubber-modified epoxies was reported by Pascault et al.¹¹ Increasing the rubber molecular weight led to a decrease in the conversion at the cloud point, a primary morphology of a low concentration of large particles, and more complete segregation of the rubber from the matrix. Park et al.¹² investigated the effects of the molecular weight of PSF on the morphology of bisphenol A dicyanate/PSF blends. They observed that the viscosity of the blends at the onset point of phase separation increased with an increase in the PSF molecular weight and determined the morphology of the blends. Merfeld et al.¹³ measured the miscibility of diglycidyl ether of bisphenol A (DGEBA) based epoxies with a series of poly(2,6-dimethyl-1,4-phenylene ether) (PPE) resins and explored the effects of the molecular weight of PPE. A lower PPE molecular weight improved the miscibility because of the larger entropic contribution to the free energy of mixing, and the dispersed phase size increased with either the PPE content or molecular weight. The phase-separation process of an epoxy prepolymer based on DGEBA with a thermoplastic PS was thermodynamically studied in the framework of the Flory-Huggins theory by Lopez et al.¹⁴ The PS/DGEBA blend showed upper critical solution temperature (UCST) behavior, the miscibility increased with the temperature, and so when the temperature decreased, the phase separation advanced. The effects of the molecular weight of carboxyl-terminated poly(ethylene glycol) adipate (CTPEGA) on

the thermomechanical and viscoelastic properties of modified epoxy networks were investigated by Samui et al.¹⁵ Although the same amount of CTPEGA was added to all the blends, the extent of the dispersed phase increased with an increase in the molecular weight of CTPEGA, as an increase in the molecular weight reduced the combinatorial entropy of mixing.

In our previous work, we found that phase separation occurred first in a high-molecular-weight PEI-modified epoxy resin and that the time of occurrence of phase separation increased as the inherent viscosity of PEI decreased. Because of their different viscosities, the blends displayed various morphologies ranging from a PEI particle dispersion to cocontinuous phases.¹⁶ The effects of the molecular weight on the phase separation of phenyl-terminated, PEI-modified tetraglycidyl-4,4'-diaminodiphenylmethane diaminodiphenylsulfone systems were also investigated. An increase in the molecular weight of PEI raised the cure rate of the modified systems and changed the morphology from PEI-rich domains in the low-molecular-weight PEI-modified system to a PEI-epoxy cocontinuous phase structure in the high-molecular-weight systems.¹⁷ Similarly, when the molecular weight of fluorocarbon-chain-terminated PEI increased, the morphology could change from a dispersed phase to a cocontinuous phase.¹⁸ This work focuses on epoxy-anhydride matrices modified with the same initial concentration (25 wt %) of thermoplastic PEIs that differed in their molecular weights (but their chemical composition was kept constant). We present and discuss the results of varying the molecular weight of thermoplastics on the phase separation of thermoplastic/thermoset systems and attempt to describe the kinetics of the evolution process of phase separation with different thermoplastic molecular weights. It is hoped that these results will aid in designing materials through control of the molecular weight and the resultant structural development in multicomponent thermosetting resins.

EXPERIMENTAL

A commercial epoxy precursor (DGEBA) with an epoxide equivalent weight of 184–194 g/equiv (DER 332, Dow Chemical, USA), a hardener [methyl tetrahydrophthalic anhydride (MTHPA)], and an accelerator [benzyl dimethylamine (BDMA; Shanghai Third Reagent Factory, Shanghai, China)] were used without further purification.

PEI was synthesized from bisphenol A dianhydride (BISA-DA) and 4,4'-[1,4-phenylenebis(1-methylethylidene)]bis(aniline) (BISP) in stoichiometric ratios of 1 : 0.985, 1 : 0.975, and 1 : 0.965 in *m*-cresol at 200°C. Afterwards, aniline was added to terminate the PEI, and the products were precipitated in

TABLE I
Properties of PEIs Synthesized with Different
BISA-DA/BISP Molar Ratios

BISA-DA:BISP (molar ratio)	M_n ($\times 10^4$) ^a	M_w ($\times 10^4$) ^a	T_g ($^{\circ}\text{C}$) ^b	IV (dL/g) ^c
1:0.985	4.60	7.52	220	0.69
1:0.975	3.63	5.73	215	0.51
1:0.965	2.87	4.66	211	0.31

IV = inherent viscosity; M_n = number-average molecular weight; M_w = weight-average molecular weight.

^a Determined by GPC.

^b Obtained by DSC.

^c Obtained at a concentration of 0.5 g/dL at 30 $^{\circ}\text{C}$ in *N*-methyl-2-pyrrolidone.

alcohol and dried at 200 $^{\circ}\text{C}$ for about 4 h. The molecular weight of PEI as measured by gel permeation chromatography (GPC) is shown in Table I.

Epoxy blends containing PEIs (25 pbw) of different molecular weights were prepared by the dissolution of PEI in DGEBA at 150 $^{\circ}\text{C}$. The mixture was cooled to 90 $^{\circ}\text{C}$, and a stoichiometric amount (80 pbw) of the cure agent MTHPA was added with 0.2 pbw BDMA; then, the blend was cooled rapidly to room temperature to avoid any further curing reaction. According to the different weight-average molecular weights of PEI—7.52 $\times 10^4$, 5.73 $\times 10^4$, and 4.66 $\times 10^4$ —the blends were designated P725, P525, and P425, respectively.

