

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

### Studies on the Phase Separation of a Polyetherimide Modified Epoxy Resin. VI. Effect of Surface Energy on Reaction-Induced Phase Separation of Epoxy Resin Modified with Polyetherimide

Hua Li<sup>a</sup>; Wenjun Gan<sup>a</sup>; Lin Zhao<sup>a</sup>; Shanjun Li<sup>a</sup>

<sup>a</sup> Department of Macromolecular Science and the Key Laboratory of Molecular Engineering of Polymers, Ministry of Education, Fudan University, Shanghai, China

Online publication date: 06 May 2003

**To cite this Article** Li, Hua , Gan, Wenjun , Zhao, Lin and Li, Shanjun(2003) 'Studies on the Phase Separation of a Polyetherimide Modified Epoxy Resin. VI. Effect of Surface Energy on Reaction-Induced Phase Separation of Epoxy Resin Modified with Polyetherimide', *Journal of Macromolecular Science, Part A*, 40: 8, 833 – 846

**To link to this Article:** DOI: 10.1081/MA-120022274

**URL:** <http://dx.doi.org/10.1081/MA-120022274>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.



JOURNAL OF MACROMOLECULAR SCIENCE®  
Part A—Pure and Applied Chemistry  
Vol. A40, No. 8, pp. 833–846, 2003

## Studies on the Phase Separation of a Polyetherimide Modified Epoxy Resin. VI. Effect of Surface Energy on Reaction-Induced Phase Separation of Epoxy Resin Modified with Polyetherimide

Hua Li, Wenjun Gan, Lin Zhao, and Shanjun Li\*

Department of Macromolecular Science and the Key Laboratory of Molecular Engineering of Polymers, Ministry of Education, Fudan University, Shanghai, China

### ABSTRACT

The effect of surface energy on the phase separation of polyetherimide modified epoxy systems is studied by time-resolved light scattering (TRLS), differential scanning calorimeter (DSC), scanning electron microscopy (SEM), and rheometer. Scanning electron microscopy shows that phase separation of F-blend system goes further and finally, smaller epoxy-rich particles and thicker polyetherimide (PEI)-rich layers are generated. Differential scanning calorimeter and TRLS experiments indicate that the F-PIP/Epoxy blend has a lower curing rate and phase separation rate than the P-PIP/Epoxy blend. Rheological behavior displays that the viscosity of F-PIP/Epoxy blend is lower than that of P-PIP/Epoxy blend. By studying the properties of different PIP surface the F-PIP and P-PIP give different surface energy and it could be concluded that kinetics is a control factor in the phase separation of the two blends due to their difference of surface energy of PEI chain.

*Key Words:* Epoxy resin; Polyetherimide; Surface energy; Phase separation.

\*Correspondence: Shanjun Li, Department of Macromolecular Science and the Key Laboratory of Molecular Engineering of Polymers, Ministry of Education, Fudan University, Shanghai, China, 200433; E-mail: sjli@fudan.edu.cn.

833

DOI: 10.1081/MA-120022274  
Copyright © 2003 by Marcel Dekker, Inc.

1060-1325 (Print); 1520-5738 (Online)  
www.dekker.com

MARCEL DEKKER, INC.  
270 Madison Avenue, New York, New York 10016



## INTRODUCTION

Epoxy resins are currently used for many important applications such as adhesives, encapsulates, and advanced composite matrixes. However, the further use of epoxies is limited because of their inherent brittleness. For blending of polymers is an effective way to obtain materials with specific properties, in recent years, the feasibility of toughening highly crosslinked networks with high modulus and high  $T_g$  thermoplastics has been investigated. Results of thermoplastic toughening of epoxy resins, such as polysulfone (PSF),<sup>[1,2]</sup> polyethersulfone (PES),<sup>[3-5]</sup> poly(ether ether ketone) (PEEK),<sup>[6]</sup> polyimide (PI),<sup>[7,8]</sup> and polyetherimide (PEI),<sup>[9-12]</sup> show that the improvement in fracture toughness is achieved without the expense of modulus at elevated temperature. It is also of special interest to scientists for theoretical importance in reaction-induced phase separation processes.<sup>[13-18]</sup> In our previous work, a series of novel PEI was synthesized and used to modify thermosetting resin, the modified resin displays toughening effect without sacrificing other important properties.<sup>[19-21]</sup>

One of the advantages of using the reaction-induced phase separation procedure is that a variety of morphologies can be obtained by changing the composition, molecular weight of the polymer, curing temperature, curing agent, and interfacial tension. Among these structures, bicontinuous or phase inverted structure can greatly increase the mechanical properties of the blends. It is reported that the interfacial tension can influence the composition range for full co-continuity and the stability of the bicontinuous structure.<sup>[22]</sup> Much work has been done to study the influence of interfacial tension on morphologies,<sup>[23-25]</sup> and block copolymers are often used to change the interfacial tension between two components in these studies. But most of these studies are based on blends of two component thermal-induced separation blend systems, not in reaction-induced phase separation ones. Interfacial tension influence on phase separation has been studied in rubber-modified epoxy systems,<sup>[26,27]</sup> and recently, it is reported that phase inversion are obtained by the low free surface energy of thermoplastic (30% of 12F-PEK).<sup>[28]</sup>

In recent years, many of studies have been done on fluorocarbon-modified polymers because under certain conditions these polymers have the inclination to self-assemble or self-stratify.<sup>[29-31]</sup> In many occasions, fluorocarbon chain with certain lengths can enrich at the surface or the interface of the polymers, and so change the surface energy of system significantly. To study the effect of surface energy on reaction-induced phase separation, a kind of fluorocarbon chain terminated PEI was synthesized and used as a modifier of epoxy resin, and some tentative explanations are provided based on the experimental results.

