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Morphology development in a thermoset/thermoplastic blend: DAP/PPE system via apparent two-step spinodal decomposition

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A thermoset/thermoplastic system, diallyl phthalate (DAP)/poly(2,6-dimethyl-1,4-phenylene ether) (PPE), was found to show upper critical solution temperature (UCST)-type phase behaviour (UCST ≈ 145°C). The system was cured by organic peroxide just above the UCST. The morphology development during curing was studied by time-resolved light scattering, Fourier transform infrared spectroscopy (*FT*i.r.) and transmission electron microscopy (TEM). A light scattering peak appeared at an early stage of curing and the scattering intensity increased with time, suggesting that the reaction-induced spinodal decomposition was caused by elevation of the UCST with the polymerization of DAP. Then the intensity gradually decreased and the peak decayed. Combining the TEM analysis, the peak decay was ascribed to a disordering in the mutual arrangement of polyDAP-rich particles in the PPE-rich matrix at a late stage of spinodal decomposition. In fully cured systems, fine polyDAP domains of the order of 10 nm were found to form in the PPE-rich matrix and fine PPE domains in polyDAP-rich particles. The fine domains could be formed by successive spinodal decomposition in both the dispersed particles and the matrix, under very deep quench after the micrometre-scale particle/matrix morphology was arrested by partial cure. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: blend; thermoset; poly(phenylene ether))

INTRODUCTION

In the past decade, many polymer–polymer pairs have been processed by reactive blending. Comparing with simple blending techniques, multiple advantage can be achieved by reactive blending[1–5]. *In situ* formation of graft and block polymers can compatibilize the immiscible components by reducing particle size and reinforcing the interface. Another class of reactive blending is the curing of thermoset/thermoplastic system. The system is usually homogeneous at the beginning of curing. With the proceeding of polymerization, i.e. with the increase of molecular weight, the system will be thrust into a two-phase region and the phase decomposition takes place either by nucleation and growth or the spinodal decomposition mechanism. Then the morphology developed by the reaction-induced phase decomposition would be fixed at a certain stage of curing by gelation and/or vitrification. Even by the spinodal decomposition mechanism, the fixed morphology would be versatile, depending on the cure condition. A variety of morphologies has been found: dispersed domain structure with uniform domain size, interconnected globule structure and bimodal domain structure[5]. In this article, a new and sophisticated morphology will be demonstrated in a thermoset/thermoplastic blend, diallyl phthalate (DAP)/poly(2,6-dimethyl-1,4-phenylene ether) (PPE). Time-resolved light scattering and transmission electron microscopy (TEM) were used to study the development of the morphology of the blend during curing. Cure kinetics were followed by Fourier transform infrared spectroscopy (*FT*i.r.). The correlation between the morphology and curing conditions was discussed.

EXPERIMENTAL

All the materials used throughout this work were from commercial sources and used as received without further treatment. Poly(2,6-dimethyl-1,4-phenylene ether) (PPE) was supplied by General Electric Co. ($M_w = 41.5 \times 10^3$). Diallyl phthalate (DAP) was supplied by Kanto Chemical Co. The cure agent for DAP was α,α-bis(*t*-butylperoxy-*m*-isopropyl)benzene (PBP) from Japan Fat Co.

The phase diagram of the DAP/PPE system was measured by the cloud point method. The DAP and PPE were dissolved at 5 wt% of the total components in trichloroethylene. The solution was cast on a cover-glass and dried at room temperature for 24 h, then further dried under a pressure of 10^{-4} mmHg for 12 h. The films on the cover-glass were annealed at different temperatures for 12 h and then the structure in the films was observed under an optical microscope. Based on the cloud point method after the long annealing, the phase diagram of the DAP/PPE blend was obtained.