The molecular weights of PEI were measured on an Agilent (Palo Alto, CA) 1100 by GPC with respect to a PS standard with tetrahydrofuran used as the eluent.

The calorimetric measurements were made on a PerkinElmer (Norwalk, CT) Pyris 1 differential scanning calorimeter in a dry nitrogen atmosphere. T_g of PEI was determined by differential scanning calorimetry (DSC) from room temperature to 300 $^{\circ}\text{C}$ at a heating rate of 10 $^{\circ}\text{C}/\text{min}$.

The final morphology of the isothermally cured blends was observed under a scanning electron microscope (XL 39, Philip, Eindhoven, The Netherlands). The samples were fractured in liquid nitrogen. All samples were coated with gold and mounted onto copper mounts. The phase-separation process taking place during the isothermal curing reaction was observed in real time and *in situ* on a self-made time-resolved light scattering (TRLS) instrument with a controllable hot chamber, which was set perpendicular to the laser beam (He-Ne laser with a 632.8-nm wavelength).¹⁹ A drop of the sample was placed between two glass slides and mounted onto a hot stage at different temperatures ranging from 100 to 150 $^{\circ}\text{C}$. The film sample for TRLS observation was prepared by melt pressing with a thickness of about 20 μm , and the phase-separation process was monitored *in situ* with an Olympus (Hamburg, Germany) BX51 camera at appropri-

ate time intervals during the isothermal cure process. The onset time of phase separation was determined as that at which a scattering peak was recorded; whereas the time for the fixing of the phase structure was determined as that at which the peak scattering vector (q_m) leveled off.

RESULTS AND DISCUSSION

Morphologies observed by scanning electron microscopy (SEM)

The morphologies of samples with PEIs of different molecular weights cured at 100, 130, and 150 $^{\circ}\text{C}$ were observed with SEM (Fig. 1). In all the images presented here, the dark regions correspond to the epoxy-rich phase, whereas the bright regions correspond to the PEI-rich phase. It is obvious that the morphologies of these systems are somewhat similar. All of the images consist of large and irregular PEI-rich domains dispersed in an epoxy-rich continuous phase that is very close to a cocontinuous-type phase structure.

However, in blends with PEIs of higher molecular weights, such as blend P525 and blend P725, many fine epoxy-rich globules, 2–3 μm in size, can be observed in the PEI-rich phase, regardless of the cure temperature, whereas in blend P425, the PEI-rich phase spreads out with no globules.

The periodic distances of the macrostructure are larger in blend P525 than those in blend P725 at the same temperature. This may be due to the fact that it is more difficult for PET of higher molecular weight to disentangle in blend P725. In blend P425, which has a lower PEI molecular weight, the periodic distances of the macrostructure decrease. Particularly at the lower temperature of 100 $^{\circ}\text{C}$, the morphology for blend P725 is between a phase-inversed structure and a cocontinuous phase structure, whereas the morphology for blend P425 is more like a dispersion phase structure. This is due to the lower PEI molecular weight in blend P425, which allows it to disentangle easily, so almost all the epoxy-rich droplets can move out to connect with one another. The disentangled PEI-rich phase spreads out, and this results in small periodic distances.

Phase separation monitored by TRLS

To describe the process of structure evolution in blends with PEIs of different molecular weights at different temperatures, phase-separation processes at 100, 110, 120, 130, 140, and 150 $^{\circ}\text{C}$ were traced *in situ* by TRLS.

Figure 2 shows a typical example of the change in the scattering profile with time t for blend P525 isothermally cured at 130 $^{\circ}\text{C}$. The scattered light

