Effect of surface energy on reaction-induced phase separation of Epoxy resin modified with polyetherimide

Shanjun Li, Hua Li, Wenjun Gan, Xinghai Yu[1]

Department of Macromolecular Science and the Key Laboratory of Macromolecular Engineering of Polymer, Ministry of Education,Fudan University, Shanghai, 200433, China

[1] Shanghai research institute of synthetic resins

SUMMARY

Phenyl terminated and fluorocarbon chain terminated polyetherimide is added to epoxy resin, and the effect of surface energy on the structure formation of polyetherimide modified epoxy systems is studied by time-resolved light scattering (TRLS), differential scanning calorimeter (DSC), scanning microscopy (SEM) and rheometer. SEM shows phase separation of F-blend system goes further and finally smaller epoxy-rich particles and thicker PEI-rich layers are generated. DSC and TRLS experiments indicate that the P-PIP/Epoxy blend has higher curing rate and phase separation rate than the F-PIP/Epoxy blend. Rheology experiment displays the viscosities of the two systems are different. The viscosity of P-PIP/Epoxy blend is higher than that of F-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 polyetherimide chain.

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 Tg thermoplastics has been investigated. Results of thermoplastic toughening of epoxy resins, such as polysulfone (PSF), polyethersulfone (PES), poly(ether ether ketone) (PEEK), polyetherimide (PI), polyetherimide (PEI) and nylon 66, show that the improvement in fracture toughness is achieved without the expense of modulus at elevated temperature. It is also of special interests to scientists for theoretical importance in reaction-induced phase separation processes[1-5]. In our previous work, a series of novel polyetherimide was synthesized and used to modify thermosetting resin, the modified resin displays toughening effect without sacrificing other important properties[6-8].

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, the molecular weight of the polymer, the curing temperature, the curing agent, and the 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[9]. Much work has been done to study the influence of interfacial tension on morphologies[10-12], 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 [13,14], and recently, it is reported that phase inversion are obtained by the low free surface energy of thermoplastic (30% of 12F-PEK)[15].

In recent years, many of studies have been done on fluorocarbon-modified polymers because under certain conditions these polymer have the inclination to self-assemble or self-stratify[16-18]. In many occasions, fluorocarbon chain with certain lengths can be enriched at the surface or the interface of the polymers, and for this reason it can change the surface energy of polymers significantly. To study the effect of surface energy on reaction-induced phase separation, a kind of fluorocarbon chain terminated polyetherimide was synthesized and used as a modifier of epoxy resin, and some tentative explanations are provided based on the experimental results.

Experimental Part

Materials

The epoxy oligmer used in the study was diglycidyl ether of bisphenol A, Dow 331 (epoxy equivalent 182-192g/eq). Perfluorooctanoic acid, PCl_5 and aluminum chloride were purchased commercially and used as received. The cure agent 4,4'-diaminodiphenyl sulphone (DDS) (Shanghai Third Reagent Factory) was used without further purification.

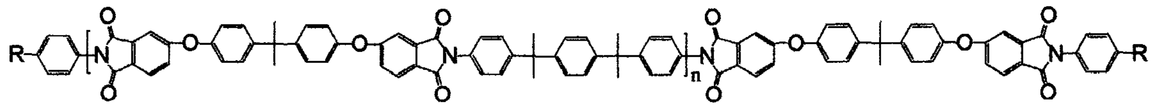
Synthesis

Perfluorooctanoyl Chloride was prepared as mentioned in literature[19].

p-Aminoperfluorooctanophenone was synthesized from perfluorooctanoyl chloride and acetanilide through Friedel-Crafts reaction under the catalysis of aluminum chloride. The product was recrystallized in mathonal and the yield was about 58% (m.p. 103-104℃). FTIR (KBr): 1701cm^{-1}(s, C=O), 1395, 1335, 1200 and 1146cm^{-1} (vs, C-F), 3064cm^{-1} (w, aromatic C-H), 3364cm^{-1} (s, NH_2). NMR ^1H ($CDCl_3$): δ8.21 ppm (d, 2H) 7.42 ppm (d, 2H), 3.56 ppm (s, 3H).

The polyetherimide (PEI) was synthesized by one step from bisphenol-A dianhydride(BISA-DA) and 4,4'-[1,4-phenylenebis(1-methylethylidene)]bisaniline (BISP) at a stoichiometric ratio of 1:0.985 in *m*-cresol at 200 ℃, 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 structure of PIP is depicted below:



R = H P-PIP

$CO(CF_2)CF_3$ F-PIP

The inherent viscosity of PIP was 0.69 dL/g and its Tg was 220℃.