DAP/PPE blends loaded with PBP were prepared as follows. The PPE was first mixed mechanically with DAP monomer at room temperature. The mixture was heated with stirring at 170°C to dissolve PPE completely in DAP. Then the mixture was cooled down to 150°C and the PBP was added with rigorous stirring to ensure PBP dispersed

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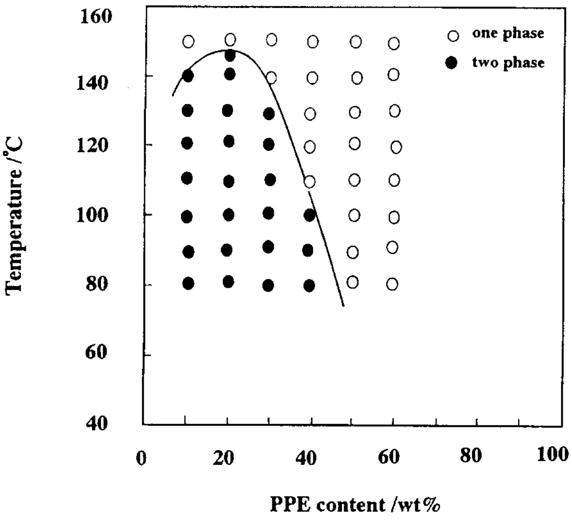


Figure 1 The phase diagram of the DAP/PPE blend

uniformly in the mixture. Two curing procedures, one-step and two-step, were applied. In the one-step curing procedure, the mixture was injected into a mould made of two glass plates sealed by a rubber gasket and cured at 150°C for 8 h. In the two-step curing procedure, the mixture was cured at 120°C for 12 h then 150°C for 5 h.

The light scattering profiles were obtained by a laser light scattering apparatus with a goniometer and a hot stage. The description of the apparatus in detail can be found elsewhere[6]. The radiation from a He–Ne gas laser of wavelength 632.8 nm was applied vertically to the film specimen. The goniometer traces of the scattering light were obtained under a V_v (parallel polarized) optical alignment. Thus during isothermal curing, the change in the light scattering intensity with time was recorded at appropriate intervals.

The morphology of the cured specimens was examined by a transmission electron microscope (JEM 100 CX, Jeol Co.) at 100 kV acceleration voltage. The ultrathin sections of thickness about 70 nm were obtained with an ultramicrotome (Ultracut N, Reichert-Nissei). The sections were stained by RuO_4 vapour for 10 min at room temperature.

The reaction kinetics of the blend was determined by a JIR-600 Fourier transform infrared spectrometer (Jeol Ltd) equipped with a hot stage. The absorbance ratio of A_{1646}/A_{746} was used to calculate the conversion of DAP, α:

$$\alpha = [(A_{1646}/A_{746})_0 - (A_{1646}/A_{746})_t]/(A_{1646}/A_{746})_0$$

where the 1646 cm^{-1} band is assigned to the C=C double bond, the 746 cm^{-1} band to the hydrogen atom in the phenyl ring (taken as the internal standard). The subscript 0 means that the reaction time is zero.

RESULTS AND DISCUSSION

The phase diagram of DAP/PPE is shown in *Figure 1*. The system exhibits upper critical solution temperature (UCST)-type phase behaviour. The UCST locates at about 145°C at DAP content of 80 wt%. It is expected that the DAP/PPE system can be cured starting from a homogeneous mixture, when a cure agent with high decomposition temperature such as PBP is used. It is also expected that, when curing proceeds, the phase boundary will shift upwards and the system will be thrust into a two-phase region.

Figure 2 shows the typical time-resolved light scattering profiles during curing at 150°C, where q is the scattering vector defined by $q = (4\pi/\lambda)\sin(\theta/2)$; λ being the wavelength of light in the specimen and θ the scattering angle.

A DAP/PPE/PBP 80/20/1.1 mixture was a single-phase system at the curing temperature of 150°C. There was no appreciable light scattering detected from the mixture in the first few minutes. A peak in the light scattering profile appeared after about 3 min, then the scattering intensity increased with time, keeping the peak position almost

