Phase Separation of Unsaturated Polyester Resin Blended with Poly(vinyl acetate)

Y. N. HSIEH, T. L. YU

Department of Chemical Engineering, Yuan-Ze University, Nei-Li, Taoyuan, 32026 Taiwan

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ABSTRACT: The behavior of phase separation during the curing reaction of unsaturated polyester (UPE) resin in the presence of low profile additive, that is, poly(vinyl acetate) (PVAc), was studied by low-angle laser light scattering (LALS) and scanning electron microscopy (SEM). The experimental results revealed that the PVAc-rich phase was regularly dispersed in the cured styrene–UPE matrix for styrene–UPE resin blended with 5 wt % of PVAc. As the PVAc content was increased higher than 10 wt %, a cocontinuous PVAc and cured styrene–UPE phase was observed for the cured systems. The LALS observations were carried out *in situ* at a curing temperature of 100°C; thus, the effect of the rate of exothermic heat released from curing reaction on the morphology of curing system was investigated and reported in this work. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 2413–2428, 1999

Key words: unsaturated polyester; poly(vinyl acetate); low-angle light scattering, scanning electron microscopy, differential scanning calorimetry

INTRODUCTION

Low-profile additives (LPAs) are used in unsaturated polyester (UPE) resin formulations to improve the surface of molding compound, compensating for resin shrinkage. Poly(vinyl acetate) (PVAc) is widely used as an LPA, particularly in sheet molding compound (SMC) and bulk molding compound (BMC) formulations. Phase separation occurs at the very beginning of the reaction.^{1–3} At low concentrations of PVAc, the final morphologies are composed of discrete particles of the LPA dispersed in the cured UPE matrix; at concentrations higher than a critical value, a cocontinuous structure is obtained.^{4,5} These cocontinuous regions promote cavitation in response to tensile stresses arising from internal thermal and cure contractions in the presence of mechanical constraints.⁶ Although there are many explanations for the observed phenomena,^{1-5,7} it is generally agreed that a major factor for the low profile behavior is due to the formation of a two-phase structure between LPA and UPE resins.

Several researchers^{1,4–16} have reported the effects of LPAs on the curing kinetics and morphology of styrene–UPE–LPA blend. Kubota⁸ found a very small effect of a LPA (cellulose acetate butyrate) on the curing kinetics. Han and coworkers⁹⁻¹¹ reported lower reaction rates and the final degree of curing in using a LPA. A decrease in the final conversion was also reported by Lee and coworkers.¹² Williams and coworkers³ reported that when the ratio of styrene to UPE unsaturation was kept constant, PVAc did not have any effect on cure kinetics. They also reported that the addition of PVAc was only effective in promoting an excellent copy of the mold surface at concentration higher than the critical one leading to cocontinuous structures. The use of PVAc at concentrations beyond the critical value did not produce further improvements in the sur-

Correspondence to: T. L. Yu.

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face quality. The lower compatibility of LPA with UPE caused a microgel formation at a lower degree of conversion and, thus, a higher gel conversion and a lower final conversion. Suspene and coworkers² and Lee and coworkers¹ separately reported that adding the LPA into a styrene-UPE prepolymer mixture might cause phase separation accompanied by a fractionation effect, which excludes a highmolecular-weight polymer from the styrene and LPA-rich phase. Bucknall and coworkers^{4,5} observed the morphology of styrene-UPE-PVAc ternary changes during curing by scanning electron microscopy (SEM). They reported that resins containing 8 wt % PVAc form composites spherical particles occupying 35 vol % of total material. It was concluded that these particles consist of resin subinclusions embedded in the continuous matrix of polyester resin. Increasing the PVAc content to 16 wt % results in a phase inversion: PVAc forms the matrix, and the resin is present as spherical particles. Han and coworkers⁹⁻¹¹ studied the structureproperty relationships of styrene-UPE matrices containing various low profile additives, such as PVAc, polyurethane, poly(methyl methacrylate), polystyrene, and polycaprolactone. They reported that the microvoids were usually observed in the polyester phase and/or the dispersed phase of the low-profile resin matrices. Microvoids were responsible for the degradation of physical properties of resin matrices. Huang and Su,^{13,14} using SEM, observed the formation of microvoids and microcracks of styrene-UPE-LPA systems at the later stage of curing. Kinkelaar and coworkers¹⁵ used a dilatometer to study the concentration effect of low profile additive and cure temperature on shrinkage control and its correlation with polymer morphology.