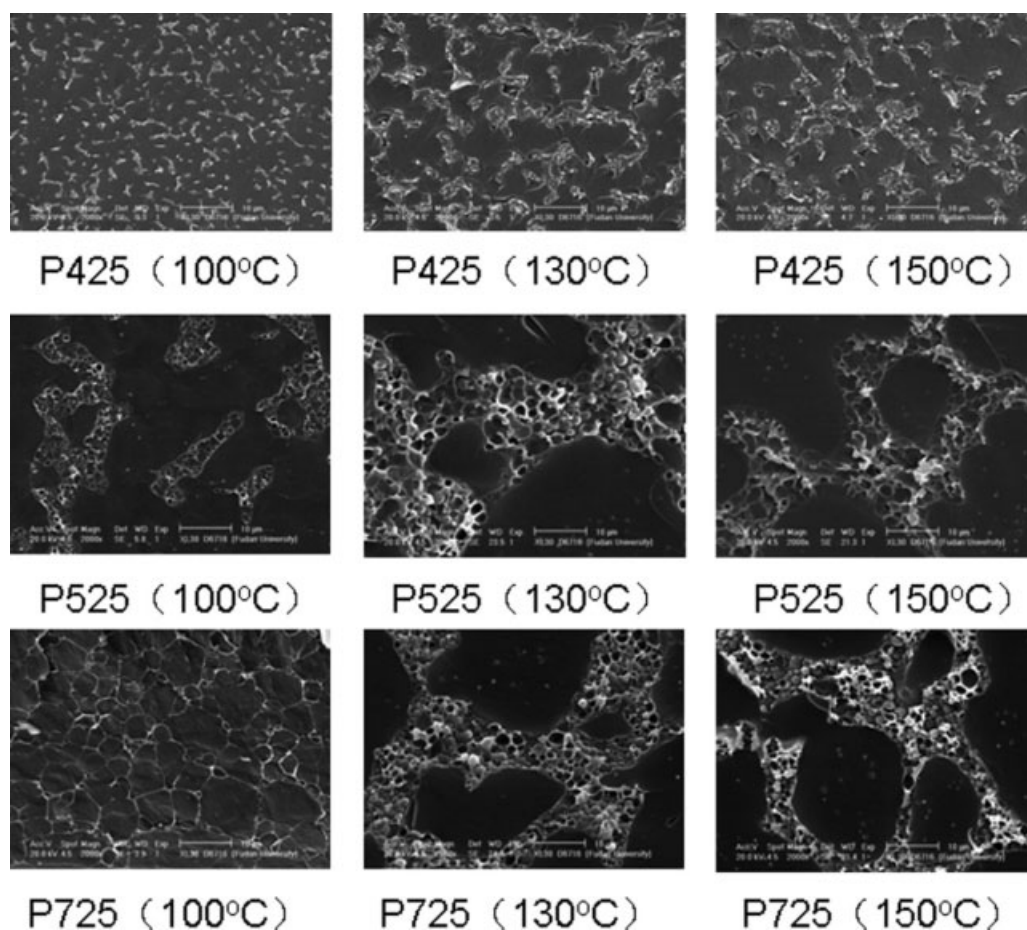


Figure 1 SEM micrographs of blends P425, P525, and P725 cured for 5 h (2000 \times).

intensity (I) is a function of the time and scattering vector (\mathbf{q}); the latter is defined by eq. (1).^{20,21}

$$\mathbf{q} = (4\pi/\lambda) \sin(\theta/2) \quad [20 - 21] \quad (1)$$

where λ is the wavelength of light in the sample and θ is the scattering angle. The reciprocal of \mathbf{q} is assigned to the periodic distance (Λ) of the dispersed particles:^{9,10}

$$\Lambda = 2\pi/\mathbf{q} \quad (2)$$

From the light scattering profiles, the \mathbf{q}_m value corresponding to an instantaneous maximum scattering intensity (I_m) was obtained. \mathbf{q}_m decreased rapidly with time and leveled off to a certain value, whereas the relative intensity of scattered light increased continually, then decreased a little, and thereafter remained constant, as described in the literature.⁴ This characteristic change in the scattering profiles indicates the development of a regularly phase-separated morphology via spinodal decomposition.^{20,21}

Note here that the light scattering profiles are similar at all temperatures, with the exception of the

differences in the onset time of the phase separation and the fixing time of the phase structure as well as the intensity of the scattered light.

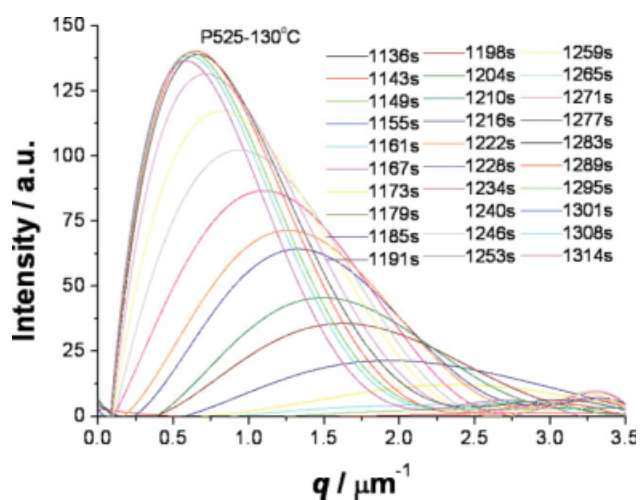


Figure 2 Changes in the TRLS profiles of blend P525 with curing at 130°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

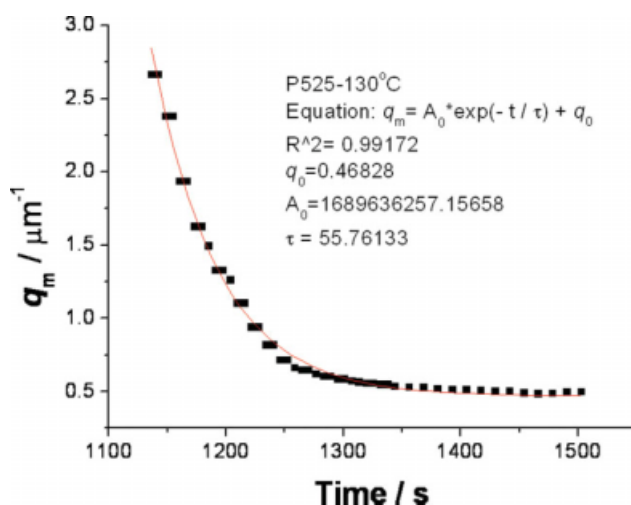


Figure 3 q_m as a function of time for blend P525 at 130°C. Symbols correspond to the experimental data, and lines correspond to the fitting with eq. (3). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Viscoelastic phase separation