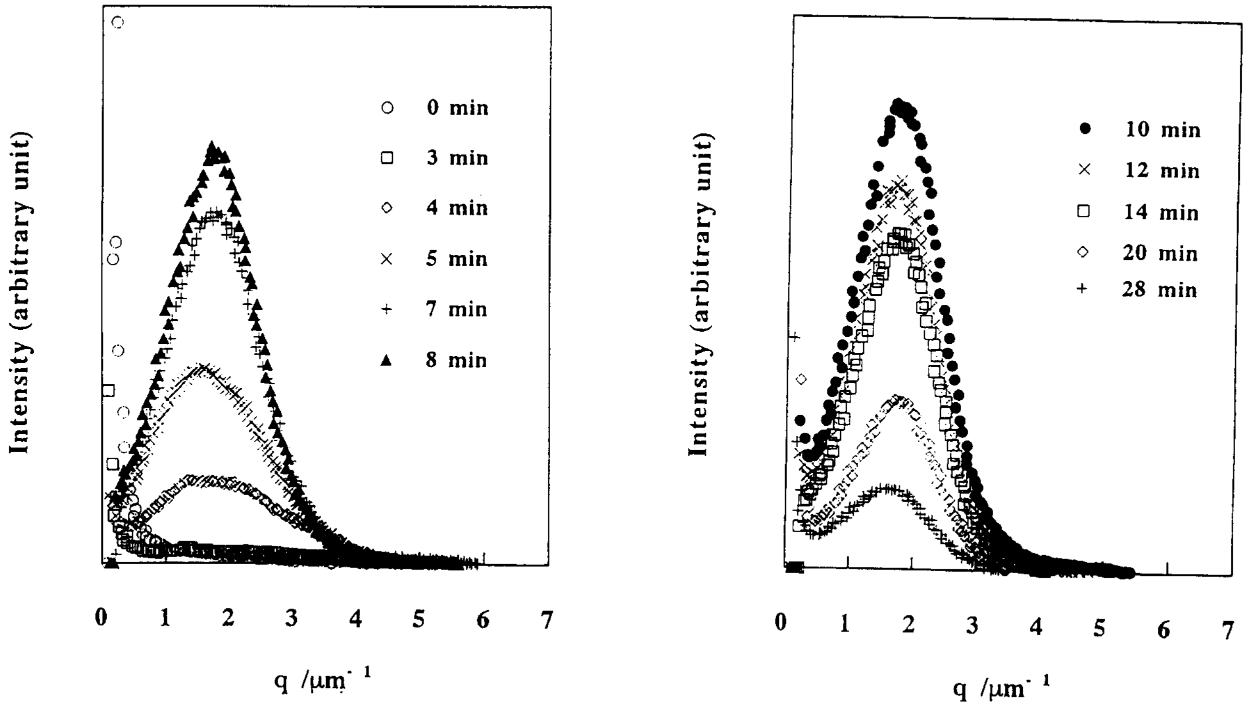


Figure 2 Time variation of light scattering profiles for a DAP/PPE/PBP 80/20/1.1 mixture during curing at 150°C

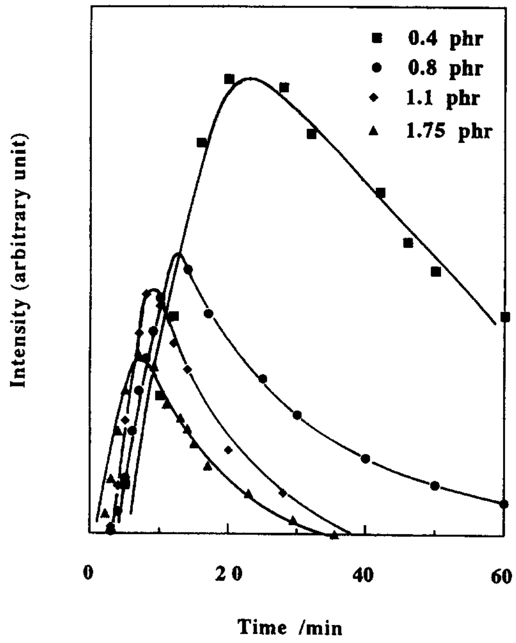


Figure 3 The peak intensity of the scattering profile *versus* cure time at 150°C for DAP/PPE 80/20 mixture with different PBP contents: ■, 0.4 phr; ●, 0.8 phr; ◆, 1.1 phr; ▲, 1.75 phr. Left, early stage; right, late stage