In the present work, we reported phase separation and morphology changes during curing for styrene–UPE–PVAc system by low-angle laser light scattering (LALS) and scanning electron microscopy (SEM). The LALS was carried out *in situ* at the curing temperature, that is, 100°C, while the SEM observations were performed at room temperature after evaporation of the residue styrene monomer from the partially cured resins. Hence, the results of LALS observations were more close to the real curing system than those of SEM observations.

EXPERIMENTAL

Materials

UPE

UPE was prepared in nitrogen atmosphere by the conventional condensation method from isoph-

 Table I
 Compositions of Samples

	Sample 1	Sample 2	Sample 3	Sample 4
Styrene (g)	33.12	31.61	29.86	28.26
UPE (g)	66.88	63.23	59.71	56.53
PVAc (g)		5.16	10.43	15.21
Initiator	1.00	1.00	0.99	1.00

thalic acid (IPA), fumaric acid (FA), and 1,2-propanediol (PG). The reaction temperature was increased by stepwise control as follows: 140°C/2h, 160°C/2h, 180°C/2h, 200°C/2h, and 220°C/2h. The polyester product was then cooled down to 100°C and mixed with styrene in a weight ratio 67/33 of polyester to styrene containing 0.1 wt % of hydroquinone inhibitor. The resin was then cooled to room temperature immediately. The mole ratio in the final composition of the solid polyester determined from nuclear magnetic resonance (NMR) was IPA/FA/PG = 1.0/1.67/3.23, with a mole ratio of 1.21 for OH/COOH and an acid value of 30.0 mg KOH/g of solid resin. The number-average molecular weight (\overline{M}_n) of the polyester determined by gel permeation chromatography (GPC) at 25°C was found to be 1800, with a polydispersity $M_{\mu}/$ $M_n = 4.3$. Tetrahydrofuran (THF) was used as the mobile phase, and narrow MWD polystyrene standards (Aldrich Chemical Co.) were used in the linear calibration method.

Initiator

The peroxide initiator was tert-butyl peroxybenzoate (Akzo Chemie Co.) with a purity of 98% and an active oxygen content of 8.07%.

Styrene

Styrene monomer (Aldrich Chemical Co.) with a purity of 99% was purified by very careful distillation several times before mixing with UPE.

PVAc

Poly(vinyl acetate) (Aldrich Chemical Co.) with $\bar{M}_n = 8.6 \times 10^4$ and $\bar{M}_w/\bar{M}_n = 2.45$ was used without further purification.

Sample Preparation

The styrene–UPE (33/67 in weight ratio) system was mixed with 5, 10, and 15 wt % of PVAc and 1 phr of tert-butyl peroxybenzoate initiator. Table I

shows the final formulations of these sample solutions.

Instrumentation

Differential Scanning Calorimetry

A Du Pont 910 DSC was applied to study the exotherms of curing. Indium was used previously as a standard calibration. Hermetic pans were used to minimize losses of volatile materials (such as the styrene monomer) during heating of the sample in the DSC cell. The size of sample was in the range from 6-10 mg. A small sample size was required in order to achieve isothermal operation during curing.

Low-Angle Laser Light Scattering

The light scattering apparatus was similar to that of Inoue et al.¹⁶ The ternary mixture (styrene-UPE-PVAc) solution was cast onto a cover glass and covered with another glass to avoid evaporation of styrene monomer. The film that was covered with glass on both sides was inserted in a heating stage kept at a temperature of 100°C. A radiation of wavelength 632.8 nm from a He-Ne laser was applied vertically to the film. The intensity of scattered light from the film was measured under an optical alignment with parallel polarization. The angular distribution of scattered light intensity was detected by a one-dimensional photometer with a 35-element photodiode array. The sampling time was ~ 15 msec. The scattered intensity profiles were the average of 16 scans and were recorded at appropriate intervals during isothermal curing, and were stored in a personal computer for further analysis. A light scattering pattern was also observed by using a photographic technique with a CCD vision camera (XC-75, Sony Co. Ltd) with 16-mm lens and 768 (H) imes 494 (V) picture elements. A Matrox Meteor PCI interface and Inspector imaging software were used for acquiring image data and data storage in a personal computer for imaging processing.

