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Morphology development via reaction-induced phase separation in epoxy/poly(ether sulfone) blends: morphology control using poly(ether sulfone) with functional end-groups

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Thermoset/thermoplastic blends, namely triglycidyl *p*-aminophenol/poly(ether sulfone) (epoxy/PES) systems, were cured using a curing agent, 4,4′-diaminodiphenylsulfone, and the morphology in the cured resins was observed by electron microscopy. In contrast to the spherical domain structure in a non-reactive PES system, a bicontinuous two-phase structure was obtained when reactive PES with amine chain ends was used. It suggests that the spinodal decomposition (SD) induced by the cure reaction is suppressed and structure coarsening is delayed by the *in situ* formation of PES–epoxy block copolymer, so that the phase-separated structure can be fixed at an early stage of SD. When a reactive PES was used, the periodic distance Λ_m of the bicontinuous structure was extremely small ($\Lambda_m \approx 20$ nm). With the non-reactive PES in the blend, Λ_m increased from 20 nm to 1 μm. In mixed PES systems, Λ_m can be reduced by the pre-reaction of PES with epoxy; e.g. from 0.7 μm to 0.1 μm for the 20/10 reactive/non-reactive system. Similar results were obtained for another reactive PES with hydroxyl chain ends.

(Keywords: epoxy; poly(ether sulfone); blend morphology)

INTRODUCTION

Some dissimilar polymers with specific interactions are miscible at low temperatures and the mixtures phase-separate at higher temperatures. This lower critical solution temperature (*LCST*) type phase behaviour is typical for polymer–polymer mixtures[1]. When the homogeneous mixture is allowed to undergo a rapid temperature jump below the *LCST* to above the *LCST* and is annealed isothermally, demixing takes place via the spinodal decomposition (SD). This yields a bicontinuous morphology with unique periodicity (*Figure 1a*). The bicontinuous morphology grows self-similarly from (a) to (b) in *Figure 1*. After the self-similar growth, the bicontinuity is lost to yield fragmented particles (*Figure 1c*) and then spherical particles (*Figure 1d*). Note here that particles are uniform in size and they are dispersed quite regularly. This is the story of morphology development by the thermally induced SD.

Similar demixing is induced by chemical reaction. This is typically illustrated by the polymerization of monomer A in the presence of polymer B[2]. For example, poly(ethylene-*co*-vinyl acetate) (EVA) is soluble in methyl methacrylate (MMA) and the EVA/MMA mixture is initially a single-phase system at the polymerization temperature (90°C); however, the system is thrust into the two-phase regime as the polymerization proceeds to form PMMA, and this elevates the upper critical solution temperature (*UCST*). Hence, the SD is expected to take place. Light scattering studies have revealed the SD nature of the reaction-induced demixing in the EVA/MMA system. A quite similar situation is seen for multicomponent thermoset resins, such as epoxy/liquid rubber and epoxy/poly(ether sulfone) (PES) systems[3–5]. The reaction-induced SD proceeds isothermally, but the quench depth, the temperature difference between the *LCST* (or *UCST*) and the reaction temperature, increases with time. Computer simulation has shown that, even under such non-isoquench depth, the SD can yield the regularly phase-separated structure in a manner similar to the SD under isoquench depth[6].

Furthermore, the effect of incorporating graft copolymer in the EVA/MMA system was investigated to

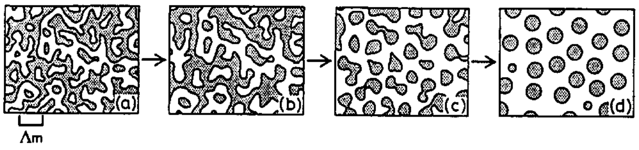

Figure 1 Schematic representation of phase separation scheme. Bicontinuous structure (a) develops at the early stage of spinodal decomposition and it grows self-similarly to yield the similar structure with longer periodic distance (b). Then the phase connectivity is interrupted to be converted to a fragmented structure (c) and further to the spherical domain structure (d)

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show that a small amount of the copolymer suppresses the demixing at the early stage of SD and delays structure coarsening; as a consequence, the copolymer incorporation readers finer morphology[2]. Such an effect could be expected also in thermoset/thermoplastic systems. In this paper, we deal with the epoxy/PES system in which the PES has reactive chain ends so that a block copolymer is formed *in situ* during cure. In the thermoset/thermoplastic system, it is particularly interesting that, with the aid of *in situ* formed block copolymer, a very fine morphology at the very early stage of SD* would be fixed by network formation in the epoxy-rich region. One has to note that various epoxy/reactive thermoplastic systems have been studied to design toughened resins with high chemical resistance[8–10].