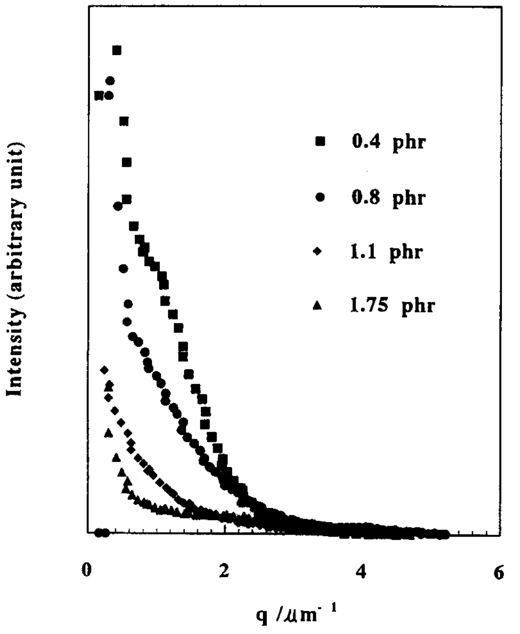


Figure 4 Light scattering profiles for the DAP/PPE 80/20 mixtures with different PBP contents after curing for 2 h at 150°C: ■, 0.4 phr; ●, 0.8 phr; ◆, 1.1 phr; ▲, 1.75 phr

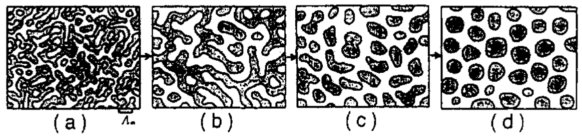


Figure 5 Schematic representation of the morphology development via spinodal decomposition

constant (left figure in *Figure 2*). About 10 min later, the peak intensity started to decrease (right figure in *Figure 2*).

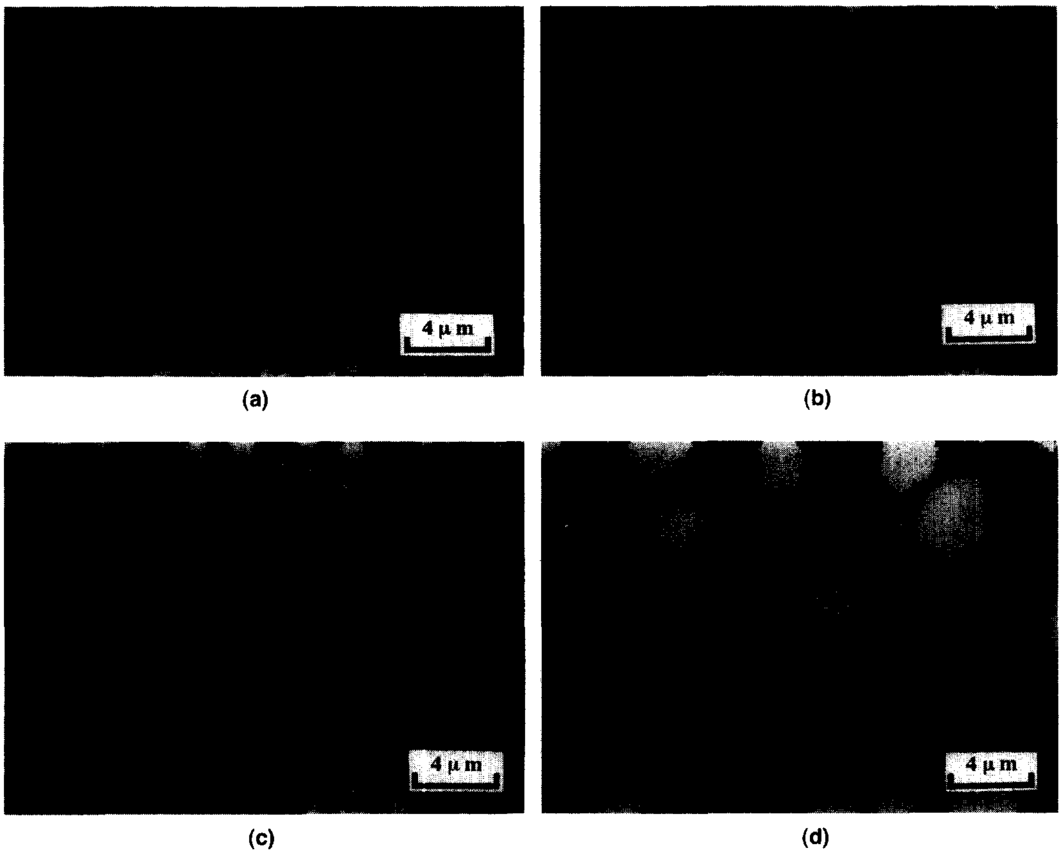
The same tendency was observed at different levels of PBP loading. The peak intensity is plotted as a function of cure time in *Figure 3*. The light scattering profiles after a long curing (2 h) are shown in *Figure 4*. One can hardly see the peak.