Scanning Electron Microscopy

Hitachi S-570 SEM with accelerated 20 kV was used to observe the fractured surface of each sample at $5000 \times$ magnification. In the morphological study, the reaction of UPE resin blended with LPA cured in DSC cell at a temperature of 100°C was stopped at a preset time by rapidly chilling the sample pan in liquid nitrogen for 5 min. The sample was then broken into several pieces and vacuumed at room temperature for 1 h to remove the unreacted residual styrene monomer. The dry sample was then gold-coated for morphological observations.

Refractometer. A refractometer (Atago No 302, Nippon Optical Works Co., Tokyo) was used to measure the refractive indexes of partially cured resins at room temperature.

RESULTS AND DISCUSSION

DSC Study

For studying the isothermal curing kinetics of thermosetting resins by DSC,¹⁷ one assumes that the amount of heat generated due to the curing reaction is directly proportional to the degree of curing α (or the extent of reaction) of the sample at that time; and then one relates the rate of curing, $d\alpha/dt$, to the rate of heat generated, dH/dt, by

$$\frac{d\alpha}{dt} = \frac{1}{H_{\text{tot}}} \frac{dH}{dt} \tag{1}$$

Integrating eq. (1) with time, one obtains the relative degree of cure α as follows:

$$\alpha(t) = \frac{1}{H_{\text{tot}}} \int_{0}^{t} \left[\frac{dH}{dt} \right]_{T} dt \qquad (2)$$

where the subscript T indicates isothermal curing reaction. In eqs. (1) and (2), the total heat of curing reaction (H_{tot}) is given by

$$H_{\rm tot} = H_t + H_r \tag{3}$$

where H_t is the heat generated during the isothermal runs at 100°C, and H_r is the residual heat that is released when the sample is heated to 220°C at a heating rate of 5°C/min after the completion of an isothermal curing reaction at 100°C.

The DSC isothermal curing profiles (α versus curing time) at 100°C for styrene/UPE system blended with 0.0, 5.0, 10.0, and 15.0 wt % of PVAc are shown in Figure 1. As indicated in Figure 1, the curing reaction rate of the resin system decreases with increasing PVAc content. The reason for the decrease in curing reaction rate with PVAc



Figure 1 Isothermal DSC curing profiles at 100°C for the styrene–UPE system blended with various contents of PVAc.

content was due to the decrease of styrene and UPE concentration.

LALS Study

The variation of the morphology for the curing reaction of styrene-UPE system blended with various content of PVAc was observed by LALS. Light scattering could be detected for these ternary blended systems with regularly phase-separated structure. A typical light scattering ring pattern obtained at room temperature for styrene-UPE blended with 5 wt % of PVAc after completion of isothermal curing at 100°C is shown in Figure 2. Similar light scattering ring patterns were also observed for styrene-UPE systems blended with 10 and 15 wt % of PVAc. However, no ring pattern was observed for pure styrene-UPE system. The ring pattern implies the development of regularly phase-separated structure, together with the characteristic change in scattering profile are the hallmarks of spinodal decomposition.



Figure 2 Light scattering ring patterns after completion of isothermal curing reaction at 100°C for the styrene–UPE systems blended with 5.0 wt % PVAc.



Figure 3 LALS profiles at various curing times for the styrene–UPE system blended with 5.0 wt % PVAc.

The LALS profiles at various curing times for styrene-UPE systems blended with 5.0, 10.0, and 15.0 wt % of PVAc isothermally cured at 100°C are shown in Figures 3, 4, and 5, respectively. For the styrene-UPE system without the presence of PVAc, no appreciable light scattering was detected during the whole period of curing. However, the scattered light was observed for the styrene-UPE system blended with PVAc. As shown in Figure 3, the LALS profile for the styrene-UPE-5 wt % PVAc system was a single-phase system in the early stage of curing, and no light scattering was detected. However, at a curing time longer than ~ 12 min, a broad light scattering pattern was observed at scattering angle around $\theta = 10-18^\circ$. At the beginning of phase separation, the scattering intensity profile was