## EXPERIMENTAL

### Materials

The epoxy oligomer used in the study was diglycidyl ether of bisphenol A, Dow 331 (epoxy equivalent 182–192 g/eq). Perfluorooctanoic acid,  $\text{PCl}_5$ , and aluminum chloride were purchased commercially and used as received. The cure agent 4,4'-diaminodiphenyl sulfone (DDS) (Shanghai Third Reagent Factory) was used without further purification.

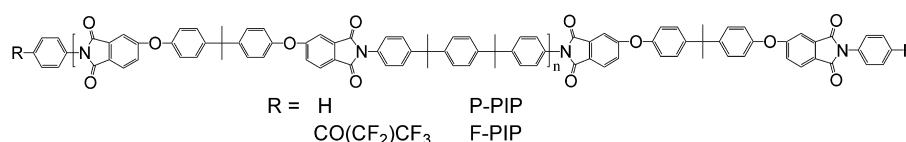


### Synthesis

Perfluorooctanoyl chloride was prepared as mentioned in the literature.<sup>[32]</sup> *p*-Amino-perfluorooctanophenone was synthesized from perfluorooctanoyl chloride and acetanilide through Friedel-Crafts reaction under the catalysis of aluminum chloride in nitromethane. Fifteen gram (0.036 mol) and 30 mL of nitromethane are placed in a 150 mL two-necked flask equipped with a mechanical stirrer, and 12.3 g (0.087 mol) of aluminum chloride was added from the open neck. Then, the acetanilide solution (3 g, 0.029 mol, acetanilide dissolved in 40 mL of nitromethane) was dropped into the above mixture with stirring in 30 min. The mixture was then heated at reflux temperature and stirring was continued for 3 h. The red-brown mixture was poured into 200 g of ice and 20 mL of concentrated hydrochloric acid was added. After the hydrolysis of the aluminum chloride, it was extracted with diethyl ether; the extract solution was washed by a 10% NaOH solution and deionized water. After removing the solvent, the crystal was refluxed in a solution of 10% NaOH for half an hour and extracted again by diethyl ether. It was then washed by deionized water and dried overnight in the presence of MgSO<sub>4</sub>. The white product obtained after removing the solvent was then recrystallized in ethanol and the yield was about 38%. (m.p. 101–102°C). FTIR (KBr): 1701 cm<sup>-1</sup> (s, C=O), 1395, 1335, 1200, and 1146 cm<sup>-1</sup> (vs, C–F), 3064 cm<sup>-1</sup> (w, aromatic C–H), 3364 cm<sup>-1</sup> (s, NH<sub>2</sub>). NMR <sup>1</sup>H (CDCl<sub>3</sub>): δ 8.21 ppm (d, 2H) 7.42 ppm (d, 2H), 3.56 ppm (s, 3H).

The PEI was synthesized in one step from *bis*phenol-A dianhydride (BISA-DA) and 4,4'-[1,4-phenylenebis(1-methylethylidene)]bis-aniline (BISP) at a stoichiometric ratio of 1 : 0.985 in *m*-cresol at 200°C, after that, aniline or *p*-aminoperfluorooctanophenone were added to terminate the PEI and the products were assigned as P-PIP for phenyl-terminated PIP and F-PIP for fluorocarbon chain terminated PIP, respectively.

The PIP structure is depicted below:



The inherent viscosity of PIP was 0.69 dL g<sup>-1</sup> and its *T<sub>g</sub>* was 220°C.

### Techniques

The inherent viscosity of PIP was obtained in the concentration 0.5 g dL<sup>-1</sup> at 30°C in *N*-methyl-2-pyrrolidone as solvent.

An epoxy blend containing 20 phr (per hundred ratio) of phenyl-terminated PIP was prepared by dissolving PIP in epoxy resins at 150°C. After a homogeneous, clear solution was obtained, the blend was then cooled to 130°C, 31 phr of DDS were added while the mixture was stirred. After the curing agent was dissolved, the blend was rapidly cooled to room temperature in order to maintain the curing reaction at a lower extent, as was the epoxy and fluorocarbon-terminated PIP specimen. The two blend systems were assigned as P-blend for epoxy/PIP and F-blend for epoxy-F-PIP, respectively.



The glass transition temperatures ( $T_g$ ) of PEI were determined by DSC (SETARAM DSC 92) from room temperature to 300°C at a heating rate of 10°C min<sup>-1</sup>. Study of conversion of the two blends was also carried out on DSC.

Scanning electron microscopy was carried out on a Philip XL39 SEM instrument. The phase separation process during curing reaction was observed at real time and in situ on the self-made TRLS with a controllable hot chamber. The films were prepared by melt pressing: a grain of the blend was sandwiched between two pieces of slide glass and heated on a heat stage at the preset curing temperature for 30 s and then quickly pressed to thin films of about 5 μm. The change of the light scattering profiles was recorded at appropriate time intervals during isothermal curing.

The rheological behavior of the blends during curing were recorded on an Ares-4A rheometer: About 1 g of the blend was sandwiched between two round fixtures and the temperature was quickly raised to the curing temperature. The two blends were tested under a parallel plate mode with a controlled strain of 1%. The testing frequency was selected at 1 Hz.

To show the different surfaces properties, the contact angles were measured by syringing deionized water on a 50 μm-thick F-PIP or P-PIP films on a NRL Contact Angle Goniometer (RH Imaging 2001, Ramé-Hart, Inc). The difference between both sides of three drops of deionized water was normally within 2°, and the results were averaged.

