Effect of molecular weight on reaction-induced phase separation of epoxy resin modified with fluorocarbon chain terminated polyetherimide

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Abstract A series of fluorocarbon chain terminated polyetherimide is added to epoxy resin, and the effect of molecular weight on the process of phase separation is studied by time-resolved light scattering (TRLS), differential scanning calorimeter (DSC), scanning microscopy (SEM). The results indicate that the phase separation rate decreases due to the preventing effect induced by low surface energy of fluorocarbon chain terminated polyetherimide. In addition, evolution time of morphology is shortened and the domain size decreases with the introduction of fluorocarbon chain terminated polyetherimide. Furthermore, when the molecular weight of fluorocarbon chain terminated polyetherimide increases, the morphology can change from dispersed phase to co-continuous phase. Thus, changing the molecular weight of fluorocarbon chain terminated polyetherimide can control the morphology of the epoxy/polyetherimide blend, which is of great significance in many industries.

Keywords: fluorocarbon chain terminated polyetherimide, epoxy, molecular weight, reaction-induced phase separation, time-resolved light scattering.

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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. Thus, the modifications of epoxy resins with rubbers, which can greatly enhance the toughness of the resin systems, have been studied for several decades. Nevertheless, the modulus and Tg are inevitably decreased with the introduction of rubber particles, which certainly confines the application of this method. Fortunately, results of thermoplastic toughening of epoxy resins, such as polysulfone (PSF)[1], polyether-sulfone (PES)[2], poly(ether ether ketone) (PEEK)[3], polyetherimide (PI)[4], polyetherimide (PEI)[5,6] and nylon 66, show that the improvement in fracture toughness can be achieved without the expense of modulus at elevated temperature.

From the 1980s, studies on the phase separation of thermoplastic modified epoxy resins have been employed[7,8], which clearly indicated the relationship between the mechanical properties and specific morphology. Among different structures, co-continuous or phase inverted structure can greatly increase the mechanical properties of the blends. As a result, it is of special interests for scientists to investigate the process of reaction-induced phase separation, from which a variety of morphologies can be obtained by changing
the composition, the molecular weight of the polymer, the curing temperature and the curing agent. Moreover, it is also reported that the interfacial tension can greatly influence the morphologies. Willemse\textsuperscript{[9,10]} found that the composition range for full co-continuity and the stability of the co-continuous structure could be improved by decreasing the interfacial tension between blends. Gerard\textsuperscript{[11-13]} suggested that the size of thermoplastic dispersed phase can be significantly changed with the introduction of compatibilizer. Besides, in the research of polyphenylene ether (PPE)- and polyetherimide (PEI)-modified epoxy networks, Pascault\textsuperscript{[13]} proposed that the size of the particles could be clearly changed when a small amount of poly(caprolactone-b-dimethylsiloxane-b-caprolactone) triblock copolymer was employed.

In our previous work, a series of novel miscible polyetherimide was synthesized and used to modify diglycidyl ether of bisphenol A (DGEBA) and tetraglycidil-4,4 -diamino diphenylmethane (TGDDM) resins\textsuperscript{[14,15]}, and the modified resin displays toughening effect without sacrificing other important properties. In addition, 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, which is able to control the final morphology of the system to some degree\textsuperscript{[16,17]}. To further study the effect of surface energy on reaction-induced phase separation, a series of fluorocarbon chain terminated polyetherimide was synthesized and used as a modifier of epoxy resin, and the influence of PEI molecular weight on the phase separation was discussed.

1 Experimental

1.1 Materials

4,4-[1,4-phenylenebis(1-methylethylidene)]bisaniline (BISP) and bisphenol-A dianhydride (BISA-DA) were provided by Shanghai Synthetic Resin Institute. Perfluorooctanoic acid, PCl\textsubscript{5} and aluminum chloride were purchased commercially and used as received. The epoxy oligmer used in the study was diglycidyl ether of bisphenol A, Dow 331 (epoxy equivalent 182 – 192 g/eq). The cure agent 4,4 -diaminodiphenyl sulphone (DDS) (Shanghai Third Reagent Factory) was used without further purification.

1.2 Synthesis

The polyetherimide (P-PIP) and fluorocarbon chain terminated polyetherimide (F-PIP) were prepared as mentioned in literature\textsuperscript{[17]}.