broader. In the progress of phase separation, the structure grew with self similarity (that is, the concentration of PVAc increased in the PVAc-rich phase, and the concentration of cured UPE increased in the UPE-rich phase as the degree of curing increased), the scattering peak intensity increased, and the peak became sharper and sharper as the curing reaction proceeded. The scattering peak intensity reached a maximum at a curing time of 54 min. After a curing time of 54 min, the peak intensity decreased slowly as the curing reaction proceeded. The reason for the decrease in scattering intensity will be explained later. The scattering angle θ_m corresponding to the scattering intensity peak maximum is an indicator of the periodic distance of the phase-separated structure. As shown in Figure 3, θ_m de-



Figure 4 LALS profiles at various curing times for the styrene–UPE system blended with 10.0 wt % PVAc.

creased with curing time and reached the lowest value at a curing time around 48 min, after which θ_m did not change as the curing reaction proceeded.

Similar LALS observations were also obtained from systems of styrene-UPE-10 wt % PVAc (Fig. 4) and styrene–UPE–15 wt % PVAc (Fig. 5). These peak intensities increased with curing time and reached a maximum at a curing time of 57 and 60 min for styrene-UPE-10 wt % PVAc and styrene–UPE–15 wt % PVAc, respectively, then decreased slowly with curing time, and the scattering pattern became broader. After completion of curing reaction, a broad light scattering profile without a sharp peak was observed. A two-phaseseparated system with one discrete phase regularly dispersed in another phase would cause a sharp light-scattering ring pattern. The formation of two irregularly dispersed phases or cocontinuous two phases would result in an increase in

the broadness of light scattering peak. The scattering angle θ_m decreased with curing time and reached a minimum value at a curing time around 51 min for the styrene–UPE–10 wt % system. At curing time between 51 and 66 min, the θ_m was fixed and did not change with degree of curing. As the time of curing reaction proceeded longer than 66 min, the scattering intensity profile became broader and after a curing time of 69 min, no clear θ_m was observed. The scattering intensity profiles were much broader for the styrene-UPE-15 wt % PVAc system than those of styrene–UPE systems blended with 5 and 10 wt %PVAc. Though the θ_m for styrene–UPE–15 wt % PVAc were not so clear as those of styrene-UPE-10 wt % PVAc and styrene-UPE-5 wt % PVAc systems, it was found to decrease with curing time and reached a minimum value at a curing time of 48 min. At a curing time between 48 and 63 min, θ_m was fixed and did not change with



Figure 5 LALS profiles at various curing times for the styrene–UPE system blended with 15.0 wt % PVAc.

degree of curing. After a curing time of 66 min, no clear θ_m was observed.

The periodic distance, Λ_m , in the phase-separated structure as a Bragg spacing can be obtained from the maximum peak intensity angle θ_m of the scattering profiles in Figures 3–5¹⁶:

$$\Lambda_m = \lambda (2 \sin \theta_m)^{-1} \tag{4}$$

where λ is the wavelength of light in the medium. The variations of Λ_m and the degree of conversion α versus curing time for styrene–UPE systems blended with 5, 10, and 15 wt % of PVAc are plotted in Figures 6, 7, and 8, respectively. In Figures 7 and 8, at the later stage of curing, since the scattering profiles were broad and no clear Λ_m were observed, dashed lines were shown in the figures to indicate the broadness of the distribution of Λ .

The integrated scattered intensity, that is, the invariant Q is defined by¹⁶

$$Q = \int_0^\infty I(q) q^2 \, dq \tag{5}$$

where q is the scattering vector, $q = 4\pi/\lambda \sin(\theta/2)$, and I(q) is the intensity of the scattered light at q. The invariant Q from an optically isotropic system with concentration fluctuation is ascribed to the mean square concentration fluctuation,¹⁸ it is an indicator for the degree of phase separation. The variation of the Q value versus curing time for styrene–UPE systems blended with 5, 10, and



Figure 6 Variation of Q, Λ_m , and α with curing time for the styrene–UPE system blended with 5.0 wt % PVAc.

15 wt % of PVAc are also plotted in Figures 6-8, respectively.