EXPERIMENTAL

Two reactive PES were supplied by Dr S. D. Jenkins, ICI Co. One has hydroxyl chain ends (PES-OH; $M_n = 12.8 \times 10^3$, 1.25 OH groups per 100 repeat units). The chain ends of the other one mostly consist of amine (PES-NH_2; $M_n = 11.3 \times 10^3$, 2.98 NH_2 and 1.25 OH groups per 100 repeat units). A non-reactive PES with 100% Cl chain ends was also used as a control polymer (PES; $M_n = 13.8 \times 10^3$). A trifunctional epoxy resin, triglycidyl *p*-aminophenol, was supplied by Ciba-Geigy Co. (MY 0510; epoxy equivalent weight $= 101\,\mathrm{g\,mol^{-1}}$, molecular weight $= 300\,\mathrm{g\,mol^{-1}}$, viscosity $\simeq 600$ cP at room temperature). A 4,4′-diaminodiphenylsulfone (DDS) supplied by Ciba-Geigy Co. (HT 976) was used as a curing agent.

PES was dissolved in a mixed solvent of methylene chloride/methanol (= 90/10 in volume ratio) and epoxy was added to the solution. After the mixture was mixed thoroughly and concentrated to ca. 40% solid content, DDS was added. The mixture was poured into an open mould set at 145°C and degassed under full vacuum for 30 min to remove residual solvent. The solvent-free mixture was inserted in a hot chamber and then cured at 180°C. After curing, the sample was allowed to cool slowly to room temperature.

The cured film (0.8 mm thick) was cut into a strip (6 mm × 20 mm) and served for the dynamic mechanical analysis (d.m.a.). The dynamic mechanical properties were measured by Rheolograph Solid (model 651, Toyo Seiki Co.). The frequency was fixed at 10 Hz and the scanning rate was $2^\circ\mathrm{C\,min^{-1}}$ over a wide range of temperature (100–350°C).

The cured film was fractured at liquid-nitrogen temperature and the fractured surface was observed by scanning electron microscopy (SEM) (JSM-T220, JEOL Co.). The fractured specimen was immersed in methylene chloride (preferential solvent for PES) at room temperature to remove PES. The fractured and etched surface was also observed by SEM.

The morphology in the cured film was also observed by transmission electron microscopy (TEM) (JEM 100CX, JEOL Co.). For TEM observation the film was cut into an ultrathin section of 70 nm thickness by ultramicrotome (Ultracut N, Reichert-Nissei) and the ultrathin section was stained by OsO_4. OsO_4 is found to stain selectively cured epoxy resin.

We also prepared a very thin film (50 μm thick) of the epoxy/DDS/PES mixture by solution casting onto a silicone wafer for *FT*i.r. spectroscopy. After the cast film was dried under a vacuum of 10^{-4} mmHg for 12 h, it was cured in a hot chamber. *FT*i.r. spectra were measured at appropriate intervals during isothermal curing by FT-IR 8100 (Shimadzu Co.).

RESULTS AND DISCUSSION

The trifunctional epoxy/non-reactive PES mixture was shown to exhibit the *LCST*-type phase behaviour as described in the previous paper ($LCST = 270^\circ$C)[11]. At the early stage of curing, the mixture was homogeneous at the cure temperature ($180^\circ\mathrm{C} < LCST$). As the cure reaction proceeds, the system was thrust into the two-phase regime by the *LCST* depression caused by the increase in the molecular weight of the epoxy-rich phase, and the phase separation took place via SD. This was confirmed by time-resolved light scattering[11]. As expected from the light scattering analysis, the cured material had the two-phase morphology fixed at the late stage of SD, as shown in *Figure 2*. One can see spherical domains of epoxy resin dispersed quite regularly in PES matrix. That is, the morphology (d) in *Figure 1* is realized.

