Hydrodynamic Effect on Secondary Phase Separation in an Epoxy Resin Modified with Polyethersulfone

Xiaolin Tang, 1 Linxia Zhang, 1 Tao Wang, 1 Yingfeng Yu, 1 Wenjun Gan, 2 Shanjun Li* 1

1 Department of Macromolecular Science and The Key Laboratory of Molecular Engineering of Polymers, Ministry of Education, Fudan University, Shanghai, 200433, China
Fax: (+86) 21-65640293; E-mail: sjli@fudan.edu.cn
2 Department of Macromolecular Materials and Engineering, College of Chemistry and Chemical Engineering, Shanghai University of Engineering Science, Shanghai, 200065, China

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Summary: The evolution of the morphologies in blends of epoxy/4,4'-methylenebis(2,6-dimethylaniline)/polyethersulfone was followed by time-resolved light scattering, optical microscopy and scanning electron microscopy. The results suggest that, once the diffusion of epoxy molecules cannot follow the geometrical growth, a secondary phase separation occurs, even in the droplet morphology, in which the size of the epoxy-rich domain grows as usual. The viscoelastic effect of polyethersulfone is also discussed.

Introduction

The secondary phase separation phenomena has been known since the beginning of the 1980’s. 1–6 Williams and co-workers investigated the phenomena of double phase separation in a polysulfone-modified epoxy resin system in 1999. 7 Recently, they explained the phenomenon of ternary thermoplastic-thermosetting blends by the evolution of phase diagrams with conversion. 8 It is well known that the increase of the domain size is mainly caused by the hydrodynamic flow and diffusion. The hydrodynamic effect on the secondary phase separation has been intensively studied from both experimental and theoretical viewpoints. Early in the 1990’s, Wiltizius found experimentally that there exists a fast mode (d ~ t^{3/2}, where \( d \) = domain size and \( t \) = time, much faster than hydrodynamic coarsening, \( d \approx t \), proposed by Siggia 9 for the bicontinuous phase separation) in the study of domain growth and wetting in the polyimide-poly(ethylene-propylene) system. 10 Tanaka et al., after studying the behavior of double phase separation in a symmetric binary fluid mixture, suggested that the double phase separation only occurs for nearly symmetric mixtures showing hydrodynamic coarsening driven by capillary instability, and is never observed for off-symmetric mixtures having a droplet morphology. 11 Subsequently, they demonstrated by numerical simulation that, in a 2D fluid mixture, high fluidity causes geometrical coarsening of the domain that is too fast for diffusion to follow. This forces the system out of equilibrium and induces secondary phase separation. They predicted that unusually fast growth of the domain (\( d \sim t^{3/2} \)) might induce a spontaneous double phase-separation phenomenon in a 3D fluid mixture. 12 By simulation, Yang et al. have shown that double phase-separation phenomena could be attributed to the coupling of hydrodynamics and a chemical reaction in a binary mixture with a reversible

Development of morphologies followed by OM: bicontinuous phase separation in the PES-15.9 blend cured at 140 °C after 80 s.
reaction system. These results imply that double phase separation will occur spontaneously in the case of low viscosity and low reaction rate.\textsuperscript{[13]} It should be noted, however, that in thermost/thermoplastic blends, actual models are not able to provide a realistic description of phase separation due to the coupling between the polymerization reaction and phase separation, as well as the occurrence of gelation of the epoxy-rich phase and vitrification of one or both phases.

For the dynamic asymmetric system, Tanaka proposed that the viscoelastic effect would play an important role in phase separation and that the diffusion flow of the fast dynamic phase was prevented by the slow dynamic phase.\textsuperscript{[14]}

In our previous work, viscoelastic effects were found in a study on reaction-induced phase separation in thermoplastic-modified thermostettings.\textsuperscript{[15,16]} Meanwhile, secondary phase separation was observed under certain conditions in the blends of polyethersulfone (PES) modified epoxy resin.

Nevertheless, so far, the hydrodynamic effect on the secondary phase separation in the dynamic asymmetric system has seldom been discussed. In the present work, phase separation of epoxy/PES/4,4′-methylenebis(2,6-dimethylaniline) blends with various PES contents was investigated by time-resolved light scattering (TRLS), optical microscopy (OM) and scanning electron microscopy (SEM) at different curing temperatures. The $T_g$ of PES is 188°C and that of the reactive epoxy resin at the cloud point is below 20°C, thus this system should be a dynamic asymmetric system. The aim of this paper is to discuss the hydrodynamic effects on secondary phase separation with varying PES content at different curing temperatures.

**Experimental Part**

**Materials and Samples Preparation**

The epoxy oligomer DER 331, a low-molecular-weight liquid diglycidyl ether of bisphenol A (DGEBA) with an epoxide equivalent of 182–192, was provided by Dow Chemical Co. Polyethersulfone (PES) was supplied by Jilin University, China, with a weight-average molecular weight of 9600 g/mol ($T_g =$ 188°C). The curing agent 4,4′-methylenebis(2,6-dimethylaniline) (DIM-DDM) was purchased from Aldrich Chemical Company Inc.