Techniques

The inherent viscosity of PIP was obtained in the concentration 0.5g/dL at 30℃ in N-methyl-2pyrrolidone 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℃. After a homogeneous, the blend was then cooled to 130℃, 31 phr of 4,4'-diaminodiphenyl sulphone (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 lower extent. So was the specimen of epoxy and Fluorocarbon-terminated PIP. The two blend systems were assigned as P-blend for epoxy/PIP and F-blend for epoxy-F-PIP respectively.

The glass transition temperatures (Tg) of Polyetherimides were determined by differential scanning calorimeter (SETARAM DSC 92) from room temperature to 300°C at a heating rate of 10°C/min. Study of conversion of the two blend systems were also carried on DSC.

Scanning electron microscopy (SEM) 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 30s and then quickly pressed to thin films of about 5μm. The change of the light scattering profiles was recorded at appropriate time intervals during isothermal curing.

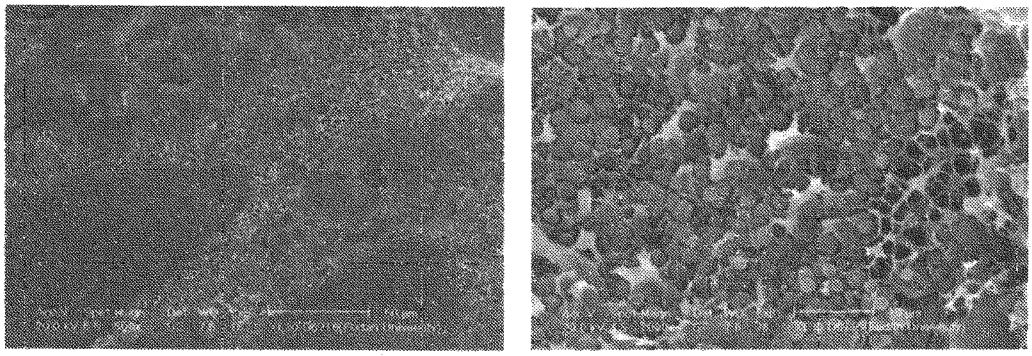
The rheology studies of the blends during curing were recorded on an Ares-4A rheometer: About 1g of the blend was sandwiched between two round fixtures and the temperature was quickly raised to the curing temperature. The two blends were tested under a parallel plate mode with a controlled strain of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

The contact angles were also measured by syringing deionized water on a 50μm-thick F-PIP or P-PIP films on a NRL Contact Angle Goniometer (RH Imaging 2001, Ramé-Hart, Inc).

Results and discussion

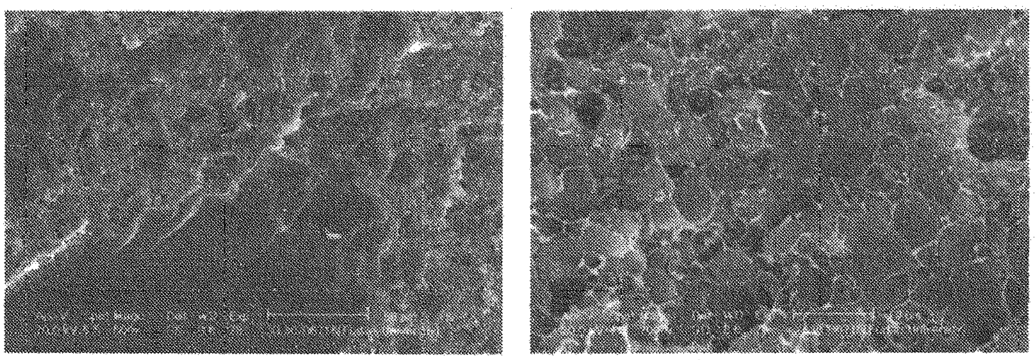
Morphology of cured blends

For SEM observation the blends are cured at 150℃ for three hours to ensure that the morphologies are fully fixed. (Figure 1, Figure 2)



(a) (b)

Figure 1. Scanning electron micrographs of F-blend cured at 150℃ for 3h (a) fracture surface; (b) magnification of the bright region



(a) (b)

Figure 2. Scanning electron micrographs of P-blend cured at 150℃ for 3h (a) fracture surface; (b) magnification of the bright region

The morphology of the two cured blends is similar to each other. There is an obvious co-continues phase in SEM of both blends. A notable fact is that the sizes of the dispersed epoxy particles of the two blend systems are different. And in contrasts of the magnification photo it can be seen the F-blend gives a thicker PEI-rich layer. Therefore, it suggests that the extent of phase separation is higher in F-blend than that in P-blend.