## RESULTS AND DISCUSSION

### Conversion and Rate of Curing Reaction

An aluminum pan containing samples was put into the DSC while the instrument reached the preset temperature of 150°C, the isothermal reaction was considered complete when there was no change on the exothermal curve. The total area under the isothermal curve was used to calculate the isothermal curing heat,  $\Delta H_{iso}$ . After that, the sample was cooled to 30°C. To determine the residual reaction heat,  $\Delta H_{res}$ , the sample after isothermal curing was heated at a heating rate of 10°C min<sup>-1</sup> from 50°C to 400°C. The sum of both isothermal heat ( $\Delta H_{iso}$ ) and residual heat ( $\Delta H_{res}$ ) of the reaction was taken to represent the total heat of cure ( $\Delta H_t$ ). The isothermal conversion at time  $t$  was defined as

$$\alpha(t) = \frac{\Delta H_{iso}(t)}{\Delta H_t}$$

The calculated conversion ( $\alpha$ ) via time curves are shown in Fig. 1. Obviously the curves of the F-blend and P-blend differ from each other already at the beginning. Compared with the system of P-blend the curing reaction of F-blend is shifted to longer curing time and slower curing rate.

### Phase Separation Observed by Light Scattering

Time resolving of light scattering was used to run after the process of phase separation. The peak scattering fact, corresponding to the wave number of concentration



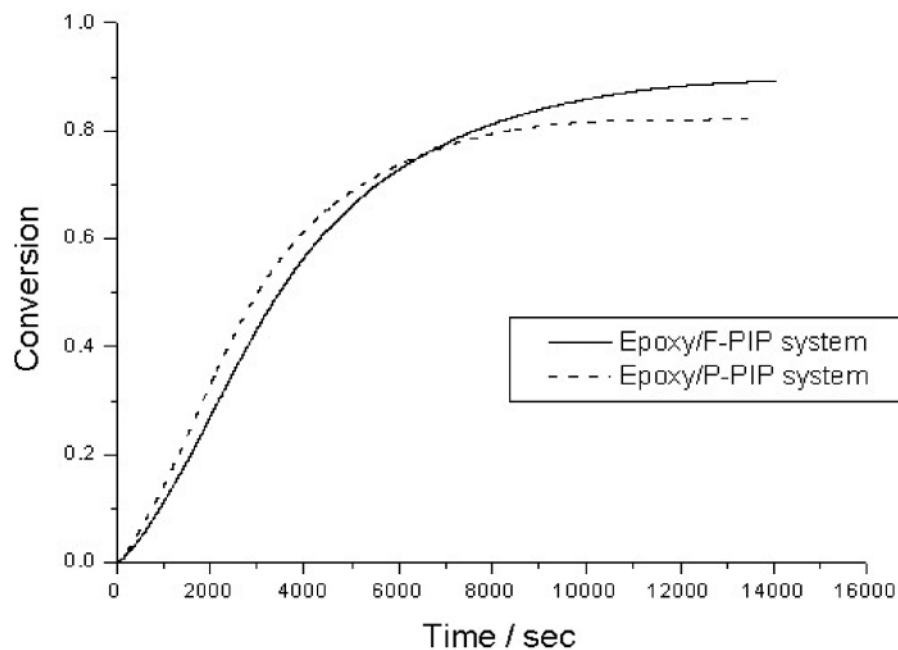


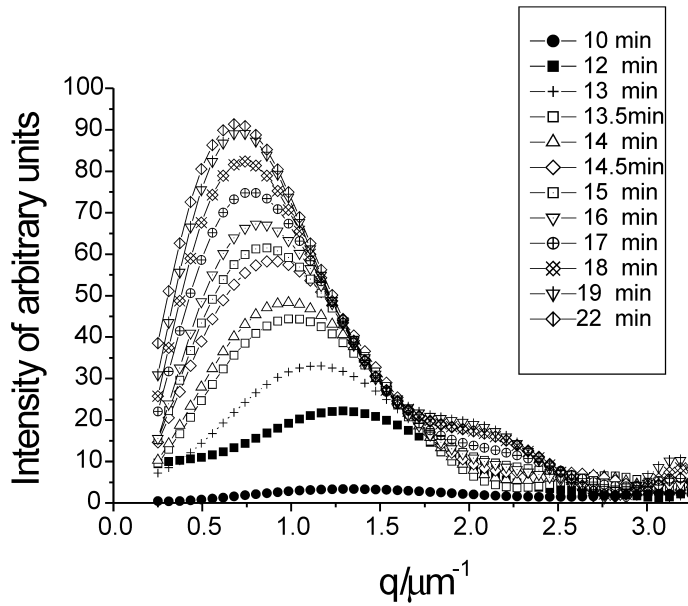
Figure 1. Conversion of F-blend and P-blend cured at 150°C.

fluctuation, is defined by  $q_m = (4\pi/\lambda)\sin(\theta_m/2)$ ,<sup>[13,33]</sup> where  $\lambda$  and  $\theta_m$  are the wavelength of scattering light in the sample and the peak scattering angle, respectively. The reciprocal of the scattering vector  $q$  is assigned to the periodic distance of the dispersed particles. The smaller the characteristic wave number  $q_m$ , the larger the periodic distance  $\Lambda_m$  of the pinned structure ( $\Lambda_m = 2\pi/q_m$ ).