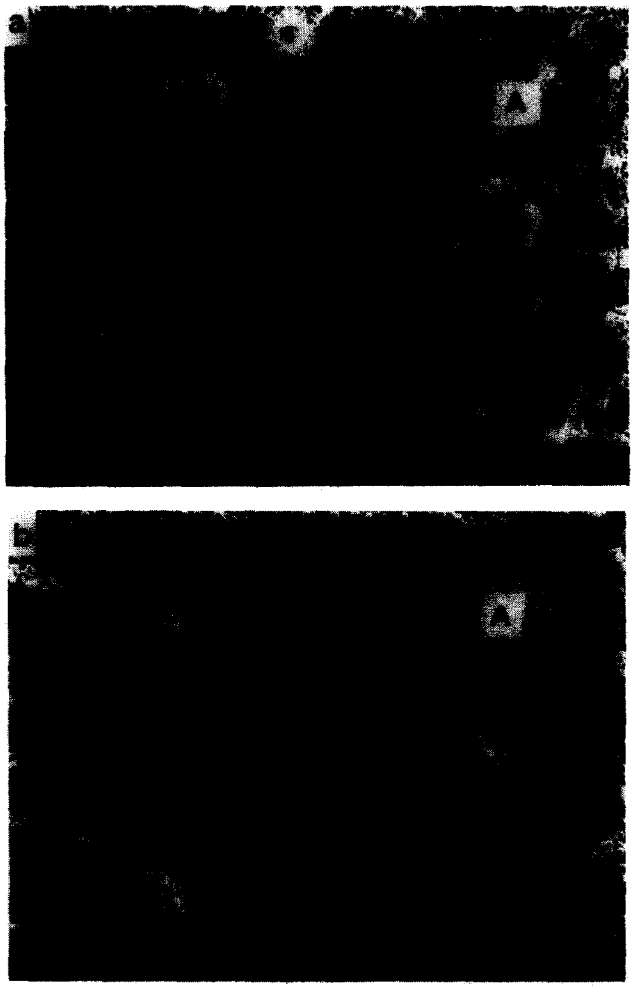

Figure 2 SEM micrographs of epoxy/DDS/non-reactive PES = 47/23/30 cured at 180°C for 3 h (resin A): (a) fractured; (b) fractured and etched

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* The periodic distance Λ_m in the bicontinuous structure (see *Figure 1a*) is expected to be of the order of 10 nm for the early stage of SD in polymer/solvent systems[7]