Conversion and curing rate difference

An aluminum pan containing samples was put into the DSC while the instrument reached the preset temperature of 150℃. 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 heat of cure (ΔH_{iso}). After that, the sample was cooled to 30℃ and then was scanned at a heating rate of 10℃/min from 50℃ to 400℃ to determine the residual heat of reaction (ΔH_t). The isothermal conversion at time t was defined as $\alpha(t) = \Delta H_{\mathrm{iso}}(t)/\Delta H_t$. (Figure 3)

℃

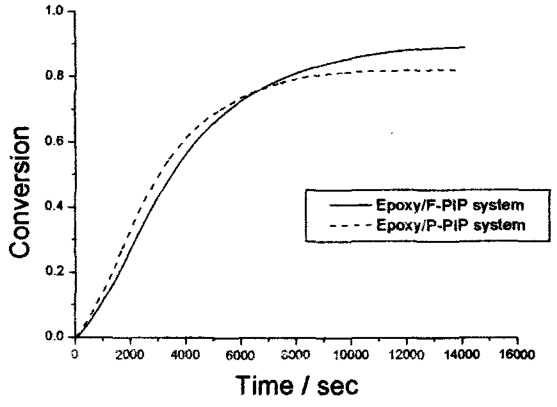
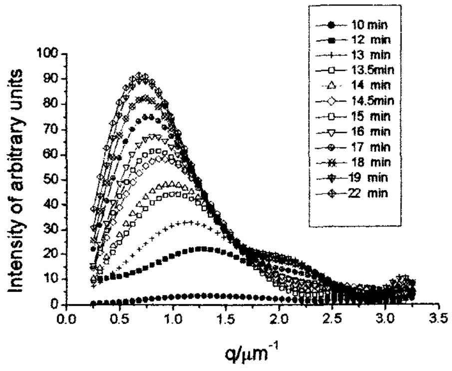


Figure 3. Conversion of Epoxy/F-PIP and Epoxy/P-PIP systems cured at 150

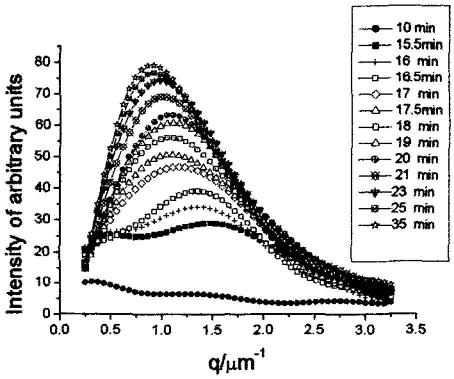
Figure 3 demonstrates the conversion via time curves of the two different systems. Obviously the P-blend shows a faster curing rate while the F-blend displays a slower one. After a certain time, the conversion of P-blend remains constant and that of F-blend continues to increase until it exceeds the conversion extent of P-blend.

Phase separation observed by light scattering

The Epoxy/PIP blend with DDS was single-phase systems at the curing temperature and showed no appreciable light scattering in the early stages of curing. After a certain time lag, scattering light appeared because of the development of a phase-separation structure. Figure 4 shows that the changes in the light scattering profiles of the blends containing different polyetherimides at 150℃. After about 12 minutes, the profile of P-blend appears a peak. The scattering intensity of the peak stops increasing after about 22 min and then begins to decrease slightly before it finally becomes invariant, which may result from the decrease in the difference of the reflection indices of the two phases[7]. The peak vector q_m is about 0.69 μm^{-1} at last (Figure 4 a), while the blends of F-blend give a peak at 15 min and finally the peak vector is about 0.91 μm^{-1}at a time lag about 35 min (Figure 4 b). 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 gives a rapidly increase shifting to a small scattering angle at the early stage of the curing reaction and finally slow down. Base on the above observation, one can estimate that the phase separation of the two blend systems both followed spinodal decomposition mechanism.



(a)



(b)

Figure 4. Change of lighting-scattering profile of blend E/PPIP (a) and E/FPIP (b) cured at 150℃

The separation rate can be characterized as the slope of linear variation of $I(q_m, t)$ at the initial stage of phase separation[6,20]. The phase separation rate of P-blend is a little faster than that of the F-blend (Tab 1), which also supports the DSC result.