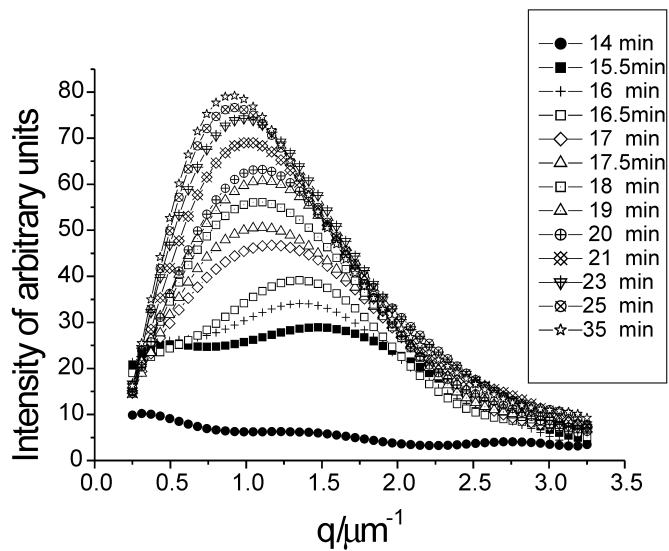
Figure 2 shows the scattering profiles of F-blend and P-blend with curing time at 150°C. The blends were single-phase systems and showed no appreciable light scattering in the early stages of curing, indicating a miscibility at the wavelength scale. After a certain time lag, scattering light appeared due to the development of a phase-separation structure. Figure 2a shows that the changes in the light scattering profiles of the P-blend. After about 12 min, a scattering peak appeared and the intensity increased, showing that the phase separation was initiated by the curing reaction. The scattering intensity of the peak stopped increasing after about 19 min and then began to decrease slightly before it finally became invariant, which may result from the decrease in the difference of the reflection indices of the two phases.<sup>[7]</sup> The peak vector  $q_m$  was about  $0.69 \mu\text{m}^{-1}$  at last (Fig. 2a), while the blends of F-blend gave a peak at 15 min and finally the peak vector was about  $0.91 \mu\text{m}^{-1}$  at a time lag of 25 min (Fig. 2b), indicating that at first the coarsening of PIP particles took place and then the morphology was fixed.

The profiles of P-blend and F-blend both exhibit one sharp peak and correspond to different scattering vectors. The intensity of the peaks of the two systems both give a rapid increase shifting to a small scattering angle at the early stage of the curing reaction and finally slow down. Based on the above observation, one can estimate that the





(a)



(b)

Figure 2. Change of lighting-scattering profile of blends cured at 150°C. (a) P-blend, (b) F-blend.

Downloaded At: 11:34 24 January 2011



**Table 1.** Rate of phase separation and peak scattering vector  $q_m$  of F-blend and P-Tr blend.

	Average rate of phase separation in $s^{-1}$	$q_m$ ( $\mu m^{-1}$ )
F-blend	$3.06 \times 10^{-3}$	0.91
P-blend	$3.96 \times 10^{-3}$	0.69

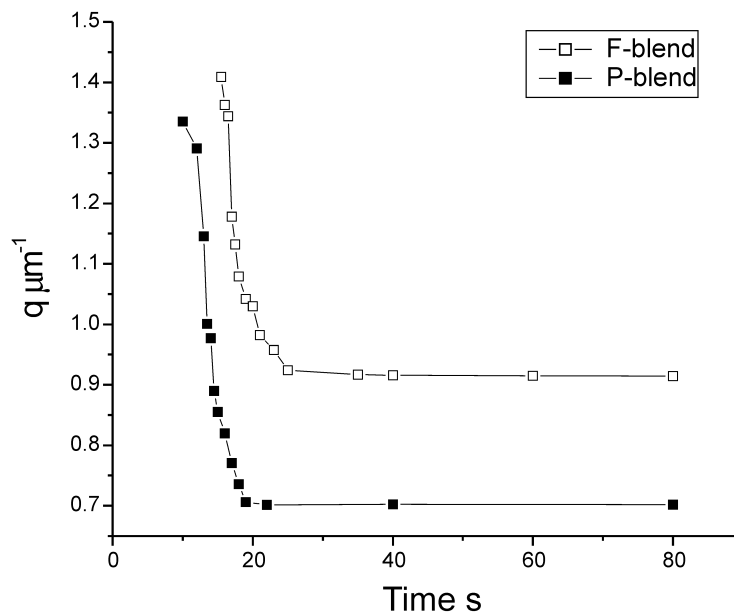
phase separation of the two blend systems both follows a spinodal decomposition mechanism.

The phase separation rate can be characterized as the slope of linear variation of  $I(q_m, t)$  at the initial stage of phase separation.<sup>[19,34]</sup> The phase separation rate of P-blend is a little faster than that of the F-blend (Table 1).

To estimate the morphology fixation time ( $t_{fix}$ ), the peak scattering vector  $q_m$  was plot as a function of curing time (Fig. 3). In the P-blend and F-blend,  $q_m$  decreased with time and the point at which  $q_m$  became invariant was recorded as  $t_{fix}$  because the morphology was then pinned up.<sup>[13,35]</sup>

**Rheological Behavior of Blend Systems During Curing Process**

Rheology is a signature of connectivity. Figure 4 shows the melt viscosity variations of the two blends with curing time at 150°C. The viscosity increases a little at the early