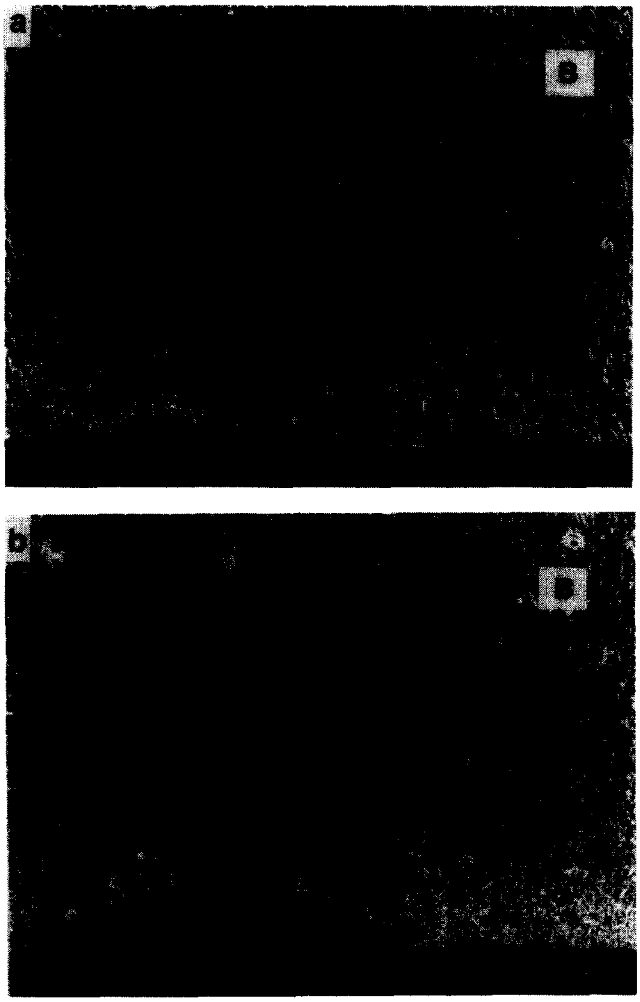

Figure 3 SEM micrographs of epoxy/DDS/PES-NH$_2$ = 47/23/30 cured at 180°C for 3 h (resin B): (a) fractured; (b) fractured and etched

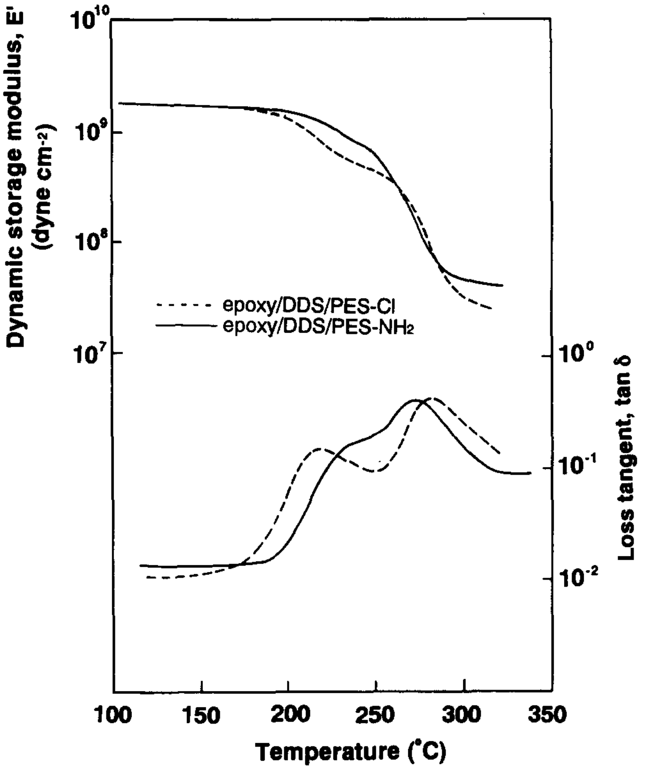

Figure 4 Temperature dependence of dynamic storage modulus E' and loss tangent, tan δ, for epoxy/DDS/PES = 47/23/30 curved at 180°C for 3 h

