Rheological Study on Structural Transition in Polyethersulfone-Modified Bismaleimide Resin During Isothermal Curing

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ABSTRACT: The structural transition in the polyethersulfone (PES)-modified bismaleimide resin, 4,4'-bismaleimidodiphenylmethane (BDM), during isothermal curing was studied by using rheological technique, different scanning calorimetry (DSC), and time resolved light scattering (TRLS). Comparing with the cure of neat bismaleimide, two separate tan δ crossover points were observed because of the phase separation during curing the blends of PES/BDM. These two structural transitions stemmed from the fixing of phase structure of the system and the chemical crosslinking of bismaleimide, respectively. The effect of curing temperature and the PES content on structural transition was discussed and found that the occurrence of two structural transition exhibited the different dependency of curing temperature and PES content. The relaxation exponent n and gel strength S were also found to be temperature-dependent and composition-dependent. Moreover, the relaxation exponent n of the second structural transition is much lower than that of the first structural transition in the PES/bismaleimide blends. ©2006 Wiley Periodicals, Inc. J Polym Sci Part B: Polym Phys 44: 3102–3108, 2006
Keywords: bismaleimide; polyethersulfone; rheology; structural transition

INTRODUCTION

Bismaleimideresins, as a kind of high-performance materials, have received more and more interest because of their good thermal stability, low water absorption, and good retention of mechanical properties at high temperatures. However, because of their highly crosslinked structures, bismaleimide resins are extremely brittle and thus are often modified with different thermoplastics, such as poly(ether imide) (PEI),1–4 poly(ether sulfone) (PES),5 poly(ether ketone)s6, and poly(arylene ether phosphine oxide).7 During isothermal curing of the blends of thermoplastic-modified thermoset, some structural transformations are expected to occur: phase separation, the vitrification of thermoplastic-rich phase, the chemical gelation of thermoset, and the vitrification of thermoset-rich phase. Unlike thermoplastic/thermoplastic blends, phase separation is induced by the increasing molecular weight of thermoset resins in the thermoset/thermoplastic blends even if the temperature is kept constant. After the occurrence of phase separation, thermoset monomers diffuse from thermoplastic-rich phase into thermoset-rich phase and result in the gradual increase of glass transition temperature \((T_g)\) of thermoplastic-rich phase. When the \(T_g\) of thermoplastic-rich phase
reaches the curing temperature, the vitrification of thermoplastic-rich phase occurs and the phase structure are fixed. As the cure proceeded, the increase in crosslinking of thermoset finally leads to the chemical gelation. The vitrification of thermoplastic-rich phase, as well as the chemical gelation of thermoset, involves a transformation from the liquid state into the solid state. Therefore, the studies on the gelation characterization of thermoplastic-modified thermoset is of crucial importance in industry applications, since it can allow the estimation of the optimal process according to which the blends should be heated or molded.

As we know, the chemical gel point is reached when the largest molecular or super molecular cluster diverges to infinity and physical gelation is reached when polymers lose their chain mobility near their glass transition temperature and molecular motion correlates over longer and longer distances. Winter and Chambon had suggested that the critical gel theory should be valid for both chemical gels and physical gels. At the gelation the stress relaxation behavior of network follows a power law:

$$G(t) = S t^{-n}$$

where $S$, the strength of the gel related to the mobility of the crosslinked chain segments, is only the material parameter depending on the flexibility of molecular chains, the crosslinks and the crosslinking density at gel point. The relaxation exponent $n$ (physically restricted for $0 < n < 1$) is related to the geometry of clusters existing at the gel point, and is a viscoelastic parameter that is related to the cluster size of the gel.