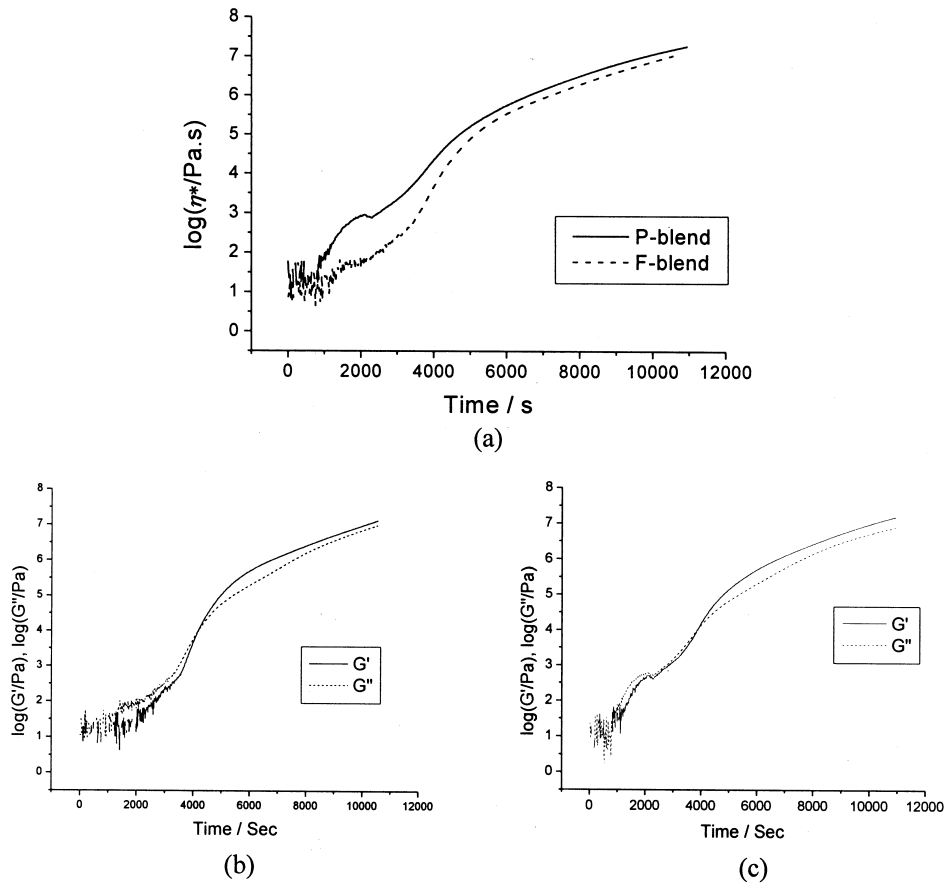
**Figure 3.** Time dependence of the peak scattering vector  $q_m$  during spinodal decomposition of F-blend and P-blend.

Downloaded At: 11:34 24 January 2011

Copyright © 2003 by Marcel Dekker, Inc. All rights reserved.







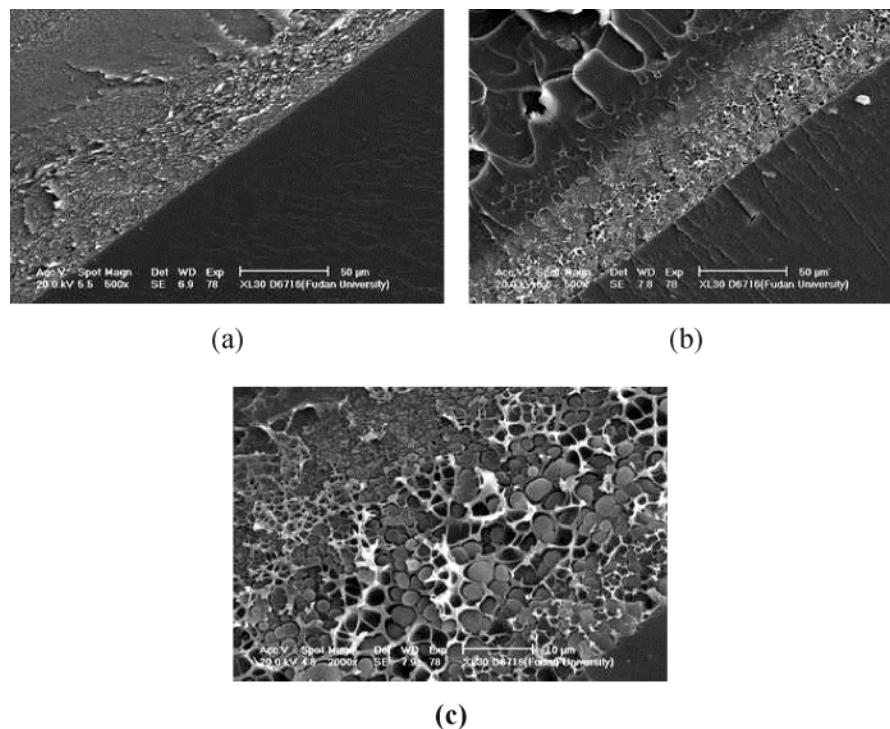
**Figure 4.** Viscosity variation of (a) F-blend and P-blend cured at 150°C,  $G'$  and  $G''$  of (b) F-blend, (c) P-blend upon curing at 150°C.

stage of curing. Then the viscosity increases abruptly because gel points are reached and three dimensional epoxy networks are formed. The gel point time  $t_{gel}$ , is obtained by the intersection point of  $G'$  and  $G''$ . It can also be found that the F-blend displays a lower viscosity than that of the P-blend during the phase separation process with the curing reaction.

### Morphology of Blend Systems

To study the compatibility between the PIP and the epoxy resins, the unreacted epoxy resin containing 31 phr DDS was poured onto a 1 mm-thick PEI film and then was cured at 150°C under pressure. The morphologies of the fracture surface of the samples were observed by SEM (Fig. 5).