For thermoplastic-modified thermoset blend P525 cured at 130°C, the change in q_m with time t is shown in Figure 3. Obviously, the curve in Figure 3 decreases exponentially. To describe the tendency of the change in q_m with time for this blend, a time-dependent version of q_m [$q_m(t)$] was also simulated according to a Maxwell-type viscoelastic relaxation equation [eq. (3)] as in our previous works.^{22–25} Note that the values of q_m were adopted from the beginning to the first lowest value for the simulation:

$$q_m(t) = q_0 + A_0 \exp(-t/\tau) \quad (3)$$

where τ is the relaxation time and A_0 is the magnifier, $q_m = q_0$ as $t = \infty$. It was found that the evolution of q_m corresponding to the morphology evolution fits eq. (3) very well.

The τ obtained by the single exponential decay of q_m cannot be the τ of the PEI segments. Tanaka²⁶ stated that the origin of the dynamic asymmetry might be the size difference in the component molecules of a mixture or the existence of another transition such as a glass transition. Because the cure temperatures are far below T_g of PEI ($\sim 215^\circ\text{C}$), the epoxy–anhydride n -mers act as a rapid dynamic phase (lower T_g component), whereas PEI is a slow dynamic phase (higher T_g component) and produces a cage effect. Thus, τ obtained by the q_m single-exponential decay should be the time for escape of the epoxy–anhydride n -mers from the so-called cage of PEI entanglement by their relaxation movements.

For blend P525, q_m decreases with time at different temperatures and is fitted with eq. (3), as shown in Figure 4 and reported in Table II.

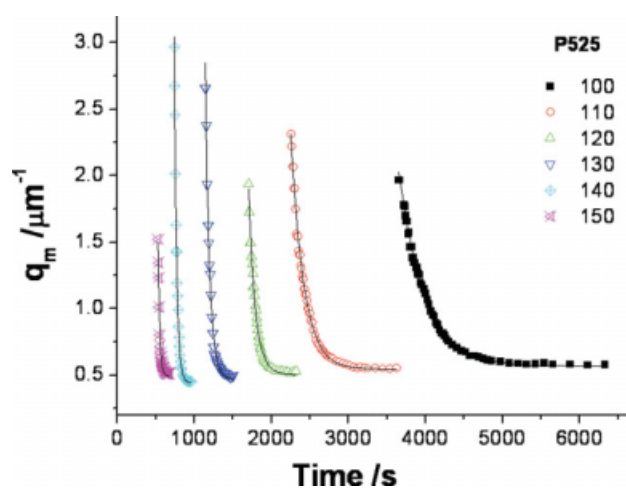


Figure 4 q_m versus time for blend P525 at different temperatures. Dots correspond to the experimental data, and lines correspond to the results simulated by eq. (3). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

As presented in Table II, the onset time of viscoelastic phase separation at different temperatures for blend P525 decreases with the cure temperature. τ obtained from fitting with eq. (3) decreases drastically with the increase in temperature and becomes progressively less sensitive to the cure temperature. This can be attributed to the acceleration of the curing reaction and the relaxation movement at higher temperatures. The higher the temperature is, the more rapidly the epoxy–anhydride n -mers escape from the cage of PEI and the more quickly the phase structure can be fixed.

To describe the variation of q_m for blends P725 and P425, the time-dependent q_m values determined by fitting with eq. (3) at different temperatures are shown in Figure 5(a,b). The resultant data are reported in Tables III and IV. Similar trends occur in blends P725 and P425; that is, the onset time of

TABLE II
Results from the Light Scattering Experiment for Blend P525

Cure temperature (°C)	100	110	120	130	140	150
t_0 (s)	3718	2251	1699	1136	736	528
t_{fix} (s)	6102	3627	2321	1503	958	674
$t_{\text{fix}} - t_0$ (s)	2384	1376	622	367	222	146
R^λ	0.997	0.995	0.993	0.992	0.994	0.986
q_0 (1/ μm)	0.57	0.54	0.50	0.47	0.44	0.49
Λ_m (μm)	11.0	11.6	12.6	13.4	14.3	12.8
τ (s)	335	166	87.7	55.8	30.3	20.7

Λ_m = periodic length; R^λ = correlation coefficient for fitting; t_0 = onset of phase separation; t_{fix} = time for fixing the phase structure; $t_{\text{fix}} - t_0$ = evolution time for the phase structure.