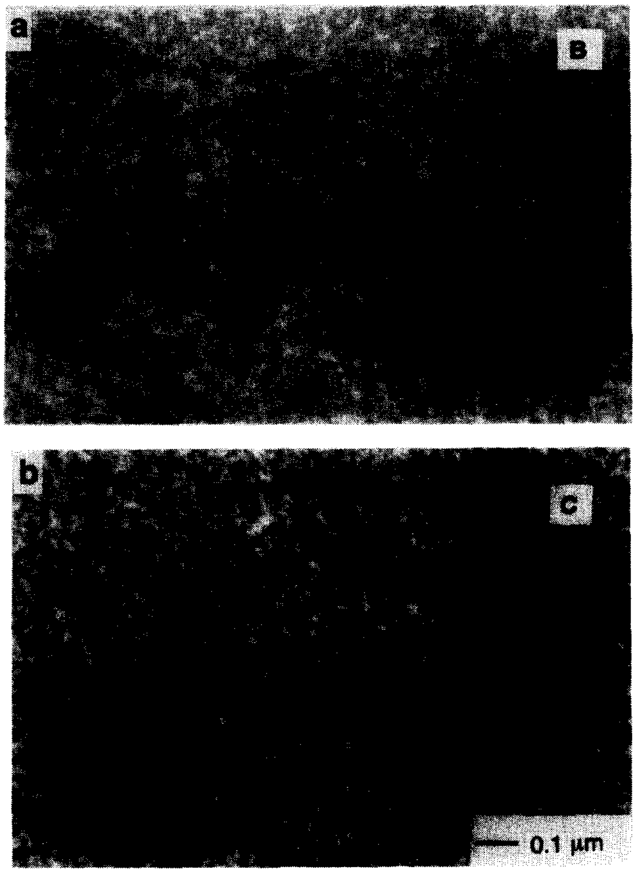

Figure 5 TEM micrographs of epoxy/DDS/PES-NH$_2$ = 47/23/30: (a) cured at 180°C for 3 h; (b) epoxy and PES-NH$_2$ pre-reacted at 180°C for 3 h, DDS added at 145°C, and then cured at 180°C for 3 h (resin C)

In contrast, when reactive PES is used, one cannot see any clear morphology under SEM as shown in *Figure 3*. One sees just a fractograph in *Figure 3a*. There is no change in the SEM micrograph with solvent etching (*Figure 3b*). It may suggest that the PES has reacted with epoxy and it is hard to rinse it away with the solvent. The d.m.a. result in *Figure 4* clearly shows the two-phase character in the cured epoxy/PES-NH$_2$ system; two tan δ (loss tangent) peaks and two-step decrease in E' (dynamic storage modulus) with increasing temperature. Then, the following morphology observation was switched from SEM to TEM.

The morphology is revealed under TEM as shown in *Figure 5a*. Here, the dark region stained by OsO_4 can be assigned to the cured epoxy phase, since a small amount of C=C bonds are formed in the epoxy network at the late stage of curing as discussed in the previous paper[11]. *Figure 5a* resembles the morphology (a) in *Figure 1*. Note that the periodic distance is quite small, $\Lambda_m \approx 20$ nm, suggesting the bicontinuous structure at the very early stage of SD is successfully fixed. Compared with the non-reactive PES system (*Figure 2*), one can see a big change in the periodic distance. It may imply the formation of PES–epoxy block copolymer, which can suppress the rate of SD at the early stage of SD. Namely, the concentration fluctuation growth has been suppressed

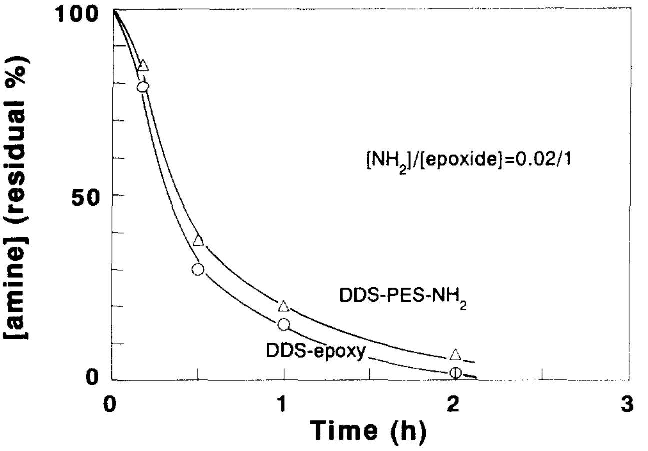

Figure 6 Time variation of residual percentage of amine groups in $PES\text{-}NH_2$ and DDS during reaction with epoxy at 180°C

until the system reaches a deep quench at which the fluctuation should have large wavenumber (small Λ_m).

In *Figure 5* is also shown a TEM micrograph of the same composition but by different procedure. *Figure 5b* is the TEM micrograph of the pre-reacted and then cured material, i.e. $PES\text{-}NH_2$ was reacted with epoxy at 180°C for 3 h to provide PES end-capped with epoxy and, after adding DDS at 145°C, the system was cured at 180°C for 3 h. One sees that the morphology is almost the same as that of one-step cure in *Figure 5a*. It may imply that the reactivity of NH_2 chain ends is almost equal to that of amine groups of DDS, so that the similar situation can be provided for the *in situ* formation of block copolymer.