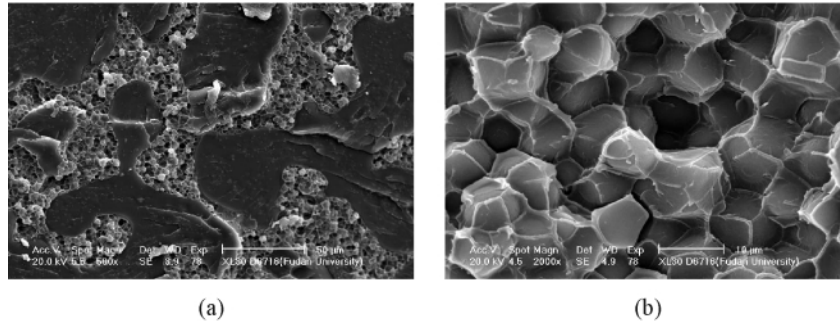


**Figure 5.** Scanning electron microscopy of interfacial structure between Epoxy and PIP cured at 150°C, (a) F-blend, (b) P-blend, (c) magnification of interfacial structure of (b).

The morphology of the interfaces on two types of PIP sheet are evidently different. In the case of the Epoxy/F-PIP/DDS system, the interface is very thin and there is no distinct morphology. However, in the Epoxy/P-PIP/DDS sample, an interface about 60 μm thick is created with dispersed epoxy-rich particles in the P-PIP matrix and a typical phase inverted morphology in the epoxy matrix. Moreover, the morphologies of the epoxy resins blend with DDS and different PIP were also studied. For SEM observation the blends are cured at 150°C for 4 h to ensure that the morphologies are fully fixed. Figures 6 and 7 show the SEM photos of fracture surfaces for the F-blend and P-blend.

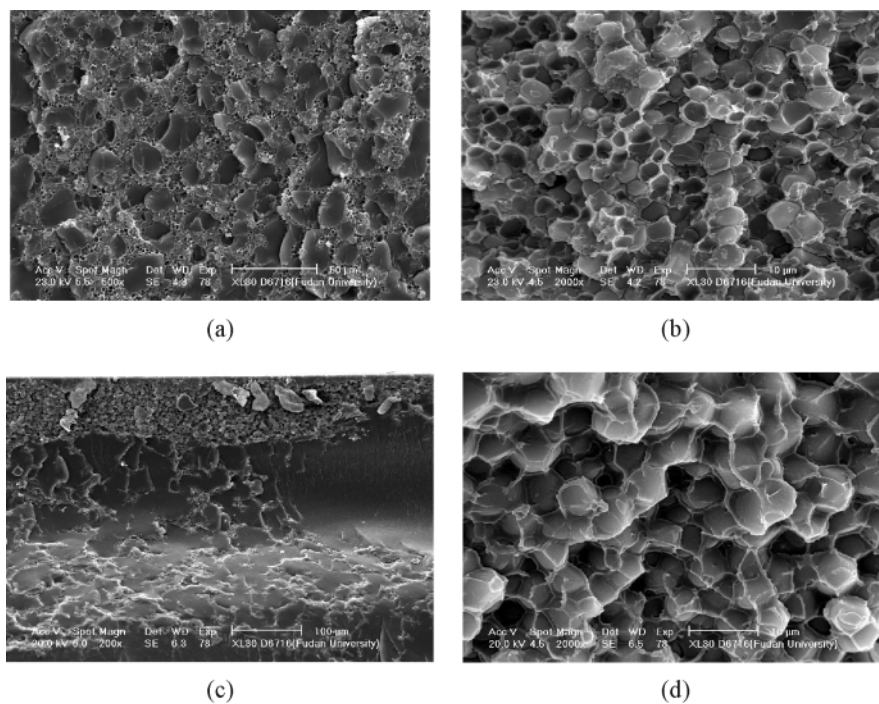
There is an obvious co-continues phase in SEM of both cured blends, moreover at the surface of F-blend, the enrichment of F-PIP was found (Fig. 7c) but no signals of such phenomena were found close to the surface of P-blend, and in bulk, it can be seen that the volume fraction of PIP in F-blend is higher than that of the P-blend. Thus, it suggests that the extent of phase separation is higher in the F-blend than that in the P-blend. This is accordance with the following fact: the lower viscosity will lead to a further extent of phase separation and the higher the viscosity, the lower the mobility of the two components and the earlier the morphologies be pinned up.





**Figure 6.** Scanning electron micrographs of P-blend cured at 150°C for 3 h. (a) Fracture surface, (b) magnification of the bright region.

Another notable fact shown in SEM is that the sizes of the dispersed epoxy particles of the two blends are different. The dispersed particles of epoxy in the F-PIP-rich phase are smaller than those in the P-PIP-rich phase, in accordance with the results observed by TRLS. These facts clearly suggest that the varieties on the morphology of F-blend systems are caused by the special property of the fluorocarbon-terminated group.



**Figure 7.** Scanning electron micrographs of F-blend cured at 150°C for 3 h. (a) fracture surface, (b) magnification of the bright region of (a), (c) surface structure of (a), magnification of the bright region of (c).

Downloaded At: 11:34 24 January 2011



**Table 2.** Contact angles of deionized water on P-PIP and F-PIP films.

	F-PIP	P-PIP
Contact angle	74.00	68.20

The contact angle measurements gave the information for the top surface, such as wettability. Data of the contact angle for the films based on the cured F-blend and P-blend are shown in Table 2, the data of pure F-PIP and P-PIP films are also listed.

Based on the results mentioned above, there exists a different curing reaction and phase separation behavior in the P-blend and F-blend. Compared with the P-blend, the F-blend has a slower curing rate which leads to the slower phase separation rate, and finally, a time lag in the phase separation induced by the curing reaction of the F-blend system. Since the components of the blends are similar, the only difference is the terminate group. The fluorocarbon chain terminated groups reduce the curing rate and the phase separation rate. The groups also lead to a lower complex viscosity which may be caused by the reducing of molecules interaction due to the existence of the fluorocarbon chain during the process of phase separation.