From the plot, one can determine the onset time of phase separation at which Q starts to increase. In the present study, LALS measurements were carried out at a time interval of 3 min (i.e., LALS intensity was measured at curing times of 0, 3, 6, 9... min). The Q and Λ_m data shown in Figures 6-8 obtained at every curing time interval are connected by a full line for easy investigation. The curing times corresponding to the first nonzero Q value for styrene–UPE blended with 5, 10, and 15 wt % of PVAc are 12, 18 and 21 min, respectively. As shown in Figures 6-8, Λ_m increases with curing time and eventually levels off, suggesting that further growth of the geometric structure is suppressed by gelation. The levelling off point is the time of geometry fixation. From the results of Figures 6-8, it is obvious that even after the geometry fixation, Qstill increased with curing time suggesting phase separation proceeds further, and a further variation in the composition difference between PVAcrich and cured styrene-UPE-rich regions. The experimental results showed that after the invariant Q attained a maximum, it started to decrease slowly, the scattering intensity profile became broader, and the distribution of Λ values became broader as time proceeded, even after the completion of curing reaction.

The reason for the decrease of Q value after completion of curing can be explained by the variations of the phase volume and refractive index. The invariant Q is proportional to the meansquare concentration fluctuation $\langle \eta^2 \rangle$ given by^{16,18}

$$Q \propto \langle \eta^2 \rangle = \phi_1 \phi_2 (\gamma_1 - \gamma_2)^2 \tag{6}$$

for the two-phase system with sharp boundary. In eq. (6), ϕ_i and γ_i are the volume fraction and the polarizability of phase *i*, respectively. Judging from the Λ_m being fixed as the degree of conversion levels off, the two-phase structure is assumed to be fixed already.

Since the curing reaction is an exothermic free radical polymerization, during curing, the exothermic reaction results a higher system temperature than that of heating stage holder. Owing to higher temperature, some of the lower molecular



Figure 7 Variation of Q, Λ_m , and α with curing time for the styrene–UPE system blended with 10.0 wt % PVAc.

weight PVAc might be dissolved in the partially cured styrene–UPE-rich phase, and some of styrene-UPE with lower degree of conversion might also be dissolved in the PVAc-rich phase. At the later stage of curing reaction, the heat released from curing system decreases due to the decrease of curing reaction rate; thus, the system cooled slowly to the temperature of heating stage holder. At a lower temperature, the low-MW PVAc phase containing a small amount of lowly cured styrene-UPE resins might be separated from the highly cured styrene-UPE-rich phase and the lowly cured styrene–UPE phase containing a small amount of low-MW PVAc might also be separated from PVAc-rich phase. It is obvious that the lowly cured styrene-UPE-low MW PVAc phase had an intermediate refractive index, which lay between those of highly cured styrene-UPE-rich phase and high-MW PVAc-rich phase.

We measured the refractive index of the pure styrene–UPE system with various degrees of conversion at room temperature. The refractive indexes for the partially cured styrene–UPE resins and the pure PVAc are summarized in Table II. These data suggested that the refractive index of styrene–UPE system varied with the degree of curing and closed to that of PVAc at the final stage of curing. The process of phase separation and variation of refractive index of each phase versus curing time, together with the variations of refractive indexes of pure PVAc and pure styrene-UPE system during curing, are plotted in Figure 9. At the beginning of the curing reaction, one homogeneous phase with a single refractive index was observed. After a certain lag of curing time, phase separation started with two phases, that is, the cured styrene-UPE-rich phase and the PVAc-rich phase, of two different refractive indexes appeared in the curing system. The refractive indexes of these two phases lay between those of pure styrene-UPE curing system and pure PVAc. As the curing reaction proceeded, owing to the decrease of refractive index of styrene-UPE with increasing degree of curing, both the refractive indexes of cured styrene-UPE-rich and PVAc-rich phases varied and approached to that of pure PVAc. Apparently, the increase in Q with curing time was due to the increase in the product of phase volume $\phi_1\phi_2$. Near the end of curing reaction, the system was cooled due to the decrease of exothermic heat released from free radical polymerization, two more phases, that is, a



Figure 8 Variation of Q, Λ_m , and α with curing time for the styrene–UPE system blended with 15 wt % of PVAc.

