Morphology Evolution during the Phase Separation of Polyetherimide/Epoxy Blends

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Introduction

Over the last two decades, attempts have been made to modify epoxy resins with a high-performance engineering thermoplastic that has a high \( T_g \) and toughness, such as polysulfone (PSU), poly(ether sulfone) (PES), poly(ether ether ketone) (PEEK), and polyetherimide (PEI). As the thermoset precursor reacts, the entropy of mixing decreases with increasing molecular weight, while the Flory–Huggins interaction parameter changes little, that is, the enthalpy almost stays constant. According to the Flory–Huggins meanfield theory, as an average molecular weight of epoxy resin is reached where a homogeneous mixture is no longer favored, the thermoplastic modified thermoset system separates into two phases. Different phase morphologies can be obtained depending on the competition between thermodynamics, kinetics of phase separation, and cross-linking chemical reactions, which are all governed by the curing conditions, composition, as well as molecular weights.

A co-continuous two phase system has been shown to exhibit unique mechanical properties, high initial modulus, large extension and complete strain recovery. To depict a clear picture of these fascinating phenomena, several models have been proposed. Inoue suggested a plausible scenario for the development of the connected-globule structure by two routes. One is that the network of epoxy-rich regions in a first formed co-continuous structure cannot be interrupted. The other is that the interruption has taken place, and the dispersed epoxy droplets grow in size and contact with each other. Chen and Chang revealed that the morphology shifted from a co-continuous structure into small epoxy-rich dispersed particles and finally into an epoxy dispersing phase with an irregular shape or continuous phase depending on the blend composition. Oyanguren et al. found that the cure reaction of epoxy

**Communication:** The results of time-resolved light scattering for the phase separation of epoxy/polyetherimide/anhydride blends show that the evolution of scattering vector \( q_m \) follows a Maxwell-type relaxation equation. The relaxation time may be suggested as the time taken for the diffusion of the epoxy-anhydride \( n \)-mers from the PEI-rich phase by their relaxation movement, and the apparent activation energy of the relaxation movement is obtained.
proceeds, the volume fraction of the epoxy-rich phase increases because of the continuous segregation of epoxy-anhydride species from the PSu-rich phase. This leads to the coalescence of epoxy-rich domains and the generation of a bicontinuous structure.

In our previous work,[10,11] a co-continuous phase structure was obtained in epoxy modified with novel polyetherimide (PEI), and the fracture toughness was improved apparently. The study of phase separation suggested that the spinodal decomposition (SD) mechanism should be the most conceivable in thermoplastic PEI modified thermoset systems.

The aim of the present work is to discuss the evolution of the morphology in PEI modified epoxy/anhydride systems and to try to describe the kinetics of the evolution process of phase separation. It was hoped that these results would aid in designing materials by the control of structure development in multicomponent thermosetting resins.

Experimental Part

A commercial epoxy precursor DGEBA (DER 332 with an epoxide equivalent weight of 184–194 g/eq.) from Dow Chemical, a curing agent methyletetrahydroadiphthalic anhydride (MTHPA), and an accelerator benzylidimethylamine (BDMA) from Shanghai Third Reagent Factory were used without further purification.

The polyetherimide (PEI) was synthesized 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 °C. After that aniline was added to terminate the PEI, and the products were precipitated in alcohol and dried at 200 °C for about 4 hours. The molecular weight of PEI measured by gel permeation chromatography (GPC) was $M_n = 29000$.

Epoxy blends containing 20 pbw (parts by weight) of PEI were prepared by dissolving the PEI in DGEBA at 150 °C. The mixture was cooled to 90 °C until a clear homogenous solution was obtained, and a stoichiometric amount (80 pbw) of cure agent MTHPA was added with accelerator BDMA (0.2 pbw), then the blend was cooled rapidly to room temperature to avoid further curing reaction.

The final morphology of the isothermal cured blends was observed under a scanning electron microscope (SEM) (Philip XL 39). The samples were fractured in liquid nitrogen. All samples were coated with gold and mounted on copper mounts.

A drop of the sample was placed between two glass slides and mounted onto a hot stage at 150 °C. The phase separation process was monitored in situ by an Olympus (BX51) camera at appropriate time intervals during isothermal curing.

The phase separation process during isothermal curing reaction was also monitored at real time on the self-made time-resolved light scattering (TRLS) with a controllable hot chamber. The change of the light scattering profiles was recorded at appropriate time intervals during isothermal curing.

Results and Discussion

Morphologies Observed by SEM

The morphologies of samples cured at 110, 130, and 150 °C were observed with SEM (Figure 1). The dark regions correspond to the epoxy-rich phase, while the bright regions correspond to the PEI-rich phase. It is obvious that the morphologies of these systems are similar regardless of different curing temperature and all consist of large irregular PEI-rich domains dispersing in epoxy-rich continuous phase.

Morphologies Evolution Observed by OM

In order to investigate the morphology evolution, optical microscopy (OM) was employed to monitor the phase separation process. Since the final morphologies at the three curing temperatures are similar (Figure 1), a sample was chosen to be monitored by OM at 150 °C. As shown in Figure 2, here the dark regions correspond to the epoxy-rich phase, while the bright regions correspond to the PEI-rich phase. The blend remains homogeneous after

![Figure 1. SEM of the blends cured for five hours (500×). (a) 110 °C; (b) 130 °C; (c) 150 °C.](image-url)
about 600 s heating at 150 °C. Then, a co-continuous phase structure is observed at 632 s, where the epoxy-rich phase and PEI-rich phase are both continuous. As the curing reaction proceeds, the epoxy-anhydride \( n \)-mers diffuse out of the PEI-rich phase and begin to coarsen rapidly. Then the periodic distance of the co-continuous structures increases and the morphology shifts into small epoxy-rich dispersed particles (632–682 s). These growing particles connect to each other to form large particles (682–772 s). At about 922 s, the epoxy-rich phase almost connected to be continuous, meanwhile, the PEI-rich phase tended to be surrounded by the growing epoxy-rich phase. Finally, irregular PEI-rich macrophase domains dispersing in the epoxy-rich matrix were formed (Figure 1), which was attributed to the low mobility of the epoxy-anhydride \( n \)-mers due to the high viscosity caused by the curing reaction.