It is well known that the formation of phase-separated morphology via spinodal decomposition can be well characterized by light scattering profiles. The appearance of a scattering peak and the continuous increase of the scattering intensity are the indications of the development of a regularly phase-separated morphology as schematically shown in *Figure 5*. After the intensity of the scattering light reaches the maximum value, the change of the scattering profile will be different depending on the further development of the morphology. When the phase-separated morphology is arrested by gelation or vitrification, the peak intensity will level off[7]. When the phase dissolution takes place[8] and the difference in the refractive index between the two phases becomes smaller with further reaction[9], the peak intensity would start to decrease. The decay of the scattering peak in the present system can be ascribed to a disordering in the mutual arrangement of dispersed particles; i.e. broader size distribution and more irregular arrangement of particles in *Figure 5d*, as shown in TEM micrographs in *Figure 6*.

In *Figure 6*, the bright region shows polyDAP-rich domains, while the dark region shows PPE-rich matrix (see Appendix A). It can be seen that, in all the specimens, spherical polyDAP-rich particles are dispersed rather irregularly in the PPE-rich matrix. The higher the PBP content, the smaller the polyDAP-rich domains. Regardless of higher or lower PBP content, no interconnected morphology (*Figure 5a,b*) is observed. This implies that the rate of phase separation was very fast, compared with the reaction rate. In other words, before the network formation of the polyDAP-rich phase, the phase connectivity had been broken and the polyDAP-rich phase had been converted to dispersed particles. Furthermore, the mutual arrangement of particles seems to become irregular by coarsening. The disordering may cause the decay of the scattering peak. Then the morphology at quite a late stage of spinodal decomposition seems to be fixed.

It should be noted that DAP has a unique gelation behaviour. Usually free radical polymerization of divinyl compounds yields a cross-linked network at only 1% conversion, while diallyl phthalate can be polymerized to 21% conversion without forming a network[10]. The delayed gelation of polyDAP may render the structure fixation at a very late stage of spinodal decomposition; without premature stopping at any stage in *Figure 5*. The lower the PBP content, the lower the reaction rate; in turn, the lower increase of viscosity in the system, which could allow the dispersed particles to coarsen to the higher degree, so that the morphology at the later stage would be arrested.

A TEM micrograph at higher magnification is shown in *Figure 7*. There are small bright domains in the matrix and small dark domains in the particles. The small domains in both the matrix and the dispersed particles may be formed by the second spinodal decomposition in individual regions after the micrometre scale structure was fixed. The situation is schematically described in *Figure 8*. That is, long waves in the concentration profile shown by the broken line are created by the first spinodal decomposition to provide the dispersed particles of micrometre diameter and then shorter waves are formed by the second spinodal decomposition to yield fine domains of the order of 10 nm in both the matrix and the dispersed particles. The morphology shown



(a) (b) (c) (d)

Figure 6 Transmission electron micrographs of the DAP/PPE 80/20 blends with different PBP contents cured at 150°C for 8 h; (a) 1.75 phr; (b) 1.1 phr; (c) 0.8 phr; (d) 0.4 phr