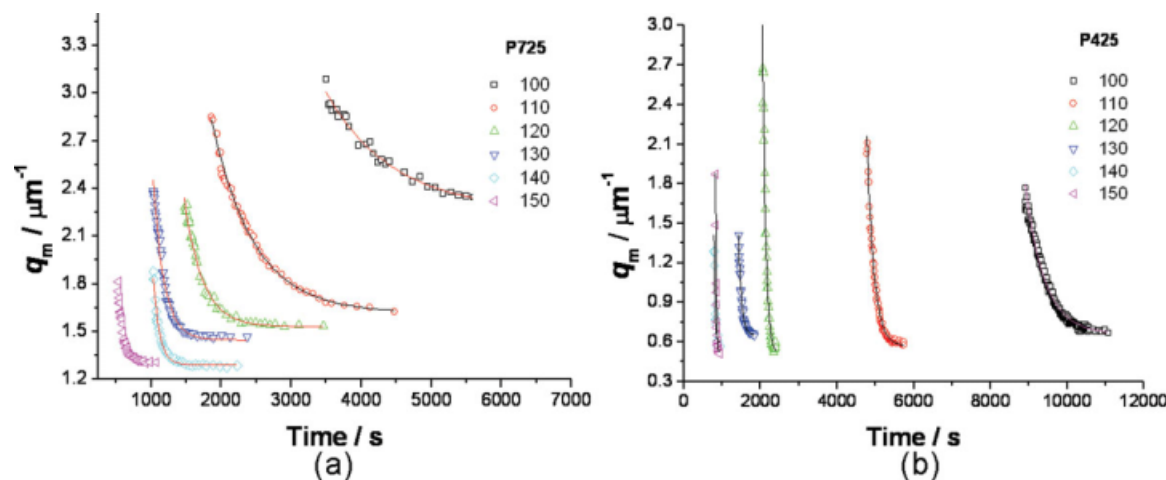


Figure 5 q_m versus time at different temperatures: (a) blend 725 and (b) blend 425. Dots correspond to the experimental data, and lines correspond to the results simulated by eq. (3). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

viscoelastic phase separation and τ in these two blends decrease drastically with the increase in temperature. Moreover, the onset time of viscoelastic phase separation and τ depend not only on the temperature of the curing reaction but also on the molecular weight of the thermoplastic modifier PEI.

Generally, thermoset and thermoplastic blends are homogeneous at the beginning of the curing reaction. In the curing process of thermoset resins, the increasing molecular weight of the thermoset component initiates the phase separation, generating various heterogeneous two-phase morphologies. Then, these morphologies, developed by the reaction-induced phase separation, would be fixed at a certain stage of curing by gelation and vitrification of the thermoset resins.

Lowering the molecular weight increases the entropic component of mixing and favors miscibility. The immiscibility window is attained at very high

conversions of the epoxy resin and causes an increase in the onset time of the viscoelastic phase separation during the curing reaction.¹³ As shown in Figure 6, the onset time of the viscoelastic phase separation is a function of the PEI molecular weight and the cure temperature (data from Tables II–IV). Phase separation occurs first in the blend with the largest PEI molecular weight, and the time of occurrence of the viscoelastic phase separation increases with a decrease in the PEI molecular weight and the cure temperature. Because these blends have the same initial amount of thermoplastic PEI (25 wt %), this means that lower molecular weights result in higher conversion for phase separation, as reported in the literature.¹¹ Then, an increase in the PEI molecular weight leads to a decrease in the onset time of viscoelastic phase separation. Provided that the conversion is not influenced by the PEI molecular weight when the composition of PEI is constant for

TABLE III
Results from the Light Scattering Experiment
for Blend P725

Cure temperature (°C)	100	110	120	130	140	150
t_0 (s)	3542	1863	1474	1030	734	536
t_{fix} (s)	6600	4478	2906	1894	1188	918
$t_{\text{fix}} - t_0$ (s)	3058	2615	1432	864	452	382
R^Λ	0.985	0.995	0.990	0.989	0.985	0.994
q_0 (1/ μm)	2.26	1.62	1.53	1.45	1.29	1.31
Λ_m (μm)	2.78	3.88	4.10	4.33	4.87	4.79
τ (s)	951	602	261	157	95.7	67.9

Λ_m = periodic length; R^Λ = correlation coefficient for fitting; t_0 = onset of phase separation; t_{fix} = time for fixing the phase structure; $t_{\text{fix}} - t_0$ = evolution time for the phase structure.

TABLE IV
Results from the Light Scattering Experiment
for Blend P425

Cure temperature (°C)	100	110	120	130	140	150
t_0 (s)	8,907	4,784	2,061	1,435	795	836
t_{fix} (s)	11,075	6,118	2,411	1,849	905	941
$t_{\text{fix}} - t_0$ (s)	2,168	1,334	350	414	110	105
R^Λ	0.984	0.995	0.983	0.994	0.973	0.994
q_0 (1/ μm)	0.67	0.57	0.67	0.65	0.57	0.52
Λ_m (μm)	9.37	11.0	9.37	9.66	11.0	12.1
τ (s)	490	178	78.9	74.8	31.6	17.4

Λ_m = periodic length; R^Λ = correlation coefficient for fitting; t_0 = onset of phase separation; t_{fix} = time for fixing the phase structure; $t_{\text{fix}} - t_0$ = evolution time for the phase structure.