From the eq 1, the frequency dependence of the dynamic shear modulus at gel point was deduced to be

$$G'(\omega) = G''(\omega) / \tan(n\pi/2) = \Gamma(1-n) \cos(n\pi/2)S\omega^n$$

Thus, the gel point can only be accurately determined at some special conditions using crossover point of $G'$ and $G''$. These conditions are that the stress relaxation in the gelation follows a power law, and the exponent $n$ of which must be exactly 0.5. However, for most network systems, though stress relaxation at gel point also follows a power law, the relaxation exponent $n$ is not 0.5. Gel point clearly does not coincide with the $G'$ and $G''$ crossover in such cases. Therefore, the general definition of the gel point is the time when the loss tangent $\tan\delta$ becomes independent of frequency because:

$$\tan\delta = G' / G'' = \tan(n\pi/2)$$

Although extensive studies of rheological study on structural transition of crosslinking polymers were carried out, such as epoxy, dicyanate resin, poly (vinyl alcohol) and polybutadiene, little literature has been reported on the structural transition of thermoplastics-modified thermoset. This work presented the study of structural transition of PES-modified bismaleimide resin during isothermal curing by using rheological measurements, different scanning calorimetry (DSC), and time resolved light scattering (TRLS).

**EXPERIMENTAL SECTION**

**Materials**

4,4'-bismaleimidodiphenylmethane (BDM; Beijing Aeronautical Manufacturing Technology Research Institute) and 2,2'-diallyl bisphenol A (DBA; Sichuan Jiangyou Insulating Material Factory). Polyethersulfone (intrinsic viscosity: 0.36 dL/g, supplied by Jilin University) (Scheme 1).

**Sample Preparation**

PES/BDM/DBA blends with various content of PES (according to Table 1) were prepared as follows. PES was dissolved in DBA at 150 °C under a nitrogen atmosphere, then BDM was
added to the blends. The ratio of BDM to DBA was kept at 57:43 wt %. The mixture was stirred continuously until a transparent blend was obtained. Then blend cooled and cured at different conditions. The blends of bismaleimide/DBA could be reacted by heat treatment without initiator or catalyst.\textsuperscript{18}

**Measurements**

All rheological tests were performed on a Rheometrics RMS 800 rheometer using 40-mm diameter plates with a gap of 1 mm. Test multifrequencies are 0.5, 1, 5, 10, 20, 50, 100 rad/s. Blends were tested with a controlled strain of 1\% to ensure that measurements were performed under dynamic equilibrium conditions.

TRLS is a kind of static light scattering technique and is described elsewhere.\textsuperscript{19} The phase separation process during isothermal curing was observed at real time and in situ on the self-made TRLS with a controllable hot chamber.

The cured samples with different curing time were dissolved in methylene chloride (CH\textsubscript{2}Cl\textsubscript{2}). The chemical gel time, \( t_{cg} \), was the time when the presence of an insoluble fraction of the blends was first observed.\textsuperscript{13}

The conversion was determined by DSC. Conversion was calculated from residual exotherms observed in scans over the temperature range of 50–350 °C, with heating rates of 20 °C/min, normalized by the total exotherms for uncured samples.

**RESULTS AND DISCUSSION**

**Rheological Behavior and the tan \( \delta \) Crossover Points**

The rheological results of BMI-15 during isothermal curing at 165 °C, as an example, were analyzed to give plots of loss tangent (tan \( \delta \)) versus time. As shown in Figure 1, there exist two crossover points of tan \( \delta \) in the curves, which means two structural transitions in the system at 13.7 and 50.5 min, respectively.

As we know, two tan \( \delta \) crossovers were already reported and identified as physical gelation and chemical gelation in the blends of poly(vinyl chloride) and polyepoxide.\textsuperscript{20} But it is the first time to find two tan \( \delta \) crossovers in the thermoplastic-modified bismaleimide blends.