Furthermore, the  $t_{gel}$  obtained by rheological study and  $t_{fix}$  obtained by TRLS (Table 3) show that in both blends  $t_{fix}$  appears earlier than  $t_{gel}$ , suggesting that the morphologies are pinned up by the low mobility of the two components rather than by gelation.

The results of SEM show obvious co-continues phases in the SEM of both blends. The surface structure of the blends are evidently different, the F-blend gives a phase-inverted structure at the surface, while the P-blend has no distinctive structure, indicating there is a higher PIP concentration at the surface of the F-blend. It can also be seen from SEM that the volume fraction of the F-blend is higher than that of the P-blend. Though TRLS results suggest that the phase separation of the two blends both follow spinodal decomposition mechanism, the lower viscosity and slower curing rate of the F-blend should lead the phase separation to advance in the PEI-rich phase of the blend. Logically, the higher phase separation extent would lead to the bigger particle size. However, the effect of low surface energy of F-PIP has the trend to keep a larger interface between the two phases, i.e., the reason the size of epoxy-rich particles in the F-blend matrix is smaller than that in the P-blend matrix. Meanwhile, the F-PIP enriches at the surface and appears as a phase inversion due to the same reason. Therefore, it is reasonable to attribute the variant morphologies to the difference of surface energy of the PIP in these two blends and it can be learned that kinetics is a control factor in the phase separation of the two blends.

**Table 3.**  $t_{cp}$  obtained by TRLS and rheology and  $t_{gel}$ .

	P-PIP	F-PIP
$t_{cp}$	780	930
$t_{fix}$	1,140 s	1,500 s
$t_{gel}$	3,900 s	4,190 s





However, there are still questions that require further investigations, the most crucial one is how the surface energy affects the behavior of phase separation of the blend systems.

### CONCLUSION

This preliminary study on the effect of surface energy on reaction-induced phase separation displays a very interesting finding that the fluorocarbon-terminated group on the PEI chain would cause such a change in both the curing reaction and phase separation. The effect of low surface energy of F-PIP has the trend to keep a larger interface between the two phases. The size of the epoxy-rich particles in the F-blend matrix is smaller than that in the P-blend matrix, meanwhile, the F-PIP enriches at the surface and appears as a phase inversion. By studying the properties of different PIP surfaces, the F-PIP and P-PIP give a different surface energy and it could be concluded that kinetics is a control factor in the phase separation of the two blends due to their difference of surface energy of the PEI chain.

### ACKNOWLEDGMENT

Project 50043011 was supported by the National Science Foundation of China.

### REFERENCES

1. Min, B.G.; Hodgkin, J.H.; Stachurski, Z.H. Reaction-mechanisms, microstructure, and fracture properties of thermoplastic polysulfone-modified epoxy-resin. *J. Appl. Polym. Sci.* **1993**, *50* (6), 1065–1073.
2. Martinez, I.; Martin, M.D.; Eceiza, A.; Oyanguren, P.; Mondragon, I. Phase separation in polysulfone-modified epoxy mixtures. *Polymer* **2000**, *41* (3), 1027–1035.
3. Bucknall, C.B.; Partridge, I.K. Phase separation in epoxy resins containing polyethersulphone. *Polymer* **1983**, *24* (5), 639–644.
4. Raghava, R.S. Development and characterization of thermosetting-thermoplastic polymer blends for applications in damage-tolerant composites. *J. Polym. Sci. Part B: Polym. Phys.* **1988**, *26* (1), 65–81.
5. Kim, B.S.; Chiba, T.; Inoue, T. Phase-separation and apparent phase dissolution during cure process of thermoset thermoplastic blend. *Polymer* **1995**, *36* (1), 67–71.
6. Bennett, G.S.; Farris, R.J.; Thompson, S.A. Amine-terminated poly(aryl ether ketone)-epoxy amine resin systems as tough high-performance materials. *Polymer* **1991**, *32* (9), 1633–1641.
7. Biolley, N.; Pascal, T.; Sillon, B. Polyimide-modified epoxy system-time-temperature transformation diagrams, mechanical and thermal-properties. *Polymer* **1994**, *35* (3), 558–564.
8. Kimoto, M.; Mizutani, K. Blends of thermoplastic polyimide with epoxy resin. *J. Mater. Sci.* **1997**, *32* (9), 2479–2483.