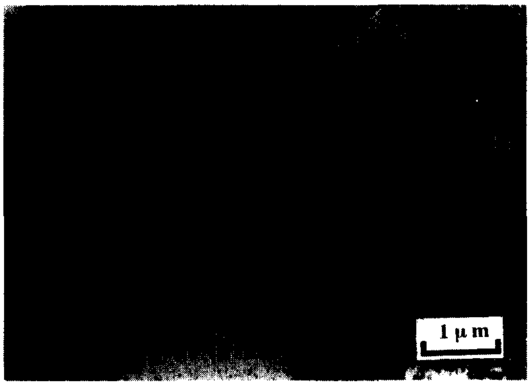


Figure 7 Transmission electron micrographs of the DAP/PPE 80/20/0.4 system (see *Figure 6d*) at high magnification

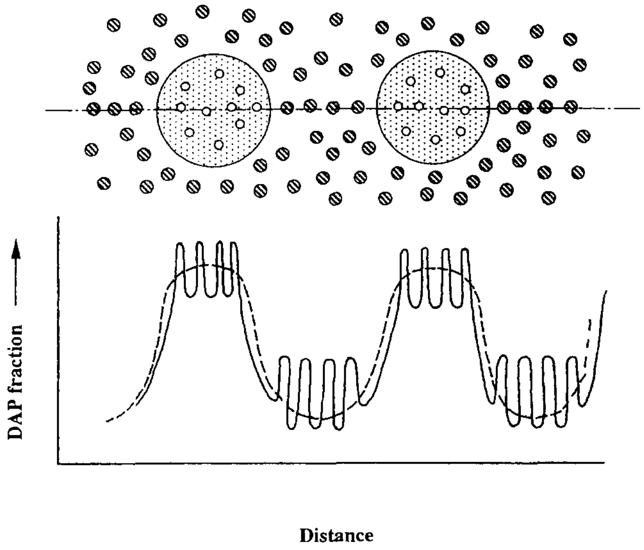


Figure 8 Schematic representation of the morphology development by the two-step spinodal decomposition and the concentration profile by the first spinodal decomposition (broken line) and that by the second one (solid line)

in *Figures 7 and 8* is a new one in thermoset/thermoplastic blends.

Note that the term second spinodal decomposition in the above discussion is used for convenience to describe the phenomenon. It is just an apparent one, because the thermodynamic quench depth may increase continuously with time during curing and one cannot expect any particular new instability to cause another decomposition. That is, the decomposition should not proceed step-wise but continuously. However, such apparent two-step spinodal decomposition is actually seen in the computer simulation of spinodal decomposition under non-isoquench depth conditions; i.e. when the quench depth increases with time[11] (as in the present case). In the simulation, as the quench depth increases with time, the long waves in the concentration profile develop to certain levels of amplitude and wavelength (as shown by the broken lines in *Figure 8*) and then short waves suddenly start to appear at a certain stage. This apparently looks like the second-step decomposition. The apparent two-step spinodal decomposition could be expected to take place especially in the thermoset system, because the morphology developed by 'the first

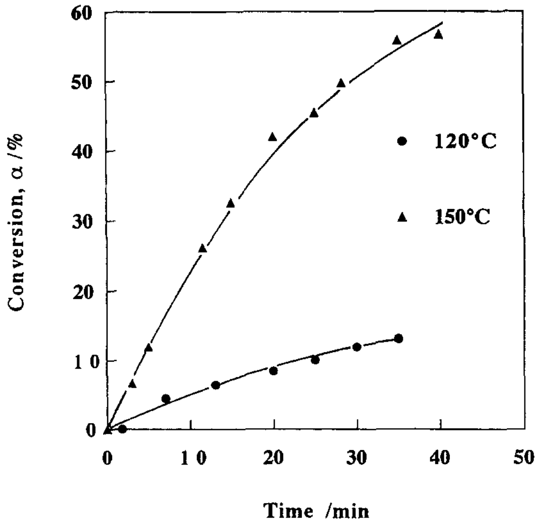
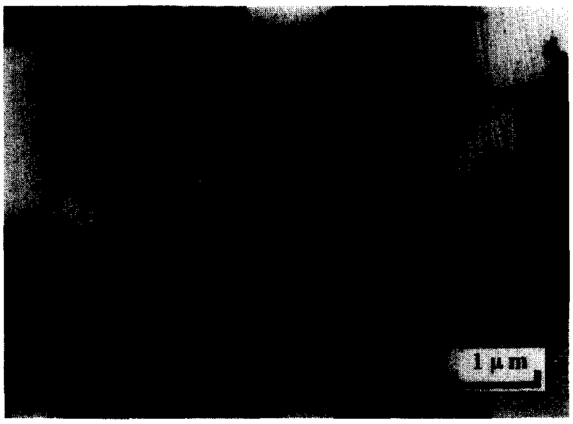