To further investigate these structural transitions, the scattering vector \( q_m \) of BMI-15 during isothermal curing at 165 °C were recorded as a function of time by TRLS. \( q_m \) is the \( q \) value of maximum peak in \( I-q \) profile. Figure 2 shows the evolution of the complex viscosity and the evolution of the scattering vector \( q_m \) with curing time. According to our previous researches,\textsuperscript{1–3} the appearance of the scattering peak, the decreasing of peak scattering vector \( q_m \) with time, and the maintaining constant of \( q_m \) were indications of the onset of spinodal decomposition phase separation, the development of a regularly phase-separated morphology, and the fixing

### Table 1. Composition of Bismaleimide Blends

<table>
<thead>
<tr>
<th>Blends</th>
<th>BMI-5</th>
<th>BMI-7</th>
<th>BMI-10</th>
<th>BMI-12</th>
<th>BMI-15</th>
</tr>
</thead>
<tbody>
<tr>
<td>PES content (wt %)</td>
<td>5</td>
<td>7.5</td>
<td>10</td>
<td>12.5</td>
<td>15</td>
</tr>
</tbody>
</table>

![Figure 1](image1.png)  
**Figure 1.** Plot of tan \( \delta \) versus curing time at various frequencies for BMI-15 at 165 °C.

![Figure 2](image2.png)  
**Figure 2.** Evolution of \( q_m \) and complex viscosity of BMI-15 cured at 165 °C.  
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DOI 10.1002/polb
of phase morphology, respectively. In Figure 2, the onset time of phase separation, \( t_{ps} \), is obtained from the jumping-off point of first rise of complex viscosity,\(^{13} \) while the times, \( t_{cp1} \) and \( t_{cp2} \), are obtained from the crossover of \( \tan \delta \).

As shown in Figure 2, the time of the onset of the phase separation corresponds to the time of the first appearance of the scattering peak, while the time of the offset of the phase separation detected by TRLS corresponds well to the time of the first \( \tan \delta \) crossover point. It demonstrates clearly that the first structural transition is caused by the fixing of phase structure, which is a form of physical gelation. Meanwhile, the fact that the time of the second crossover points is comparable to the time of chemical gelation, \( t_{cg} \), in the reasonable range of error means the second structural transition stemmed from the crosslinking of BDM/DBA.

Based on the two crossover points time and the onset time of phase-separate determined by rheometry, the evolution of complex viscosity of blends during isothermal curing can be divided into four stages as shown in Figure 3.

Initially, the blends are homogeneous. They can be described as the miscible polymer systems. With the curing reaction proceeding, phase separation takes place, and the blends move into the two-phase region. In this stage, cure reaction induces an increase of complex viscosity. The phase separation and the growth of the particles continue until the phase structure was fixed (the first structural transition). Finally, with the increase of the degree of the crosslink of BDM/DBA, the second structural transition occurs.

### Curing Conversions at the \( \tan \delta \) Crossover Points

The curing conversions of BMI-15 at two \( \tan \delta \) crossover points at different temperature were recorded as a function of time.

In Figure 4, the curing conversions of two \( \tan \delta \) crossover points at different temperatures are clearly separated. The curing conversions of first structural transition are quite low and vary with curing temperature in the range of 0.1–0.2. They are much lower than the curing conversions of the second structural transition, which are almost independent of curing temperature and locate at about 0.54, which agree with the theoretical conversion of chemical gelation of bismaleimide/DBA.\(^{21} \)

It was shown in the literature that apparent activation energy for the crosslinking reaction can be calculated from the measurement of \( \tan \delta \) crossover point time at different temperatures.\(^{22} \) Since the second structural transition occurred at a constant conversion, the activation energy could be obtained from the second crossover point time\( (t_{cp2}) \) at various temperatures by using Arrhenius expression.

\[
\frac{t_{cp2}}{t_{cp1}} = \frac{Ae^{E_a/R}}{RT}
\]  

\( t_{cp2} \) where \( E_a \) is the activation energy, \( T \) is the absolute temperature of reaction, and \( R \) is the universal gas constant. Figure 5 shows an Arrhenius plot obtained using eq 4, the slope of which gives an activation energy (\( E_a \)) of 98.7 kJ/mol. The activation energies of blends with different PES content are listed in Table 2, which shows a slight increase of values with the increase of PES content.

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**Figure 3.** The evolution of complex viscosity of BMI-15 during isothermal curing: square, onset of phase separation; circle, first structural transition; triangle, second structural transition.