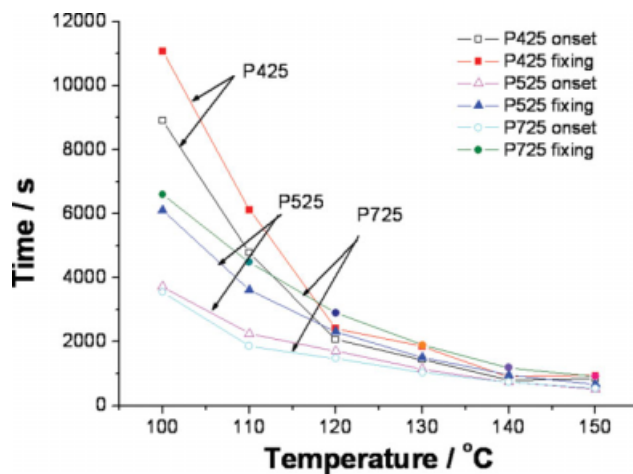


Figure 6 Temperature dependence of the onset time of viscoelastic phase separation and the fixing time of the phase structure for blends P425, P525, and P725 (data from Tables II–IV). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

the three blends, then an increase in the PEI molecular weight results in a decrease in the cloud-point conversion.

On the other hand, the fixing times for the three blends at the same cure temperature are very close at high temperatures such as 140 and 150°C. Because their chemical compositions are all kept constant at 25 wt %, the gelation time at the same temperature might be very close for the three blends. This result might be due to the high viscosity near gelation, which is the predominant factor at higher temperatures.

However, the fixing times of the phase structure at lower temperatures are different, and it is interesting that the fixing time of the viscoelastic phase separation for blend P725 is between those of blend P425 and blend P525 at lower temperatures. Although viscoelastic phase separation for blend P725 occurs earlier than for blend P525 because of the lower miscibility resulting from its high molecular weight, the phase structure for blend P725 fixes later at almost all temperatures investigated. Then, what is the key factor affecting the fixing time of the phase structure? Does this mean that the conversion at gelation has been changed by the effect of the molecular weight of PEI?

Phase separation is believed to be caused by the epoxy molecular weight climbing to a threshold value during the reaction, and gelation is similarly linked to the epoxy molecular weight; these two responses would be expected to have a similar temperature dependence if the mass transfer of the phase separation is fast in comparison with the rate of reaction. The miscibility of this PEI/epoxy blend is altered continuously because the phase diagram

moves upward for the upper critical solution temperature system. At the same temperature, the blend with higher molecular weight PEI has a deeper quench depth.^{11,13,19} Then, with the UCST-type phase boundary being elevated by an increase in the molecular weight of epoxy, the thermodynamic quench depth increases. It might be a reasonable explanation for the order of the fixing time of the phase structure of blends P725 and P525.

When the cure temperature is low enough, such as 100 or 110°C, the viscosity may again be the key factor affecting the evolution of the phase structure. In comparison with blends P525 and P725, lowering the PEI molecular weight in blend P425 results in lower viscosity and allows the phase structure to be fixed later.

Viscoelastic phase separation occurs after the curing reaction and fixes before gelation. As reported in our previous work,²⁵ the evolution of the phase structure in a PEI-modified epoxy system is caused by the movement of epoxy–anhydride *n*-mers. As the curing reaction proceeds, the epoxy–anhydride *n*-mers diffuse out of the PEI-rich phase and begin to coarsen. Then, the periodic distance of the cocontinuous microstructures increases, and the morphology shifts to a small, epoxy-rich, dispersed, inversed phase structure. These growing particles connect to one another to form irregular PEI-rich macrophase domains, eventually dispersing into the epoxy-rich matrix.

The periodic distance also depends on the temperature and PEI molecular weight (Fig. 7). Blend P725 has the smallest periodic distances. As the periodic distance is a function of the quench depth and an increase in the quench depth is expected to suppress structure coarsening,¹⁹ it is reasonable that blends with higher molecular weight PEI will yield a shorter periodic distance. However, the periodic distance in blend P425 is shorter than that in blend P525. This might be attributed to the very low molecular weight PEI molecules used in blend P425, which were almost completely disentangled. This is consistent with the SEM micrographs shown in Figure 1.

Williams–Landel–Ferry (WLF) function

As shown previously, q_m was a function of time t and fitted the Maxwell-type viscoelastic relaxation equation very well. τ was obtained at different temperatures for the three blends and varied with the temperature. The viscoelastic properties were assessed further with the temperature superposition principle.

The τ values (from Tables II–IV) versus temperature T for the three blends were fitted with the WLF equation:

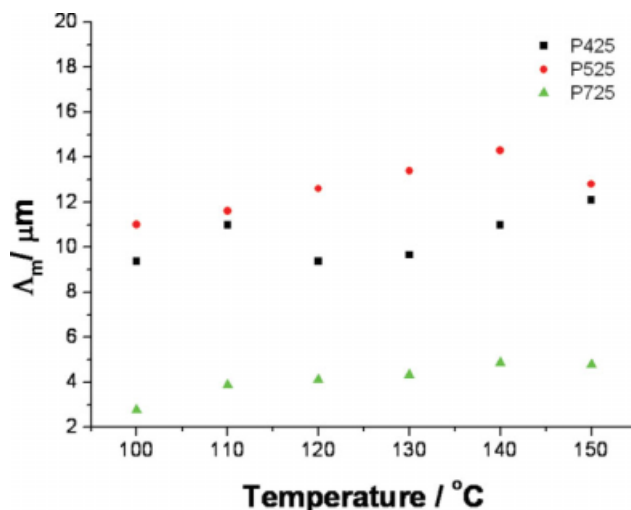


Figure 7 Periodic distance (Λ_m) of the phase structure (data from Tables II–IV) versus the cure temperature for three blends with PEIs of different molecular weights. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