lower cured styrene–UPE-rich phase, which contained a small amount of the low-MW PVAc (designated by the dashed line in Fig. 9) and the low-MW PVAc-rich phase, which contained a small amount of lowly cured styrene–UPE (designated by a full line in Fig. 9), were separated from the PVAc-rich phase (designated by a dashed line in Fig. 9) and a highly cured styrene–UPE-rich phase (designated by a full line in Fig. 9), respectively. It is obvious that the refractive indexes of these two new phases, that is, a lowly cured styrene–UPE-rich with a small amount of low-MW PVAc and low-MW PVAc-rich with small amount

Table II	Refractive Indexes at Room			
Temperature of Styrene–UPE at Various				
Degrees of	of Conversion			

Degree of Conversion (%)	Refractive Index	
0.0	1.644	
12.1	1.533	
15.8	1.516	
18.6	1.467	
33.9	1.384	
34.8	1.380	
48.0	1.376	
53.4	1.375	
63.8	1.373	
66.9	1.372	
74.5	1.371	
PVAc	1.356	



Figure 9 Variation of the refractive index and phase separation of the styrene–UPE–PVAc system versus curing time. The variations of refractive indexes of the pure styrene–UPE curing system and pure PVAc are also shown for comparison.

of low cured styrene–UPE phases, were between those of highly cured styrene–UPE-rich (which contained less PVAc) and high MW PVAc-rich (which contained less styrene–UPE) phases. Thus, the Q value decreased during the system cooled, and the Λ value became broader.

SEM Study

The morphology of styrene–UPE systems with various contents of PVAc during curing was observed by SEM. The SEM micrographs of the fracture surfaces of styrene–UPE systems blended with 5, 10, and 15 wt % of PVAc after evaporating the residual styrene monomer are shown in Figures 10–12, respectively.

Figure 10 shows the micrography of styrene-UPE in the presence of 5 wt % of PVAc at various stages of curing. The SEM micrography showed that at a curing time of 15 min, a heterogeneously fractured surface appeared due to the phase separation of PVAc with the partially cured resin. Fig. 10(a) shows that the surfaces of small UPE globules were coated with PVAc-rich phase (bright region). Both the resin matrix (dark region) and the PVAc phases were continuous [Fig. 10(a)]. The smooth surface of the globule was first identified as LPA by Pattison et al.¹⁹ At a curing time of 50 min, the curing system was at vitrification, and the SEM micrography showed that the PVAc particles were separately dispersed in the cured styrene–UPE matrix [Fig. 10(b)]. Figure 10(c) shows the micrography of the styrene-UPE-5 wt % PVAc system at a curing time of 70 min. Owing to the similar degree of conversion, the micrography of Figure 10(c) was similar to that of Figure 10(b). However, LALS data revealed that the scattering intensity profile was broader, and the Q value was lower for the curing system at a curing time of 70 min than that at a curing time of 50 min. The SEM observations were carried out at room temperature after evaporating the residue styrene monomer from the partially cured resins, while the LALS observations were performed in real time at 100°C; thus, the effect of rate of heat released from the free radical polymerization on the morphology of cured resin was demonstrated in the LALS study.

Figure 10 Micrographies of styrene–UPE–5 wt % PVAc at various curing times (\times 5000). Curing time: (a) 15, (b) 50, and (c) 70 min.













Figure 11 Micrographies of styrene–UPE–10 wt % PVAc at various curing times (×5000). Curing time: 72 min.

A similar morphology of the styrene–UPE system blended with 10 wt % of PVAc, as that of the styrene–UPE system blended with 5 wt % of PVAc, was obtained by SEM. The morphology of the styrene–UPE system blended with 10 wt % of PVAc at a curing time of 72 min was shown in Figure 11. Owing to the higher content of PVAc, Figure 11 shows that PVAc particles more or less overlapped with each other in the styrene–UPE matrix. Thus, the LALS intensity profiles were broad after curing for 69 min (Fig. 4).