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

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

Rheological behavior of blend system during curing process

Rheology is a signature of connectivity. Figure 5 gives two plotted curves of the complex viscosity η*. For P-blend (20phr) the curve process a gradual increase in viscosity and after several minutes a decrease of η* was observed (Figure 5).

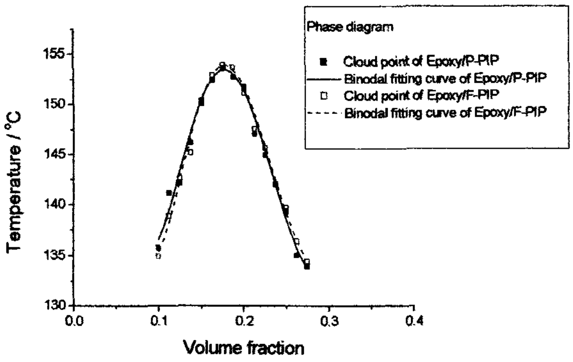


Figure 5 Cloud points and binodal fitting curves of F-blend and P-blend

Figure 5 also demonstrates that there is no great difference at the beginning of curing process, but the systems' difference increases as the curing reaction proceeds, the viscosity of P-blend is higher than the F-blend.

Phase diagram

To discuss the phase separation behavior, the phase diagrams were plotted by measuring cloud point of different concentrations of PEI (Figure 6). P-PIP and F-PIP was dissolved in a kind of home-made epoxy resin (epoxy equivalent 500g/eq) at 150℃ and then cast on glass. The samples were observed by a Leitz optical microscopic which has a controllable hot chamber.

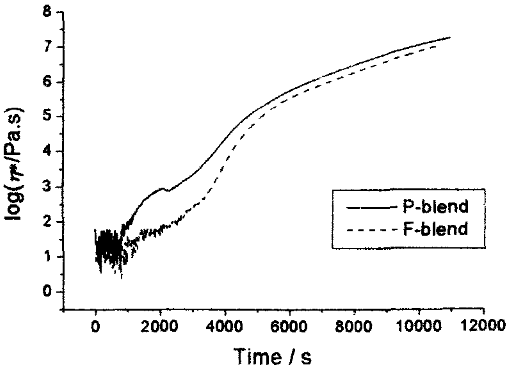
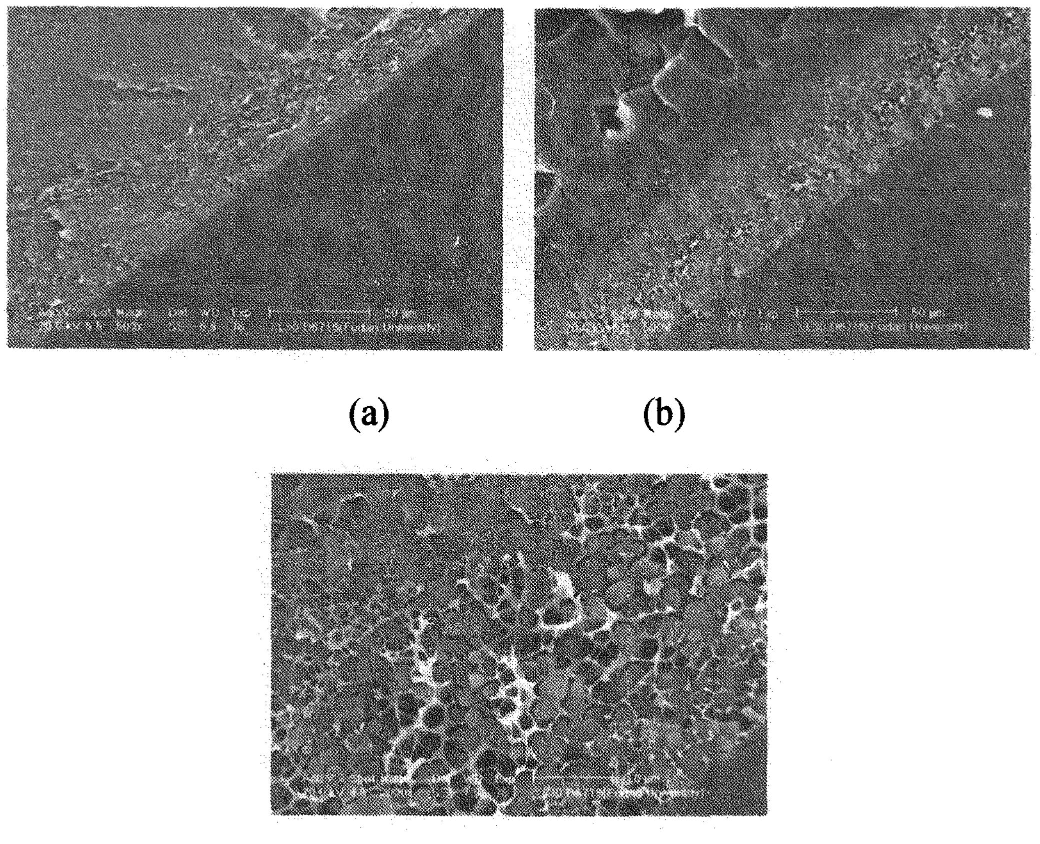