The reactivity of $PES\text{-}NH_2$ with epoxy is shown and compared with that of DDS in *Figure 6*. Here, $PES\text{-}NH_2$ and DDS were charged at the same amine/epoxy molar ratio (0.02/1) and the reaction was carried out at 180°C. The residual percentage of amine groups was estimated by using the absorbance of phenyl group at $1602\,\mathrm{cm}^{-1}$ (as an internal standard), A_{1602}:

$$\text{residual amine groups (\%)} = \frac{(A_{1720}/A_{1602})_t}{(A_{1720}/A_{1602})_{t=0}} \times 100$$

where $(A_{1720})_t$ is the absorbance of amine (N–H bending) band at $1720\,\mathrm{cm}^{-1}$ at reaction time t and $(A_{1720})_{t=0}$ is that at $t=0$. One sees that the amine end-group of PES reacts with epoxy and the rate is almost the same as that of DDS; the latter is slightly more reactive than the former.

In *Figure 7* are shown the effects of blending of non-reactive PES with reactive PES and of pre-reaction. *Figure 7a* is the TEM micrograph of epoxy/PES/PES-NH_2/DDS = 47/20/10/23 cured at 180°C for 3 h. Compared with the 100% reactive PES system in *Figure 5a*, the periodic distance of the bicontinuous structure is much larger ($\Lambda_m = 1\,\mu\mathrm{m}$). It may suggest that the lower amount of $PES\text{-}NH_2$ yields less *in situ* formed block copolymer. A higher amount of the copolymer could be expected by the pre-reaction. For the same compound as in *Figure 5a*, PES and $PES\text{-}NH_2$ were reacted with epoxy at 180°C for 3 h and then cured with epoxy at 180°C. The result is shown in *Figure 5b*. As expected, the periodic distance is reduced to $0.7\,\mu\mathrm{m}$ by the pre-reaction. Note that, in *Figures 7a* and *7b*, small spherical domains are seen in both PES- and epoxy-rich regions. The occluded spherical domains could be assigned to the microdomains of block copolymer and the larger domains solubilized with homopolymers. *Figure 7c* shows that, by increasing the charge amount of reactive PES, the periodic distance can be reduced very much ($\Lambda_m = 0.1\,\mu\mathrm{m}$) in the pre-reacted system.

So far, we have discussed the results for $PES\text{-}NH_2$ systems. For PES-OH systems, the results were almost the same as for the $PES\text{-}NH_2$ systems, as shown in *Figures 8* and *9*. The results in *Figure 8* are essentially the same as those in *Figure 5*, i.e. PES-OH system provides the