Figure 12 shows the SEM micrography for the styrene–UPE–15 wt % PVAC system. The SEM micrography for the system at a curing time of 40 min [Fig. 12(a)] shows lots of small cured styrene–UPE globule particles with a PVAc thin film coated on the particle surface. Both the PVAc-rich and styrene–UPE-rich phases were continuous. The micrography at a curing time of 50 min [Fig. 12(b)] showed that more cured styrene–UPE globule particles with their surface coated with PVAc film were dispersed in the PVAc-rich phase. A similar phase inversion phenomenon was also re-

ported by Bucknall et al.⁴ At a curing time of 72 min, the degree of conversion of styrene-UPE was higher than that at a curing time of 50 min. The PVAc-rich phase had a lower content of cured styrene–UPE at a curing time of 72 min than that at a curing time of 50 min. The SEM micrography [Fig. 12(c)] showed that both the PVAC-rich and the styrene–UPE-rich phase were continuous, and the cured styrene-UPE globule particles sizes were larger for the system at a curing time of 72 min than that at a curing time of 50 min. For the two-phase-separated system with a regular repeat distance, the LALS result would show a sharp ring pattern with a maximum peak intensity profile. The system with irregularly dispersed or cocontinuous phases would cause a broad LALS scattering intensity profile. The results of LALS showed that there was a broad peak with a peak maximum θ_m in the scattering intensity profiles at curing times around 48-57 min. However, the LALS result showed that the scattering intensity profile at a curing time of 72 min was broad, and no scattering peak maximum was observed. Thus, the results of SEM and LALS observation were consistent.

Discussion

Based on the above observations, we developed the phase separation mechanism at a curing temperature of 100°C for styrene–UPE in the presence of various contents of PVAc. The ternary mixtures are single-phase systems at the very early stage of curing. The curing reaction caused an increase in the molecular weight of UPE and a decrease in the concentration of styrene monomer, which induced phase separation, and the system was thrust into a two-phase region during curing. The phase separation process during curing for styrene-UPE-5 wt % PVAc system is shown in Figure 13. Figure 13(a) shows that the ternary system is a homogeneous phase at the beginning of curing. Demixing took place at a curing ~ 12 min (as shown by LALS profiles in

Figure 12 Micrographies of styrene–UPE–15 wt % PVAc at various curing times (\times 5000). Curing time: (a) 40, (b) 50, and (c) 72 min.

Figure 13 Phase separation mechanism of styrene–UPE–5 wt % PVAc: (a) Before curing, a homogeneous system; (b) early stage of curing, a bicontinuous phase separation taking place; (c) formation of a fragmented structure; (d) formation of a spherical structure; (e) end of curing, in which the system cooled down to 100°C, with further phase separation of the lowly cured UPE phase (dark dots around the bright region) and low MW PVAc phase (gray region).

(a)



(b)



(c)



Figure 12









(c)











Figure 13



Figure 14 Phase separation of styrene–UPE–10 wt % PVAc, after completion of exothermic curing reaction and the system cooled down to 100°C. The highly cured UPE-rich phase (dark region); high-MW PVAc-rich phase (bright region); lowly cured UPE phase (dark dots); and low-MW PVAc-rich phase (gray region).

Fig. 3) and yielded a bicontinuous morphology [Fig. 13(b), where the bright region is the PVAcrich region and the dark region is the UPE-rich region). The bicontinuous morphology grew selfsimilarly (LALS profiles in Fig. 3 at a curing time 12-36 min). After the self-similar growth, the bicontinuity was lost, yielding discrete PVAc-rich fragment particles dispersed in UPE-rich matrix [Fig. 13(c) and LALS profiles in Fig. 3 at curing times of 36-54 min) and then to spherical particles [Fig. 13(d) and LALS profile in Fig. 3 at curing time ~ 54 min). During curing, owing to the exothermic reaction, the temperature of the system was higher than that of sample holder, that is, 100°C. After completion of curing, no exothermic heat released from the curing reaction and the system cooled to 100°C, the lowly cured UPE-rich phase containing a small amount of low-MW PVAc separated from the high-MW PVAc-rich phase (lowly cured UPE-rich phase, designated by dark dots around the bright region in Fig. 13(e); the process of phase separation is also shown in Fig. 9 by dashed line after end of curing) and the low-MW PVAc-rich phase containing small amount of the lowly cured UPE separated from the highly cured UPE-rich phase



Figure 15 Phase separation mechanism of styrene– UPE–15 wt % PVAc: (a) before curing, a homogeneous system; (b) early stage of curing, a bicontinuous phase separation taking place; (c) a more UPE-rich phase separated from the PVAc-rich phase; (d) formation of the fragmented structure; (e) end of curing, in which the system cooled down to 100°C, and further phase separation of lowly cured UPE phase (dark dots around the bright region) and low-MW PVAc phase (gray region).