Figure 6. Rheological behavior of blend P-blend and F-blend

The two diagrams are similar, which means there is no obvious difference in the effect of thermodynamics on phase separation of the two systems. They are both typically UCST systems and the cloud points of same concentration of the two systems are close to each other. It is known that the phase separation mechanism is relevant to the type of phase diagram[21], based on these facts we consider that the kinetic factor, which is induced by change in surface energy, is the first cause lead to the different phase separation behavior during the curing processes.

Study on properties of PEI surface

To explain the difference of phase separation of the two blends, the unreacted epoxy resin containing 31phr DDS was poured onto a 1mm-thick PEI film and then was cured at 150℃ under pressure. The fracture surface of the samples were studied by SEM (Figure 7).



(a) (b)

(C)

Figure 7. SEM of interfacial structure between Epoxy and PIP cured at 150℃, (a) F-blend blend (b) P-blend blend (c) magnification of interfacial structure of (b)

In the case of the F-blend, the interface is very thin and no distinct morphology is observed. However, in the P-blend sample, an interface about 60μm or thicker is created with dispersed epoxy-rich particles in the P-PIP matrix, which is typical phase inverted morphology.

The contact angles were measured on both sides of 3 drops of deionized water, the difference was normally within 2°, and the results list in Tab 2 were averaged.

The results show that the change in surface energy leads to a lower matrix viscosity in this system, finally affecting the morphology of the cured blend.

	F-PIP	**P-PIP**
Contact angle	**74.00**	**68.20**

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

Discussion

Based on the results mentioned above, we try to make some tenable explanations of the difference between the blend systems.

The morphology of the two cured blends is similar to each other. There is evident co-continues phase in SEM of both blends, but the sizes of the dispersed particles of the two blend systems are different, F-blend gives a thicker PEI-rich layer and smaller epoxy-rich particles. Thermodynamics of phase separation of the two blends should be similar based on their phase diagrams, so it is reasonable to attribute the variant morphologies to the kinetic factor induced by the difference of surface energy of the two blends.

Obviously the contact angles of deionized water on the two PEI films are different from each other. The dissimilar wetting shows that the films have different surface energy, which can be defined as the enrichment of the fluorocarbon chains on the surface. For this reason, the epoxy resin is hard to infiltrate into the F-PIP films. On the contrary, the epoxy resins go into the P-PIP film easily and ultimately generate a full phase inversion structure

The rheology curves of the two systems are also distinct. They suggest that the decrease of η^* in P-blend is due to the beginning of the phase separation process: The initially dissolved highly viscous P-PIP component separates from the epoxy-rich matrix[4] and the viscosity declines, then the viscosity is gradually increases with cure. But the decrease disappears in the curve of F-blend system, which also displays a lower viscosity than that of P-blend during the phase separation process. The fluorocarbon chains counteract the diffusion of the molecules and the phase separation process of this system is slower.

When the co-continuous is originally formed, the lower surface energy weakens the interaction between the epoxy-rich phase and PEI-rich phase. The lower viscosity and curing rate of F-blend system will bring on a time lag in phase separation. For the same reason, the phase separation in PEI-rich phase of F-blend system can go further and finally smaller epoxy-rich particles and thicker PEI-rich layers are generated. At the same time, from the structure of P-blend, it is obvious that this system has a lower phase separation extent.

So it could be concluded that kinetics is a control factor in their phase separation due to their difference of surface energy of polyetherimide chain.

In this study, we have made some preliminary studies on the effect of surface energy on reaction-induced phase separation of epoxy resin modified with polyetherimide. However, there are still questions that require further investigations. The most crucial one is that there is not an explicit theory about change in surface energy affecting the morphologies of the blend systems yet. More studies will be carried out to get a better interpretation.

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