$$\log \frac{\tau}{\tau_s} = \frac{-C_1(T - T_s)}{C_2 + (T - T_s)} \quad (4)$$

If we assume $C_1 = 8.86$ K and $C_2 = 101.6$ K, the WLF equation can be written as follows:

$$\tau = \tau_s \exp[-\ln 10 \times 8.86 \times (T - T_s)/(101.6 + (T - T_s))] \quad (5)$$

As shown in Figure 8, the simulation results give a good fit to the experimental data. This means that τ follows the time–temperature superposition principle and can be described by the WLF function. Then, it can be suggested that the coarsening process of epoxy droplets is mainly controlled by the viscoelastic flow. The values of T_s and τ_s (temperature and relaxation time at a reference condition) are 297.0 and 8.08E6, 306.8 and 1.06E6, and 329.4 and 2.25E5 for blends P725, P525, and P425, respectively. As the molecular weight of PEI in the blend decreases, the value of T_s increases, whereas τ_s decreases.

According to the WLF equation, when C_1 and C_2 are selected to be the empirical constants 8.86 and 101.6 K, T_s may be related to the flow temperature of the polymer chain, which should be 50°C higher than T_g of this polymer. The T_g value of epoxy monomers (including hardener MTHPA and accelerator BDMA) in the absence of PEI was measured to be 248.2 K.²² The values of $T_s - 50$ are 247.0, 256.8, and 279.4 K for blends P725, P525, and P425, respectively. This implies that the value of $T_s - 50$ reflects T_g of epoxy–anhydride n -mers that conduct the viscoelastic relaxation movement. Then, T_s might also be related to the order of the onset time of the

viscoelastic phase separation. The higher T_g is, the higher the average extent of polymerization is and the later the viscoelastic phase separation occurs. At the same temperature, when the extent of polymerization reaches the critical point of viscoelastic phase separation for blend P725, blends P525 and P425 remain homogeneous. From this point, the order of the onset time for viscoelastic phase separation is $P725 < P525 < P425$. Obviously, this is very consistent with the results obtained experimentally.

Thermodynamic analysis

Thermodynamic factors have been taken into account in the interpretation of the miscibility and the molecular weight effect.^{7,11,13} In terms of the Flory–Huggins theory,²⁷ the mixing free energy (F) of the blend can be determined as follows:

$$\frac{F}{kT} = \sum_1^r \frac{\phi_i}{n_i} \ln \phi_i + \sum_{i < j}^r \sum_{i < j}^r \chi_{ij} \phi_i \phi_j \quad (6)$$

where n_i and ϕ_i are the weight-averaged polymerization degree and volume fraction of component i , respectively, and χ_{ij} is the Flory–Huggins interaction parameter. The symbols i and j represent species of different molecular masses corresponding to components 1 and 2. The first term on the right-hand side represents the combinatorial contribution to the free energy (entropic contribution), whereas the second term represents the excess contribution to the free energy. The main driving force for phase separation is the decrease in the absolute value of the entropic contribution to the free energy of mixing. Other factors can also contribute to the demixing process, such as a change in the interaction parameter due to

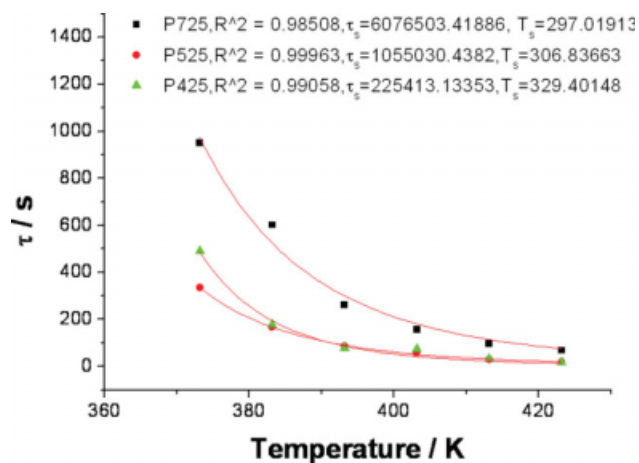


Figure 8 Plot of τ versus the temperature for three blends with PEIs of different molecular weights. Symbols correspond to the experimental data, and solid lines correspond to the fitting with eq. (5). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

changes in the chemical structure produced by polymerization.

Because the statistical approaches to the average molecular weight and distributions of molecular sizes of the thermoset monomers (including hardeners) are kept unchanged during chainwise polymerization at a low conversion before gelation, thermoset monomers can be simplified as a component or a solvent ($n_s = 1$) in the early stage of viscoelastic phase separation with a volume fraction labeled ϕ_s (i.e., the volume fraction of the solvent).