(low MW PVAc-rich phase, designated by the gray region in Figure 13(e); the process of phase separation is also shown in Figure 9 by a full line after the end of curing). The lowly cured UPE-rich and low-MW PVAc-rich phases form the interfacial layer between high-MW PVAc and highly cured UPE-rich phases. Figure 13(e) shows that the particles of gray phase with bright phase inside the middle are dispersed in the dark phase. Thus, a peak scattering intensity maximum was observed in the light scattering intensity profiles. However, due to the presence of interfacial layer, the Q value decreased upon cooling the curing system to the sample holder temperature, that is, 100°C (LALS profiles in Fig. 3 at curing time of 54–81 min). The phase separation mechanism of the styrene-UPE-10 wt % PVAc system was similar to those shown in Figure 13(a)-(d) for the curing reaction from beginning to end. However, owing to a higher content of PVAc, a bicontinuous morphology (as shown in Fig. 14) was present while the exothermic reaction was completed, and the system cooled to the sample holder temperature, that is, 100°C.

Increasing the PVAc content to 15 wt % resulted in a phase inversion: the PVAc-rich phase formed the matrix, and the UPE-rich phase was dispersed in the matrix. Figure 15 shows the phase separation mechanism of the styrene-UPE-15 wt % PVAc system. Before curing, the ternary system was homogeneous [Fig. 15(a)]. Demixing took place at a curing time of 24–30 min (as shown in Fig. 5), and a bicontinuous morphology is obtained [Fig. 15(b)]. In contrast to Figures 13 and 14 with the UPE-rich phase as the matrix phase, in this system, the PVAc-rich phase (bright region in Fig. 15) was the matrix phase. As curing reaction proceeded, more and more highly cured UPE (dark region in Fig. 15) separated from PVAc-rich phase and the bicontinuous morphology grew self-similarly [as shown from Fig. 15(b) to (c)]. After the self-similar growth, the continuity is lost to form fragmented particles [Fig. 15(d) and LALS profiles in Fig. 5 at curing times from 48-60 min, which show broad peaks with θ_m]. After the completion of curing, no exothermic heat released from the curing reaction, and the system cooled to 100°C. The phases of low cured UPE phase (dark dots around the bright region in Fig. 15(e) contained small amount of low-MW PVAc and the low-MW PVAc phase (gray region in Fig. 15(e) contained a small amount of lowly cured UPE separated from high-MW PVAcrich and highly cured UPE-rich phases, respectively (the process of phase separation is also shown in Figure 9 by full and dashed lines, respectively). Figure 15(e) shows that the gray and bright regions form a bicontinuous morphology. Thus, a broad scattering intensity profiles without θ_m were obtained in LALS at a curing time from 60–81 min.

CONCLUSION

Both LALS and SEM were used to investigate the phase separation during the curing reaction of the styrene-UPE system in the presence of PVAc. The SEM results revealed that the PVAc-rich phase was regularly dispersed in the cured UPE matrix while the styrene-UPE system was blended with 5 wt % of PVAc. However, as the PVAc content was increased to higher than 10 wt %, a cocontinuous PVAc and UPE phases was observed in the final isothermal cured system. The LALS data showed that during curing the scattering intensity profiles with maximum peak intensities were observed, indicating a regularly discrete phase dispersed in a continuous matrix phase. The scattering intensity profile became broader as the PVAc content was increased from 5 to 15 wt % suggesting that the increase of PVAc content resulted in an increase of the chance for the ternary blend to be a cocontinuous phase. The LALS observations also counted the effect of the rate of heat released from the exothermic curing reaction on the morphology of curing system. Our LALS results suggested that at the end of curing, the system cooled down due to the cessation of exothermic heat released from the curing reaction and caused the phase of low-MW PVAc-lower cured UPE to separate from styrene–UPE-rich and high-MW PVAc-rich phases.

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