The structure of PIP is depicted in Fig. 1. The viscosity and T\textsubscript{g} of different PEI with different BISA-DA/BISP content are listed in Table 1.

Table 1  The viscosity and Tg of polyetherimide

<table>
<thead>
<tr>
<th>BISA-DA: BISP (mol: mol)</th>
<th>n (dL·g(^{-1}))</th>
<th>Tg((^{\circ}\text{C}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1: 0.985</td>
<td>0.69</td>
<td>220</td>
</tr>
<tr>
<td>1: 0.975</td>
<td>0.51</td>
<td>215</td>
</tr>
<tr>
<td>1: 0.955</td>
<td>0.31</td>
<td>211</td>
</tr>
</tbody>
</table>

a) The inherent viscosity of PIP was obtained at the concentration 0.5 g/dL at 30\(^{\circ}\text{C}\) in N-methyl-2-pyrrolidone as solvent. b) The glass transition temperatures (Tg) of polyetherimides were determined by a differential scanning calorimeter (SETARAM DSC 92) from room temperature to 300\(^{\circ}\text{C}\) at a heating rate of 10\(^{\circ}\text{C}/\text{min}\).

Epoxy blends containing 20 phr (per hundred resin) of phenyl-terminated PIP were prepared by dissolving PIP in epoxy resins at 150\(^{\circ}\text{C}\). After a homogeneous, the blend was then cooled to 130\(^{\circ}\text{C}\), 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

![Fig. 1. Chemical structure of PEI.](image-url)
Fluorocarbon-terminated PIP. The two blend systems were preserved at 0°C and assigned as P-blend (x) for P-PIP/DGEBA/DDS and F-blend (x) for F-PIP/DGEBA/DDS respectively, where x presented the viscosity of PIP.

1.3 Techniques

(i) An aluminum pan containing samples was put into the differential scanning calorimeter (SETARAM DSC92) 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 heat of cure \( \Delta H_{iso} \). After that, the sample was cooled to 30°C and then was scanned at a heating rate of 10°C/min from 50 to 400°C to determine the residual heat of reaction \( \Delta H_r \). The sum of \( \Delta H_{iso} \) and \( \Delta H_r \) gives the total heat of cure \( \Delta H_t \). The isothermal conversion at time \( t \) \( (\alpha(t)) \) was defined as

\[
\alpha(t) = \frac{\Delta H_{iso}(t)}{\Delta H_t}.
\]

(ii) Scanning electron microscopy (SEM) was carried out on a Philip XL39 SEM instrument.

(iii) The phase separation process during curing reaction was observed at real time and in situ on the self-made time resolved light scattering (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.

(iv) The contact angles were measured by syringing deionized water on 50 µm-thick F-PIP or P-PIP films, which are put on a NRL Contact Angle Goniometer (RH Imaging 2001, Ramé-Hart, Inc.). The difference between both sides of 3 drops of deionized water was normally within 2°, and the results listed in Table 2 were averaged.

2 Results and discussion

2.1 The influence of fluorocarbon-terminated group on the surface energy

The contact angles were measured on the films of different systems that all cured at 180°C, and the results are listed in Table 2.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Contact angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>F-PIP</td>
<td>74.0</td>
</tr>
<tr>
<td>P-PIP</td>
<td>68.4</td>
</tr>
<tr>
<td>F-blend</td>
<td>71.1</td>
</tr>
<tr>
<td>P-blend</td>
<td>64.1</td>
</tr>
</tbody>
</table>

It is well known that the bigger the contact angle, the lower the surface energy is. Thus, conclusion can be drawn from Table 2 that the surface energy of the blend is lowered with the introduction of fluorocarbon chain terminated PEI.

2.2 The influence of molecular weight of Fluorocarbon chain terminated PIP on morphology

For SEM observation, the blends are cured at 150°C for three hours to ensure that the morphologies are fully fixed. In Fig. 2, relatively white areas present PIP rich phase, while dark areas present epoxy rich phase. It is clear that F-blend (0.31) and P-blend (0.31) both exhibit PIP dispersed phase, which is unfavorable for excellent mechanical properties and thus the systems with 0.31 viscosity value are not further studied. While the systems with 0.51 and 0.69 viscosity value all present co-continuous phase structure. Furthermore, on each given viscosity system, the domain size of F-blend is smaller than that of P-blend, and the domain sizes in these systems all decrease with increasing molecular weight, especially for F-blend.