**Figure 4.** The curing conversions of BMI-15 at the two crossover points at different temperatures.
Effect of Curing Temperature on the tan δ Crossover Points

Figure 3 shows that the times of the occurrence of two structural transitions decrease with the increase of curing temperature. To further discuss the effect of curing temperature on the structural transition, the log $G'$ and log $G''$ against log $\omega$ at the crossover points for BMI-15 cured at 160 °C were plotted in Figure 6. At tan δ crossover point, the self-similar relaxation governs the rheological behaviors. The characteristics of shear moduli ($G'$ and $G''$) are predicted by power law expressions: $G' \propto G'' \propto \omega^n$. The relaxation exponent $n$ is determined from the slope of plotting log $G'$ and log $G''$ versus log $\omega$, meanwhile the gel strength $S$ can be calculated from the interception of log $G'$ and log $G''$ versus log $\omega$ according to eq 2. It is seen that the structural transition of our system obey the universal power law independent on temperature, with different power index values for each transition though. In the two tan δ crossover points of this system, a linear dependence of the logarithm of the $G'$ and $G''$ with the log $\omega$ is observed following the relation of $G \propto \omega^n$ at the wide range of frequency. The values of $n$ and $S$ at different temperature are listed in Table 3, which shows a narrow range of values for $n_1$ from 0.58 to 0.68, and for $n_2$ from 0.28 to 0.33. Moreover, the relaxation exponent $n$ increases with curing temperature for both the first structural transition and the second structural transition. It implies that the higher cure temperature would result in lower strength or loose network.

The relaxation exponent $n$ has been investigated experimentally by several authors. There are various theories to explain the value of the exponent. For the Zimm case, in the system dominated by hydrodynamic interactions between segments of the macromolecules, the relaxation exponent $n$ is near 2/3, which is very close to $n$ of the first structural transition at all temperatures in this work. Therefore, it demonstrated further that the first structural transition related to the fixing of the phase structure, in which the thermoplastic are surrounded by the solvents (BDM/DBA monomers).

However, an relaxation exponent $n \approx 0.7$ was reported on the chemical gelation of epoxy and cyanate, which is far higher than the $n$ of the second structural transition in this work. The reason could be attributed to the occurrence of the first structural transition, which would greatly influence the second structural transition. With the restriction from the thermoplastic phase formed by phase separation, the crosslinking network was much “tight”, and reduced significantly the $n$ of the second structural transition. Therefore, it could be concluded that relaxation exponent $n$ of the second structural transition is much lower than that of the first structural transition in the blends of thermoplastic-modified thermoset.

Furthermore, as shown in Table 3, the gel strength $S$ decreases with curing temperature for both the first structural transition and the second structural transition. Despite, no strong theoretical interpretation of gel strength $S$ existed, it is believed that $S$ reflects the mobility of chain segments. Thus, the decrease of the gel strength $S$ with the increase of temperature in this work could be attributed to the enhanced chain mobility.

Effect of PES Content on the tan δ Crossover Points

The effects of PES content on the tan δ crossover point time are illustrated in Figure 7. It is notable that the time of the occurrence of second structural transition increases with the increase

Table 2. The Reaction Activation Energy of the Curing Reaction for the BMI/PES Blends

<table>
<thead>
<tr>
<th>System</th>
<th>The Activation Energy (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BMI-5</td>
<td>91.5</td>
</tr>
<tr>
<td>BMI-7</td>
<td>90.3</td>
</tr>
<tr>
<td>BMI-10</td>
<td>92.1</td>
</tr>
<tr>
<td>BMI-12</td>
<td>94.5</td>
</tr>
<tr>
<td>BMI-15</td>
<td>98.7</td>
</tr>
</tbody>
</table>

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of PES content, while the time of the occurrence of first structural transition decreases initially and after then increases. The occurrence of structural transition of blends is determined by the competition of two factors: on the one hand, high content of PES can enhance the initial chemical quench depth, which facilitates the evolution of phase separation and the occurrence of first structural transition; on the other hand, the higher content of PES may result in dilutedness effect,\(^2\) which causes the lower cure rate and delays the occurrence of first structural transition.