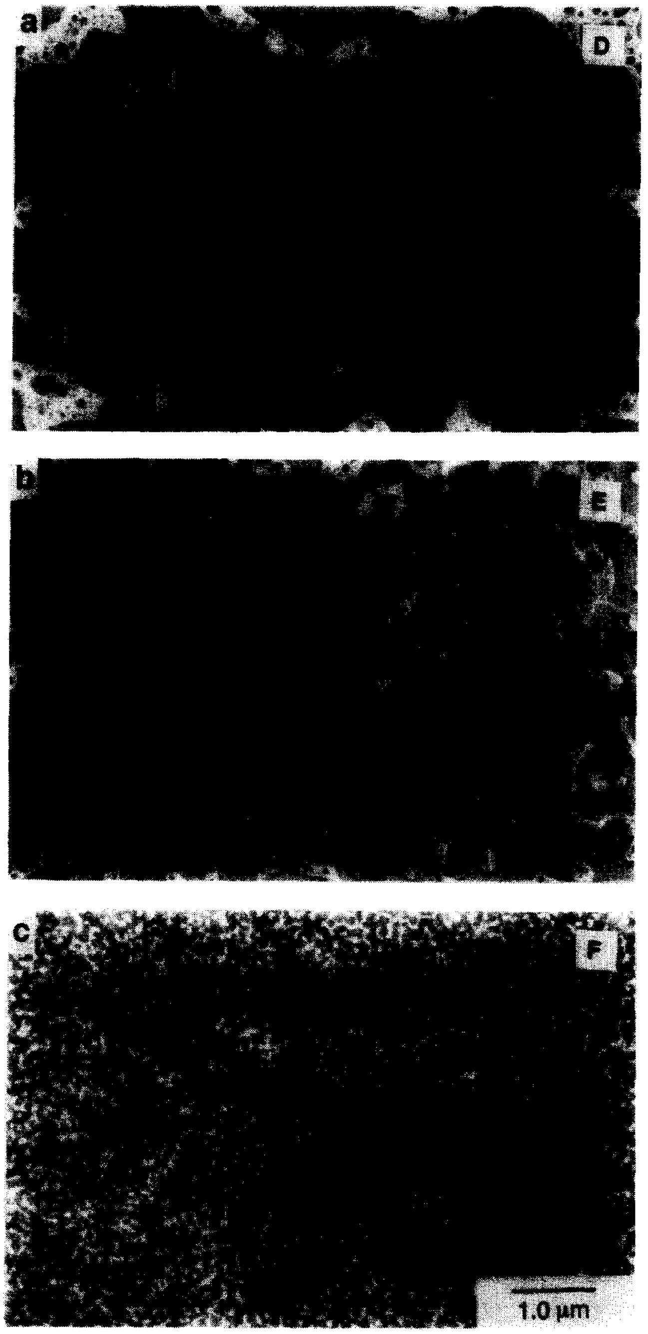

Figure 7 Effects of PES/$PES\text{-}NH_2$ blend ratio and pre-reaction: (a) epoxy/DDS/PES/$PES\text{-}NH_2$ = 47/23/20/10 cured at 180°C for 3 h (resin D); (b) same compound, pre-reacted at 180°C for 3 h and then cured at 180°C for 3 h (resin E); (c) epoxy/DDS/PES/$PES\text{-}NH_2$ = 47/23/10/20, pre-reacted at 180°C for 3 h and then cured at 180°C for 3 h (resin F)

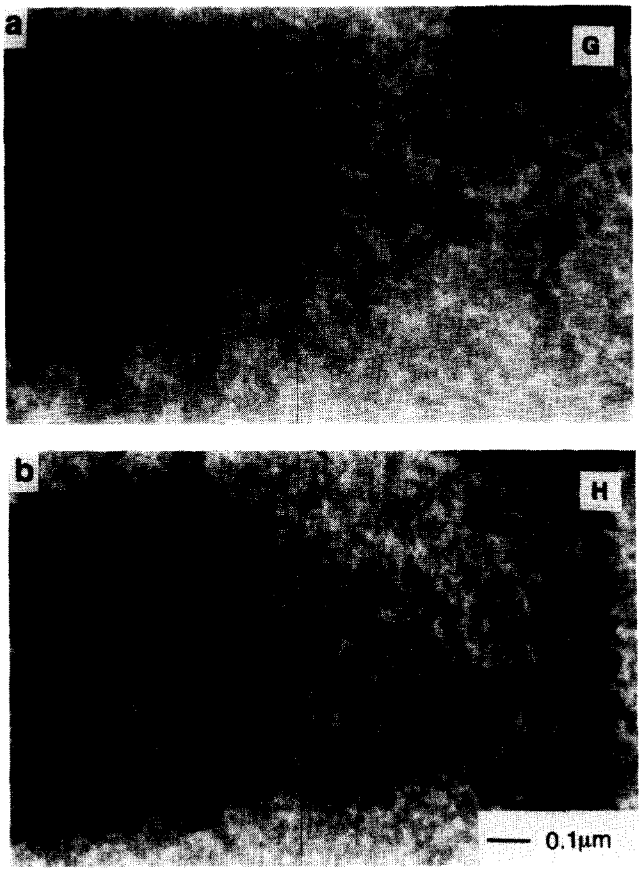

Figure 8 TEM micrographs of epoxy/DDS/PES-OH = 47/23/30: (a) cured at 180°C for 3 h (resin G); (b) epoxy and PES-OH pre-reacted at 180°C for 3 h, DDS added at 145°C, and then cured at 180°C for 3 h (resin H)