Figure 9 Conversion curves in a DAP/PPE/PBP 80/20/1.75 blend measured by *FT*i.r. at (a) 150°C and (b) 120°C.

(a)



(b)

Figure 10 Transmission electron micrograph of a DAP/PPE/PBP 80/20/1.75 system cured at 120°C for 12 h then at 150°C for 5 h: (a) low and (b) high magnification

spinodal decomposition' would be arrested by partial cross-linking at a certain stage and then the quench depth further increases without significant change in morphology for a while; finally, 'the second spinodal decomposition' would start to yield much smaller domains.

As has been discussed, the morphology developed in the DAP/PPE system seems to be the structure fixed at a very late stage of spinodal decomposition. We tried to fix the structure at an earlier stage to provide the bicontinuous structure as shown in *Figure 5b* or *c*. The strategy was as follows. If the unreacted homogeneous mixture undergoes a temperature drop from the single-phase region to 120°C and an isothermal annealing at 120°C, the rate of phase separation is expected to decrease drastically; e.g. following the WLF-type temperature dependence of the chain mobility, while the reaction rate does not decrease so much. As generally expected, the rate slows down to a half by a 10°C depression. Actually, the reaction rate estimated by *FT*i.r. did not decrease so much as shown in *Figure 9*. Then, the structure at an earlier stage is expected to be fixed by the 120°C cure and then the reaction could be completed by a post-curing at higher temperatures. Thus we undertook a two-step cure programme: the first cure at 120°C for 12 h and the post-cure at 150°C for 5 h. The results are shown in *Figure 10*. As expected, the bicontinuous nature is preserved in the fully cured material (*Figure 10a*). Also in this material, the fine domains of scale 10 nm are seen in both regions (*Figure 10b*), implying that the morphology developed by a two-step spinodal decomposition.

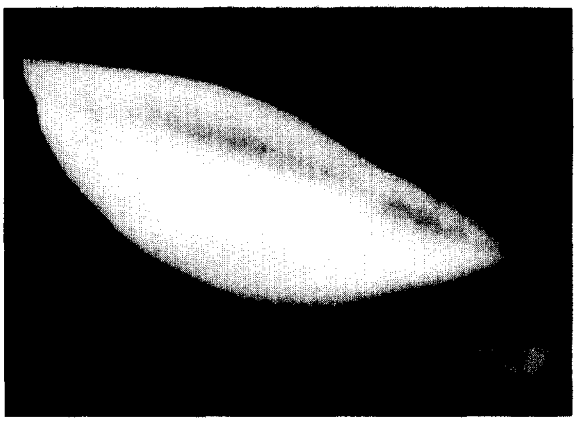


Figure 11 Transmission electron micrograph of the physical blend of cured DAP particle and PPE to show the preferential staining of PPE matrix by RuO_4

APPENDIX A: RuO_4 STAINING FOR THE PPE/DAP SYSTEM

Since both PPE and DAP have phenyl rings, it is not clear which phase in the DAP/PPE blend will be stained preferentially by RuO_4. This was checked by an experiment. First, neat DAP was fully cured and the cured DAP was ground into small particles of about 5 μm. Then a small amount of the particles was melt-blended with PPE. The blend was pressed into a 2-mm-thick sheet. The sheet was microtomed and the ultrathin section was stained with RuO_4, following the procedure in the experimental section. A typical TEM micrograph is shown in *Figure 11*. It can be clearly seen that the cured DAP particle is not stained by RuO_4, and it appears as the bright region, while the PPE matrix is stained, in the dark region.

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