J Mater Sci (2007) 42:2150–2156
DOI 10.1007/s10853-006-1219-9

Study on the polyethersulfone/bismaleimide blends: morphology and rheology during isothermal curing

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Received: 16 November 2005 / Accepted: 23 January 2006 /

Abstract The morphology and rheological behave of the polyethersulfone/bismaleimide blends during isothermal curing was investigated by rheological instrument, different scanning calorimetry (DSC), scanning electronic microscopy (SEM) and time resolved light scattering (TRLS). The influences of the PES content, the PES molecular weight and the curing temperatures on the complex viscosity of the blends were discussed in detail, which suggested that the fluctuation of the complex viscosity at the beginning of phase separation was largely dependent on the PES content, while the PES molecular weight mainly influenced the onset of phase separation and had relatively less influence on the evolution of complex viscosity. Moreover, the evolution of complex viscosity of blends with high PES content was relatively less sensitive to the curing temperature. In addition, it was found that the phase morphology as well as the composition of continuous phase played an important role in the rheological behavior of PES modified bismaleimide resin during isothermal curing.

Introduction

Bismaleimide resins, as a kind of high-performance thermoset 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, thermosets tend to have a characteristic low resistance to brittle fracture. As a result, much work has been made to toughen them with high modulus, high glass transition temperature thermoplastics [1–7]. Due to the highly crosslinked structures, bismaleimide resins are also extremely brittle and thus are often modified with different thermoplastics, such as polyetherimide(PEI)[1, 2, 6] and poly(arylene-ether ketone)s [7].

It is well known that the rheological characterization of thermoset and 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. The chemorheology of thermosets have reviewed by Halley and Mackay [8]. Some thermosets, such as epoxy [9–11] and dicyanate [12, 13], have been carefully studied, which indicated that profound rheological changes were inevitably exhibited during polymerization [14]. However, the modification of thermoset with thermoplastics would change their rheological behaviors completely. It has been reported by Pascault et al. [15] that the initially low complex viscosity increased abruptly during curing of polyetherimide (PEI) modified epoxy (diglycidyl ether of bisphenol A, DGEBA) systems, and the interdependence between morphology and initial composition was exhibited. When PEI content was lower (dispersed structure), phase separation induced a rapid decrease

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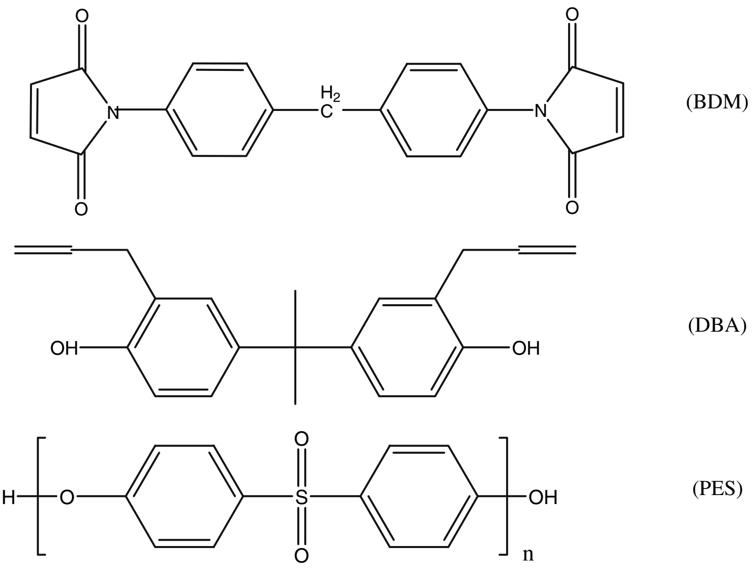

Scheme 1 Chemical structures of BDM, DBA and PES

of the viscosity. When thermoplastic concentration was higher (phase inversion), however, phase separation led to a gradual increase in the viscosity. Kim et al. [16] noted that there was a fluctuation on the viscosity just before the abrupt viscosity's increase, which was due to the phase separation of thermoplastic from the thermoset matrix induced by curing reaction. In the blends with PES modified dicyanate resin, Kim et al. [17] reported that the gelation time of the dicyanate resin system decreased with increasing isothermal curing temperature and with decreasing PES content.

Although extensive studies were carried out on rheology of thermoplastic modified epoxy and dicyanate resin, little literature has been reported on that of thermoplastics modified bismaleimide resin. The aim of present work was to study the morphology and rheological behavior of PES modified bismaleimide resin during isothermal curing, and to discuss the effects of the PES content, the molecular weight of PES and curing temperatures on complex viscosity by the combination of results from different scanning calorimetry (DSC), scanning electronic microscopy (SEM) and time resolved light scattering (TRLS).