2.3 The influence of molecular weight of fluorocarbon chain terminated PIP on conversion and curing rate

Fig. 3 demonstrates the conversion via time curves of different systems. Obviously, profiles of systems with different PEI molecular weight share the same
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Fig. 2. SEM of (a) F-blend (0.31); (b) P-blend (0.31); (c) F-blend (0.51); (d) P-blend (0.51); (e) F-blend (0.69); (f) P-blend (0.69) cured at 150°C for 4 h.

tendency. The values of curing rates are close to each other in the initial stage of cure, after which P-blend shows a faster curing rate while F-blend displays a slower one. This is because the low surface energy of F-PIP prevents the epoxy from diffusion, thus decreases the curing rate.

2.4 Phase separation observed by time resolved light scattering (TRLS)

Time resolved light scattering was used to run after the process of phase separation. The peak scattering fact, \( q_m \), corresponding to the wave number of concentration fluctuation, is defined by \( q_m = (4\pi\lambda)\sin(\theta_m/2) \) \(^{17,18}\), 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 is assigned to the periodic distance of the dispersed particles (domain size), \( \Lambda_m \), which is defined by \( \Lambda_m = 2\pi\theta_m \). The smaller the characteristic wave number, the larger the periodic distance of the pinned structure (domain size) is. Fig. 4 shows the scattering profiles of
Fig. 3. Conversion of epoxy resin versus curing time at 150°C.

F-blend (0.51 and 0.69) and P-blend (0.51 and 0.69) with curing time at 150°C.

The profiles of these systems all exhibit one sharp peak and correspond to different scattering vectors.

The intensities of the peaks of these systems all 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 observations, one can estimate that the phase separation of these systems follows a spinodal decomposition mechanism\[18]\.

According to the TRLS results, separation rate \((v_p)\) can be characterized as the slope of linear variation of \(I(q_m, t)\) at the initial stage of phase separation. Besides, induction period \((t_{ind})\), fixed time of morphology \((t_{fix})\), evolution time of morphology \((t_{evol})\) and \(q_m\) all can be obtained (as shown in Table 3).

Obviously, on a given molecular weight of PEI, the phase separation rate of P-blend is a little faster than that of the F-blend due to the slow curing rate of F-blend. Besides, F-PIP with low surface energy prevent
the diffusion of epoxy and thus decrease the phase separation rate.

In addition, the value of \( q_m \) can be used to estimate the domain size. The larger the \( q_m \), the smaller the domain size is. The results listed above are well consistent with the results from SEM figures, which indicates that the domain size of F-blends is smaller than that of P-blends owing to the low surface energy of F-blend that prevents the epoxy from diffusion and coarsening.

Compared with the P-blend, the induction period of F-blend is longer, thus its \( t_{\text{ind}} \) is smaller than that of P-blend. It is well accepted that the phase separation process of PIP/epoxy systems is phase conversion, co-continuous phase, dispersed phase. In other words, during the whole phase separation process, the domain size increases gradually. Therefore, the domain size of F-blend is small because the gelation occurs before the final morphology can be obtained, which is in accordance with SEM figures.

On increasing the molecular weight of PEI, phase separation is speeded up, evidenced by the short induction period and large \( q_m \) (correspond to the small domain size), which results from the less compatibility between PEI and epoxy for the Flory-Huggins parameter is changed due to different degree of polymerization. When PEI with relatively high molecular weight is employed, the terminal fluorocarbon chain will play a more important role in the system and make a large difference on the process of phase separation between different systems.

### 3 Conclusion

Owing to the low surface energy induced by fluorocarbon chain terminated polyetherimide, the curing rates and final morphologies of the systems all have been influenced by the fluorocarbon chain. Compared with P-blend, F-blend exhibits lower curing rate after the initial stage of curing, lower phase separation rate, shorter evolution time of morphology and smaller domain size. With the increasing F-PEI molecular weight, the diffusion rate of epoxy decreases, followed by low curing rate; meanwhile, the compatibility between epoxy and PEI also decreases, which leads to a fast phase separation rate and thus the domain size is further diminished. Therefore, according to the results obtained here, it is possible to control the morphology of the epoxy/polyetherimide blend through fluorocarbon chain terminated polyetherimide with different molecular weight.

### References

5. Bonnet, A., Pascault, J. P., Sautereau, H. et al., Epoxy-diamine