The blends with PES 15.9 wt.-% (DGEBA/PES/DIM-DDM: 100:25:32 wt.-%, PES-15.9 blend), PES 18.5 wt.-% (DGEBA/PES/DIM-DDM: 100:30:32, PES-18.5 blend) and PES 21.0 wt.-% (DGEBA/PES/DIM-DDM: 100:35:32, PES-21.0 blend) were prepared by dissolving the PES in DiGDBA at 150°C. The mixture was cooled to 100°C until a homogeneous solution was obtained. After that a stoichiometric amount of curing agent DIM-DDM was added, with stirring, and the blend was then cooled rapidly to room temperature to avoid further curing.

**Results and Discussion**

**SEM Morphologies**

SEM micrographs of the fracture surface of the cured samples are shown in Figure 1. The PES-15.9 blend cured at 140°C (Figure 1a) displays the usual phase-in-phase morphology similar to that described previously.\textsuperscript{[4–7]} The secondary phase separation took place in both phases, which might be due to the interfacial quench-effect proposed by Tanaka.\textsuperscript{[11]}

The SEM micrographs of the PES-18.5 blend show an inversion morphology: epoxy-rich domains (≥5 μm) dispersed in a PES-rich matrix. In the membrane-like, PES-rich matrix, there are few smaller epoxy-rich particles at a curing temperature of 120°C (Figure 1b). However, the number of smaller epoxy particles increased with curing temperature as shown in Figure 1c and 1d and a number of smaller epoxy particles (about 2–4 μm) at 170°C (Figure 1d) in the PES-rich matrix. This indicates that there is probably a secondary phase separation in the droplet morphology at higher curing temperatures.

For the PES-21.0 blend, the smaller epoxy-rich particles (about 1–2 μm) are found in the PES-rich matrix particles at 170°C (Figure 1f). The secondary phase separation does not occur at a curing temperature of 140°C (Figure 1e).

**Evolution of Phase Morphologies (OM)**

Figure 2 shows that a bicontinuous phase structure appears at the beginning of the phase separation in the PES-15.9 and PES-18.5 blends, the conversion of which at the cloud point ($x_{cp}$) is 0.22 for PES-15.9 at 140°C, 0.39 for PES-18.5 at 120°C, and 0.23 for PES-18.5 at 140°C. The $T_g$ of the reactive epoxy resin for the PES-15.9 blend at 140°C, the PES-18.5 blend at 140°C and the PES-18.5 blend at 120°C is about 7°C, 7°C and 18°C, respectively. For this LCST (lower critical solution temperature) system, it is easy to understand the above results.
Meanwhile, there exists an elastic regime, in which the elastic force balance dominates the morphology, rather than the interface tension, and this leads to the anisotropic shape of the domain (as indicated in Figure 2 (b1)), and a clear phase inversion occurs. This coincides well with the feature of viscoelastic phase separation proposed by Tanaka.\textsuperscript{[14]}

Figure 2a clearly shows that the size of the epoxy-rich domains grows rapidly and many small droplets appear in the PES-rich matrix at the late stage of phase separation for the PES-15.9 blend at 140°C. When this system is cured at 120°C, however, except for the fact that phase-separation process takes more time, the morphology evolution is similar to that of the PES-15.9 blend at 140°C.

It is noticeable that the morphologies of the PES-18.5 blend cured at 120°C (Figure 2b) are clearly different from that cured at 140°C (Figure 2c). In the former case, the size of the epoxy-rich domain increase is probably retarded strongly by the elastic force of the PES-rich matrix, in which the secondary phase separation does not occur. However, in the latter case, the size of the epoxy-rich domain grows rapidly (Figure 2c), and a secondary phase separation is clearly found in the PES-rich matrix.

\textit{Evolution of an Epoxy-Rich Domain (TRLS)}

In light of the TRLS results, the temporal changes of the peak scattering vector, $q_{\text{m}}$, versus time, $t$, are plotted in Figure 3. In the PES-15.9 blend (Figure 3a), there is a minimum in the curve of peak scattering vector versus time before attaining a constant value at all curing temperatures,
which means that the appearance of many secondary droplet domains makes the average domain-size decrease. Upon increasing the curing temperature from 120 °C to 170 °C, the slope of log \( q_m \) versus log \( t \) increases from 1.14 to 1.51. These unusually steep slopes mean that the size of the epoxy-rich domain grows rapidly in a short time. The results show that secondary phase separation may be spontaneously induced by the unusually fast growth mode.\(^{[12]}\)

In the PES-18.5 blend (Figure 3b), the slope of log \( q_m \) versus log \( t \) is 1.10 at 150 °C and 1.17 at 170 °C. It is possible that the secondary phase separation occurs because of the unusually high hydrodynamic flow, which is similar to the PES-15.9 blend. The results of slopes of log \( q_m \) versus log \( t \) are summarized in Table 1.