**Morphologies Evolution Monitored by TRLS**

As illustrated in Figure 2, the evolution of the morphology was caused by the movement of epoxy-anhydride \( n \)-mers. To describe the process of morphology evolution, phase separation processes at 100, 110, 120, 130, 140, and 150 °C were traced in situ by TRLS respectively.

Figure 3 showed a typical example of a scattering profile with time \( t \) for the P720 system cured at 120 °C isothermally. The scattered light intensity \( I \) is a function of time and scattering vector \( \mathbf{q} \); the latter is defined by Equation (1).\[^{[12,13]}\]

\[
q = \frac{4\pi}{\lambda} \sin(\theta/2)
\]

Where \( \lambda \) is the wavelength of light in the sample, and \( \theta \) is the scattering angle. The reciprocal of the scattering vector \( \mathbf{q} \) is assigned to the periodic distance of the dispersed particles. From the light scattering profiles, the peak scattering vector \( q_m \) corresponding to an instantaneous maximum scattering intensity \( I_m \) was obtained. The \( q_m \) decreased rapidly with time and leveled off until fixed to a certain value, while the relative intensity of scattered light increased continually, then, decreased a little, and thereafter remained constant as mentioned in the literature.\[^{[4]}\] It indicates the development of a regularly phase-separated morphology by spinodal decomposition.\[^{[13,14]}\]

It can be noticed that the morphology evolution observed by TRLS was in agreement with that observed by OM (Figure 2). In addition, similar light scattering profiles were exhibited at all the temperatures.

**Morphology Evolution Kinetics**

In order to describe the tendency of the \( q_m \) changing with time, the time dependent \( q_m \) was simulated according to the Maxwell-type relaxation Equation (2).

\[
q_m(t) = q_0 + A_0 \exp\left(-t/\tau\right)
\]

As \( t = \infty \), \( q_m = q_0 \). Here \( \tau \) is the relaxation time, \( A_0 \) is a magnifier. It can be seen that the values of \( q_m \) were adopted from the beginning to the first lowest value for simulation.

As shown in Figure 4(a), the \( q_m \) at different temperature fits well with Equation (2) respectively.

The relaxation time \( \tau \) simulated with Equation (2) at different temperatures is reported in Table 1.

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**Figure 2.** The process of phase separation of PEI/epoxy blends monitored by an optical microscope at 150 °C, 500×.
As presented in Table 1, the relaxation time $t$ decreases drastically with increasing temperature and becomes progressively less sensitive to the curing temperature. It is clear that the relaxation time $t$ depends upon the temperature of the curing reaction.

The relaxation time $t$ obtained by single exponential decay of $q_m$ could not be the relaxation time of the PEI segments. Tanaka\(^{[15]}\) stated that the origin of the dynamic asymmetry may be caused by the size difference in component molecules of a mixture or the existence of another transition such as glass transition. Since the cure temperatures are far below the $T_g$ of PEI (210°C), the epoxy-anhydride $n$-mers act as a rapid dynamic phase (lower $T_g$ component), while PEI is a slow dynamic phase (higher $T_g$ component) and produces "cage effect". Thus, the relaxation time $t$ obtained by $q_m$ single exponential decay should be the time for escape of the epoxy-anhydride $n$-mers from the "cage" of PEI entanglement by their relaxation movement. Furthermore, it also demonstrates that it is epoxy anhydride $n$-mers that diffuse out of the

Table 1. The relaxation time $t$ at different temperatures.

<table>
<thead>
<tr>
<th>Curing Temperature ($T$) ($^\circ$C)</th>
<th>100</th>
<th>110</th>
<th>120</th>
<th>130</th>
<th>140</th>
<th>150</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R^2$(^{[a]})</td>
<td>0.995</td>
<td>0.997</td>
<td>0.995</td>
<td>0.990</td>
<td>0.992</td>
<td>0.989</td>
</tr>
<tr>
<td>$t$ (s)</td>
<td>345</td>
<td>156</td>
<td>87.1</td>
<td>48.2</td>
<td>33.4</td>
<td>23.7</td>
</tr>
</tbody>
</table>

\(^{[a]}\) The correlation coefficient.
PEI-rich phase and connect with each other, as observed in Figure 2. From Table 1, the apparent activation energy of the relaxation movement can thus be obtained. The plot of ln τ versus 1/T is satisfactorily linear (Figure 4b). The slope is $8.42 \times 10^3$, from which the apparent activity energy calculated by the Arrhenius equation is 69.9 kJ mol$^{-1}$.

This apparent activation energy of the relaxation movement may be a key factor in affecting the phase separation process and be somewhat influenced by the activation energy of curing reaction of epoxy resin.

**Conclusion**

The phase separation of polyetherimide/epoxy blends takes place by spinodal decomposition. The morphology evolution begins with a co-continuous structure, then, shifts to a phase inversion structure, and finally irregular PEI-rich macrophase domains are formed, which disperse in the epoxy-rich matrix by connecting epoxy particles. The evolution of scattering vector $q_m$ corresponding to the morphology evolution follows the Maxwell-type relaxation equation. The relaxation time may be suggested as the time for the diffusion of the epoxy-anhydride $n$-mers from the PEI-rich phase by their relaxation movement, and thus the apparent activation energy of the relaxation movement is obtained.

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