9. Bucknall, C.B.; Gilbert, A.H. Toughening tetrafunctional epoxy resins using polyetherimide. *Polymer* **1989**, *30* (2), 213–217.
10. Hourston, D.J.; Lane, J.M. The toughening of epoxy-resins with thermoplastics. 1. Trifunctional epoxy-resin polyetherimide blends. *Polymer* **1992**, *33* (7), 1379–1383.
11. Varley, R.J.; Hodgkin, J.H.; Hawthorne, D.G.; Simon, G.P. Toughening of a trifunctional epoxy system. 2. Thermal characterization of epoxy/amine cure. *J. Appl. Polym. Sci.* **1996**, *60* (12), 2251–2263.
12. Kim, Y.S.; Kim, S.C. Properties of polyetherimide/dicyanate semi-interpenetrating polymer network having the morphology spectrum. *Macromolecules* **1999**, *32* (7), 2334–2341.
13. Inoue, T. Reaction-induced phase-decomposition in polymer blends. *Prog. Polym. Sci.* **1995**, *20* (1), 119–153.
14. Rong, M.Z.; Zeng, H.M. Polycarbonate-epoxy semi-interpenetrating polymer network. 2. Phase separation and morphology. *Polymer* **1997**, *38* (2), 269–277.
15. Liang, H.; Favis, B.D.; Yu, Y.S.; Eisenberg, A. Correlation between the interfacial tension and dispersed phase morphology in interfacially modified blends of LLDPE and PVC. *Macromolecules* **1999**, *32* (5), 1637–1642.
16. Bonnet, A.; Pascault, J.P.; Sautereau, H.; Camberlin, Y. Epoxy-diamine thermoset/thermoplastic blends. 1. Rates of reactions before and after phase separation. *Macromolecules* **1999**, *32* (25), 8517–8523.
17. Bonnet, A.; Pascault, J.P.; Sautereau, H.; Camberlin, Y. Epoxy-diamine thermoset/thermoplastic blends. 2. Rheological behavior before and after phase separation. *Macromolecules* **1999**, *32* (25), 8524–8530.
18. Kim, S.C.; Ko, M.B.; Jo, W.H. The effect of the viscosity of epoxy prepolymer on the generated morphology in rubber-toughened epoxy-resin. *Polymer* **1995**, *36* (11), 2189–2195.
19. Cui, J.; Chen, W.J.; Zhang, Z.C.; Li, S.J. Studies on the phase separation of polyetherimide-modified epoxy resin. 1. Effect of curing rate on the phase structure. *Macromol. Chem. Phys.* **1997**, *198* (6), 1865–1872.
20. Cui, J.; Yu, Y.F.; Li, S.J. Studies on the phase separation of polyetherimide-modified epoxy resin, 3-Part 1-Morphology development of the blend during curing. *Macromol. Chem. Phys.* **1998**, *199* (8), 1645–1649.
21. Wu, X.G.; Cui, J.; Ding, Y.F.; Li, S.J.; Dong, B.Z.; Wang, J. Studies on the phase separation of poly(ether imide)-modified epoxy resin, 5-phase separation behavior of a Quasi-binary system. *Macromol. Rapid. Commun.* **2001**, *22* (6), 409–413.
22. Willemse, R.C.; Posthuma de Boer, A.; Van Dam, J.; Gotsis, A.D. Co-continuous morphologies in polymer blends: the influence of the interfacial tension. *Polymer* **1999**, *40* (4), 827–834.
23. Ton-That, C.; Shard, A.G.; Bradley, R.H. Effects of annealing on the surface composition and morphology of PS/PMMA blend. *Macromolecules* **2000**, *33* (22), 8453–8459.
24. Tran-Cong, Q.; Kawakubo, R.; Sakurai, S. Effects of chemical labeling on the phase-behavior of poly(2-chlorostyrene) poly(vinyl methyl-ether) blends. *Polymer* **1994**, *35* (6), 1236–1241.
25. Li, Z.H.; Zhang, X.M.; Tasaka, S.; Inagaki, N. The interfacial tension and morphology of reactive polymer blends. *Mater. Lett.* **2001**, *48* (2), 81–88.





26. Moschiar, S.M.; Riccardi, C.C.; Williams, R.J.J.; Verchere, D.; Sautereau, H.; Pascault, J.P. Rubber-modified epoxies. 3. Analysis of experimental trends through a phase-separation model. *J. Appl. Polym. Sci.* **1991**, *42* (3), 717–735.
27. Chen, J.P.; Lee, Y.D. A real-time study of the phase-separation process during polymerization of rubber-modified epoxy. *Polymer* **1995**, *36* (1), 55–65.
28. Brostow, W.; Cassidy, P.E.; Hagg, H.E.; Jaklewicz, M.; Montemartini, P.E. Fluoro-polymer addition to an epoxy: phase inversion and tribological properties. *Polymer* **2001**, *42* (19), 7971–7977.
29. Yoon, S.C.; Ratner, B.D.; Ivan, B.; Kennedy, J.P. Surface and bulk structure of segmented poly(ether urethanes) with perfluoro chain extenders. 5. Incorporation of poly(dimethylsiloxane) and polyisobutylene macroglycols. *Macromolecules* **1994**, *27* (6), 1548–1554.
30. Ming, W.H.; Laven, J.; Van der Linde, R. Synthesis and surface properties of films based on solventless liquid fluorinated oligoester. *Macromolecules* **2000**, *33* (18), 6886–6891.
31. Sun, F.; Castner, D.G.; Mao, G.; Wang, M.; McMeown, P.; Grainger, D.W. Spontaneous polymer thin film assembly and organization using mutually immiscible side chains. *J. Am. Chem. Soc.* **1996**, *118* (8), 1856–1866.
32. Li, M.; Jiang, M.; Zhang, Y.; Qin, F. Fluorescence studies of hydrophobic association of fluorocarbon-modified poly(n-isopropylacrylamide). *Macromolecules* **1997**, *30* (3), 470–478.
33. Chen, W.J.; Li, X.L.; Dong, T.; Jiang, M. Spinodal decomposition induced by cross-linking reaction in a binary polymer mixture. *Macrol. Chem. Phys.* **1998**, *199* (2), 327–333.
34. Hashimoto, T.; Itakura, M.; Hasegawa, H. Late stage spinodal decomposition of a binary polymer mixture. I. Critical test of dynamical scaling on scattering function. *J. Chem. Phys.* **1986**, *85* (10), 6118–6128.
35. Kim, B.S.; Nakamura, G.; Inoue, T. Structure development in the phenolic resin poly(methyl methacrylate-co-ethyl acrylate) copolymer blends. *J. Appl. Polym. Sci.* **1998**, *68* (11), 1829–1837.

Received September 2002

Revised February 2003