For the chainwise polymerization reaction, the systems are quite complicated as in a pseudoternary blend (PEI/growing thermoset/monomers). At a low conversion (before gelation), the molecular weight of the growing thermoset epoxy–anhydride n -mers is distributed with a Poisson distribution^{28,29} and increases with conversion.²⁹ The additional degree of freedom due to the molecular weight distribution results in the destabilization of the polymer mixture.³⁰ It has been found that the monodisperse assumption gives a reasonable approximation when macroscopic separation is considered, although the effect of polydispersity must be taken into account to realize a more exact analysis.¹⁴ Then, the growing thermoset epoxy–anhydride n -mers could be simplified as polymeric components with an average polymerization degree labeled n_{gt} (i.e., the weight-averaged polymerization degree of the growing thermoset) and a volume fraction labeled ϕ_{gt} (i.e., the volume fraction of the growing thermoset).

Following Tompa,³¹ we assumed that there is no interaction between the epoxy monomer and the growing thermoset epoxy–anhydride n -mers and that the interaction between a segment of a thermoplastic [the molecular weight of the thermoplastic (n_p) and the volume fraction of the thermoplastic (ϕ_p)] and a solvent molecule epoxy monomer is the same as that between segments of the two polymers. The spinodal curve is given by

$$(1 - 2\chi n_p \phi_p)[1 - 2\chi(\phi_s + n_{gt}\phi_{gt})] = 1 \quad (7)$$

The critical point, at which the third derivative with respect to the composition is equal to zero, is determined from

$$n_{gt}(1 - \phi_p)(1 - 2\chi n_p \phi_p)^3 + (n_{gt} + 1)n_p \phi_p (1 - 2\chi n_p \phi_p)^2 - n_p^2 \phi_p = 0 \quad (8)$$

The critical values of the Flory–Huggins interaction parameter (χ_c), which mark the threshold at which immiscibility sets in, are obtained as follows:

$$\chi_c = \frac{1}{2}(n_{gt}^{-1/2} + n_p^{-1/2})^2 \quad (9)$$

Provided that χ is only a function of temperature, immiscibility is caused by the entropy reduction due to the molecular weight increase of the growing thermoset (n_{gt}); thus, χ_c equals χ_0 (where χ_0 is the initial Flory–Huggins interaction parameter). For a specific value of n_p , the following equation can be obtained:

$$n_{gtc} = \frac{n_p}{[(2n_p\chi_0)^{1/2} - 1]^2} \quad (10)$$

or

$$n_{gtc} = \frac{1}{[(2\chi_0)^{1/2} - \frac{1}{n_p^{1/2}}]^2} \quad (11)$$

That is, with an increase in n_p , n_{gtc} (the critical value of n_{gtc}) drops, whereas χ_0 , which is a function of temperature, decreases with the cure temperature in a UCST system and thus causes earlier viscoelastic phase separation.

In these blends of PEI and epoxy resin, for a specific blend with the same PEI molecular weight (or n_p), increasing the cure temperature results in a decrease in χ ; then, it is very clear from eq. (10) that the critical value of n_{gtc} decreases as well. This indicates that the onset time for viscoelastic phase separation will decrease with the cure temperature increasing. As for blends with different PEI molecular weights, the values of n_p are different. When the blends cure at the same cure temperature, χ is considered to be constant. Then, from eq. (11), it can be determined that increasing n_p decreases the critical value of n_{gtc} . This means that the onset time for viscoelastic phase separation decreases with increasing PEI molecular weight. These predictable theoretical results have been observed experimentally with good agreement.

CONCLUSIONS

The morphologies of epoxy–anhydride matrices modified with thermoplastic PEIs (25 wt %) all consist of large and irregular PEI-rich domains dispersed in an epoxy-rich continuous phase that is very close to the cocontinuous-type phase structure.

The processes of phase separation at different temperatures for three blends with PEIs of different molecular weights were monitored by TRLS. It has been found that the phase separation of PEI/epoxy blends takes place via spinodal decomposition, which is initiated by the increasing molecular weight of the thermoset epoxy resin and stopped by the very high viscosity of the blend before gelation. The lower the molecular weight is, the higher the conversion is for phase separation. Then, an increase in the

PEI molecular weight leads to a decrease in the onset time of phase separation and cloud-point conversion. Blends with higher molecular weight PEI yield a shorter periodic distance, whereas the periodic distance in blend P425 is shorter than that in blend P525. This may be attributed to the very low molecular weight PEI molecules, which were almost completely disentangled.

The evolution of q_m corresponding to the morphology evolution follows a Maxwell-type viscoelastic relaxation equation. The obtained τ has been fitted with the time-temperature superposition principle, and it has been found that the temperature-dependent τ can be described by the WLF function. It is suggested that the coarsening process of epoxy droplets is mainly controlled by the viscoelastic flow. On the other hand, the obtained T_s may be related to the flow temperature of the polymer chain, which conducts the viscoelastic relaxation movement. Thus, it might also be related to the order of the onset time of viscoelastic phase separation.

The fact that the onset time for viscoelastic phase separation is affected by the PEI molecular weight and cure temperature has been analyzed according to the Flory-Huggins theory. The results are in good agreement with those obtained experimentally.

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