In the PES-18.5 blend cured at 120 °C and the PES-21.0 blend cured at 140 °C, the maximal slope of log \( q_m \) versus log \( t \) is 0.30 and 0.26, respectively; secondary phase separation does not occur. However, the maximal slope is 0.90 at 140 °C for the PES-18.5 blend (Figure 3b), and 0.62 at 150 °C and 0.93 at 170 °C for the PES-21.0 blend (Figure 3c), meaning that the size of the epoxy-rich domain increases in the usual manner but that secondary phase separation takes place. Thus, the hydrodynamic flow is probably not the only mechanism to induce a secondary phase separation in a dynamic asymmetric system.

Based on the above results, a possible scenario for secondary phase separation in the PES-modified epoxy blend could be as follows: in a dynamic asymmetric system, the diffusion of the fast dynamic phase is prevented by the slow dynamic phase, and the size growth of the fast-dynamic-rich domain is retarded by the elastic force of the slow-dynamic-rich matrix. Therefore, the fast-dynamic-rich domain increases in size slowly in the higher viscosity blend due to the stronger elastic force, and thus the diffusion of the fast dynamic phase can follow geometrical growth and establish a local concentration equilibrium; secondary phase separation does not occur. With a decrease of system viscosity, the size growth of the fast-dynamic-rich domain turns fast, and once the diffusion is not able to keep up with the geometrical growth, secondary phase separation takes place, even in the droplet morphology in which the size of the fast-dynamic-rich domain grows in the normal manner. Tanaka has suggested that the secondary phase separation occurs because the high hydrodynamic flow due to the interface motion makes the geometrical coarsening too fast for diffusion to follow and therefore the local concentration equilibrium is broken.\(^{[12]}\) Thus, the results of this paper reveal that the high hydrodynamic flow due to interface motion causes the geometrical coarsening to become too fast for diffusion to follow and leads to spontaneous secondary phase separation. Furthermore, the viscoelastic effect of the slow dynamic phase cannot be ignored in a dynamic asymmetric system. SEM micrographs of the fracture surface in this system show a very sharp interface between the epoxy-rich phase and the PES-rich phase. In a conventional scaling law, it is considered that a sharp interface between two phases can be observed when the system is at equilibrium. For the unusual phenomenon of these systems,
the concentration equilibrium will be broken again as the polymerization proceeds (deeper quench depth), therefore the phase separation will occur again if the system is not frozen by gelation of the curing reaction or vitrification. A study of the effect of the molecular weight of PES and the curing reaction rate on the secondary phase separation is currently underway.

### Conclusion

A secondary phase separation was observed in the phase separation evolution of epoxy/4,4'-methylenebis(2,6-dimethylaniline)/polyethersulfone blends with various PES contents at different curing temperatures. In the case of higher viscosity, the slopes of log $q_m$ versus log $t$ are about 0.3 and the diffusion of epoxy molecules can follow the growth of the size of the epoxy-rich domain, thus secondary phase separation does not occur. As the viscosity of the system decreases, the size growth of the fast-dynamic-rich domain becomes more rapid, and once the diffusion is no longer able to follow the geometrical growth, secondary phase separation takes place, even in the droplet morphology, in which the size of the fast-dynamic-rich domain grows in the usual manner. This phenomenon could be aggravated by a further viscosity decrease. Therefore, these results suggest that the high hydrodynamic flow due to interface motion causes the geometrical coarsening to become too fast for diffusion to follow and leads to spontaneous secondary phase separation. Meanwhile, the viscoelastic effect of the slow dynamic phase cannot be ignored in a dynamic asymmetric system.

### Acknowledgements

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**Table 1. Summary of the experimental results (✓ secondary phase separation occurs; x does not occur).**

<table>
<thead>
<tr>
<th>Blend</th>
<th>Temperature</th>
<th>Slope</th>
<th>Secondary phase separation</th>
</tr>
</thead>
<tbody>
<tr>
<td>PES-15.9</td>
<td>120°C</td>
<td>1.14</td>
<td>✓</td>
</tr>
<tr>
<td></td>
<td>140°C</td>
<td>1.24</td>
<td>✓</td>
</tr>
<tr>
<td></td>
<td>170°C</td>
<td>1.51</td>
<td>✓</td>
</tr>
<tr>
<td>PES-18.5</td>
<td>120°C</td>
<td>0.30</td>
<td>x</td>
</tr>
<tr>
<td></td>
<td>140°C</td>
<td>0.90</td>
<td>✓</td>
</tr>
<tr>
<td></td>
<td>150°C</td>
<td>1.10</td>
<td>✓</td>
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<tr>
<td></td>
<td>170°C</td>
<td>1.17</td>
<td>✓</td>
</tr>
<tr>
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<td>x</td>
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<td></td>
<td>150 °C</td>
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</tr>
<tr>
<td></td>
<td>170 °C</td>
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</table>

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**Figure 3. The changes of peak scattering vector, $q_m$, versus time, t: (a) PES-15.9 blend; (b) PES-18.5 blend; (c) PES-21.0 blend.**

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