Effects of PES content on relaxation exponent \(n\) and gel strength \(S\) are shown in Table 4. The gel strength \(S\) increases with PES content for both the first structural transition and the second structural transition implies the reduced chain mobility with high PES concentration.

The value of \(n\) slightly decreases with the increase of PES content and are located in the range of 0.62–0.68 for \(n_1\) and 0.30–0.42 for \(n_2\). In the case of high PES content, the entanglement effects of PES will probably reduce the value of \(n_1\) and \(n_2\). This kind of the reduction of the relaxation exponent with increasing polymer content in the semidilute regime was also reported by Scanlan and Winter.\(^8\) Anna Lena\(^1\) and Koike\(^2\) indicated that the relaxation exponent \(n\) decrease with increasing entanglement density in the study on chemical gelation, whereas in unentangled prepolymer solutions.

![Figure 6](image)

![Figure 7](image)

Table 3. The \(n\) and \(S\) Value for BMI-15 at Different Curing Temperatures

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>(n_1)</th>
<th>(S_1)</th>
<th>(n_2)</th>
<th>(S_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>0.58</td>
<td>95.5</td>
<td>0.28</td>
<td>1.05 E 5</td>
</tr>
<tr>
<td>155</td>
<td>0.59</td>
<td>51.3</td>
<td>0.28</td>
<td>0.56 E 5</td>
</tr>
<tr>
<td>160</td>
<td>0.62</td>
<td>26.9</td>
<td>0.30</td>
<td>0.29 E 5</td>
</tr>
<tr>
<td>165</td>
<td>0.64</td>
<td>21.4</td>
<td>0.32</td>
<td>0.20 E 5</td>
</tr>
<tr>
<td>170</td>
<td>0.68</td>
<td>10.6</td>
<td>0.33</td>
<td>0.14 E 5</td>
</tr>
</tbody>
</table>

Table 4. The \(n\) and \(S\) Value for Blends with Different PES contents (cured at 160 °C)

<table>
<thead>
<tr>
<th>Blends</th>
<th>(n_1)</th>
<th>(S_1)</th>
<th>(n_2)</th>
<th>(S_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BMI-5</td>
<td>0.68</td>
<td>20.12</td>
<td>0.42</td>
<td>1.76 E 4</td>
</tr>
<tr>
<td>BMI-7</td>
<td>0.65</td>
<td>22.90</td>
<td>0.37</td>
<td>2.19 E 4</td>
</tr>
<tr>
<td>BMI-10</td>
<td>0.65</td>
<td>22.99</td>
<td>0.33</td>
<td>2.35 E 4</td>
</tr>
<tr>
<td>BMI-12</td>
<td>0.63</td>
<td>25.11</td>
<td>0.31</td>
<td>2.57 E 4</td>
</tr>
<tr>
<td>BMI-15</td>
<td>0.62</td>
<td>26.9</td>
<td>0.30</td>
<td>2.94 E 4</td>
</tr>
</tbody>
</table>

\(S_1\) and \(n_1\): \(S\) and \(n\) in the first structural transition; \(S_2\) and \(n_2\): \(S\) and \(n\) in the second structural transition.
the value of $n$ was found to be independent of polymer concentration. Therefore, the results in this work imply that the blends are entangled between the PES molecular and the BDM/DBA molecular.

CONCLUSIONS

Two tan δ crossover points observed in the isothermal curing of the blends of PES/BDM/DBA were identified as the first structural transition due to the fixing of the phase structure and the second structural transition due to the chemical crosslink reaction of BDM/DBA, respectively. It is notable that the time of the occurrence of first structural transition was a function of curing conversion and depended on the curing temperature, whereas the second structural transition occurred almost at the constant conversion at different curing temperatures. The occurrence of the second structural transition delayed with the increase of PES content, while the time of the occurrence of the first structural transition decreases initially and after then increases. It is also found that the relaxation exponent $n$ and gel strength $S$ dependent on temperature and composition of the blends. Moreover, the relaxation exponent $n$ of the second structural transition is much lower than that of the first structural transition due to the phase separation during isothermal curing.

REFERENCES AND NOTES