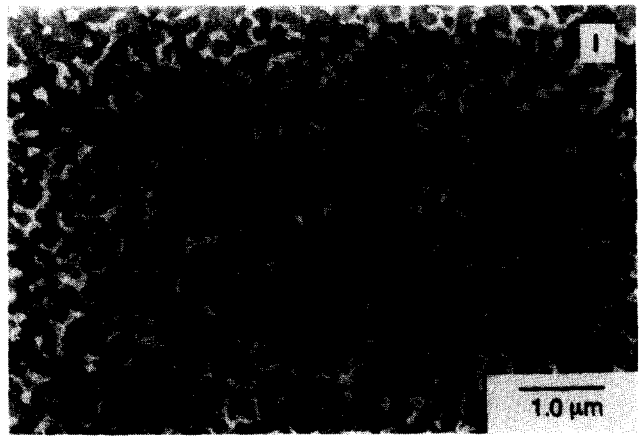

Figure 9 TEM micrographs of epoxy/DDS/PES/PES-OH = 47/23/10/20; epoxy and PES-OH pre-reacted at 180°C for 3 h and then cured with DDS at 180°C for 3 h (resin I)

bicontinuous two-phase morphology with very short periodic distance ($\Lambda_m = 50\,\text{nm}$) by both the one-step curing and the curing after pre-reaction. Similarly, the result in *Figure 9* corresponds to that in *Figure 7b*, showing again the non-reactive PES/reactive PES blend system provides the bicontinuous morphology with longer periodic distance ($\Lambda_m = 0.3\,\mu\text{m}$)

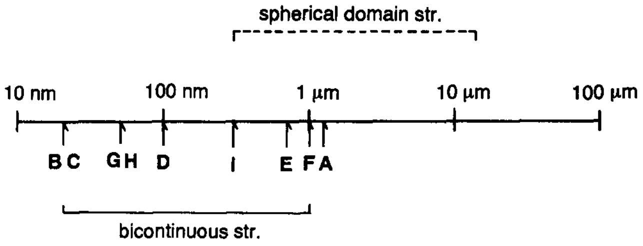

Figure 10 Two-phase morphology obtained by the reaction-induced SD in epoxy/PES systems

CONCLUSION

In this paper, just one example of spherical domain structure with periodic distance of 1.3 μm was shown for non-reactive PES system (resin A). In the previous paper[3], we have shown that the periodic distance of spherical domain structure can be changed in a wide range ($0.3\,\mu\text{m} < \Lambda_m < 14\,\mu\text{m}$) by controlling the cure program, as shown by the broken line in *Figure 10*. Employing the reactive PES, the bicontinuous structure with shorter periodic distance ($20\,\text{nm} < \Lambda_m < 1\,\mu\text{m}$) was shown to be obtained in this paper, as shown by the solid line in *Figure 10*. In the overlapping range ($0.3\,\mu\text{m} < \Lambda_m < 1\,\mu\text{m}$), both spherical domain and bicontinuous structures can be prepared by the reaction-induced SD. The latter is by the incorporation of reactive PES. The reduction of interfacial tension by the *in situ* formed block copolymer may be the reason why the bicontinuous character can be maintained in the latter system.

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REFERENCES

1 Olabisi, O., Robeson, L. M. and Shaw, M. T. (Eds.) 'Polymer–Polymer Miscibility', Academic Press, New York, 1979
2 Chen, W., Kobayashi, S., Inoue, T., Ohnaga, T. and Ougizawa, T. *Polymer* 1994, **35**, 4015
3 Yamanaka, K. and Inoue, T. *Polymer* 1989, **30**, 662
4 Yamanaka, K., Takagi, Y. and Inoue, T. *Polymer* 1989, **30**, 1839
5 Yamanaka, K. and Inoue, T. *J. Mater. Sci.* 1990, **25**, 241
6 Ohnaga, T., Chen, W. and Inoue, T. *Polymer* 1994, **35**, 3774
7 McMaster, L. P. *Adv. Chem. Ser.* 1975, **142**, 43
8 Hedrick, J. L., Yilgor, I., Jurek, M., Hedrick, J. C., Wilkes, G. L. and McGrath, J. E. *Polymer* 1991, **32**, 2020
9 Hourston, D. J. and Lane, J. M. *Polymer* 1992, **33**, 1379
10 Kubotera, K. and Yee, A. F. *ANTEC* 1992, 2610
11 Kim, B. S., Chiba, T. and Inoue, T. *Polymer* submitted