Experimental

Materials

4,4′-bismaleimidodiphenylmethane (BDM, Beijing aeronautical manufacturing technology research institute,). 2,2′-diallyl bisphenol A (DBA, Sichuan Jiangyou Insulating Material Factory). Two kinds of polyethersulfone (intrinsic viscosity: 0.36 and 0.53 dm^3/kg (determined in *N*,*N*-dimethylformamide and at 25 °C), supplied by Jilin University) (Scheme 1).

Sample preparation

PES/BDM/DBA blends containing different content of PES and different molecular weight of PES (according to Table 1) were prepared as follows. PES was dissolved in DBA at 150 °C under protection of nitrogen. After mixtures had cooled to 120 °C, BDM was added. The ratio of BDM to DBA was kept at 57:43 pbw (1:0.85 mole ratio). The mixture was stirred continuously until a transparent blends was obtained. Then blends cooled and cured at different conditions.

Measurements

The melt viscosity variations of the blends during isothermal curing were recorded on an Ares-9A rheometry instrument under the parallel plate mode with the controlled strain of 1%, test frequency of 1 rad/s and the gap of 1 mm. These test parameter, which are usually used for high viscosity, were used in

Table 1 Composition of bismaleimide blends

Blends	PES content (wt%)	PES intrinsic viscosity (dm^3/kg)
BMI-0	0	–
BMI-5	5	0.36
BMI-7	7.5	0.36
BMI-12	12.5	0.36
BMI-15	15	0.36
BMI-5H	5	0.53
BMI-15H	15	0.53

here because the higher strain may destroy the morphology formed by phase separation during isothermal curing. Meanwhile, to avoid running the test below the minimum torque, we specially used 40 mm diameter plates (usually 8 mm diameter plates were used) and found they are sensitive enough for the system with low viscosity. The scattering vector with maximum scattering intensity, q_m, was obtained by the self-made TRLS with a controllable hot chamber. The TRLS technique is described elsewhere [18]. The morphology of the fully cured blends was examined by SEM (TS 5136 MM). The cured samples were fractured in liquid nitrogen and coated with a layer of gold before observation. The reaction conversion of blends was measured by using a Perkin-Elmer DSC (Pyris 1). 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

Effect of the PES content

Figure 1 shows the evolutions of complex viscosities observed at curing temperature of 160 °C. Obviously, in the early stage of cure reaction, complex viscosities of all blends increase slightly. Then complex viscosities increase quickly for blends BMI-12 and BMI-15, while drop abruptly for blends BMI-5 and BMI-7.

For comparison, the evolution of the complex viscosity and scattering vector q_m of BMI-12 cured at 160 °C, as an example, were plotted in Fig. 2. According to our previous researches [1–3], the appearance of the scattering peak and the evolution of the peak scattering vector q_m are the indication of the onset of phase separation and the evolution of a regularly phase-separated morphology, respectively. In Fig. 2, the onset of the phase separation is corresponding to the first fluctuations of complex viscosity profiles, which implies that the fluctuations were caused by the phase separation. Moreover, the onset of phase separation observed by rheometer is earlier than that observed by TRLS, which is reasonable for the rheology technique is more sensitive to phase separation than light scattering technique [19]. The phase separation mechanism of BMI-12 follows spinodal mechanism and we can get the q_m trace. The same mechanism was found for BMI-15. However, Phase separation of BMI-5 and BMI-7 follows nucleation growth mechanism and their cloud points were determined by change of the light intensity of light scattering experiments.

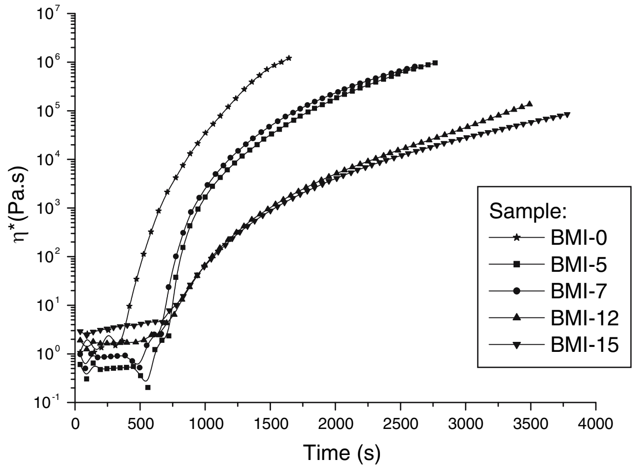

Fig. 1 Influence of PES content of PES on complex viscosity: curing at 160 °C

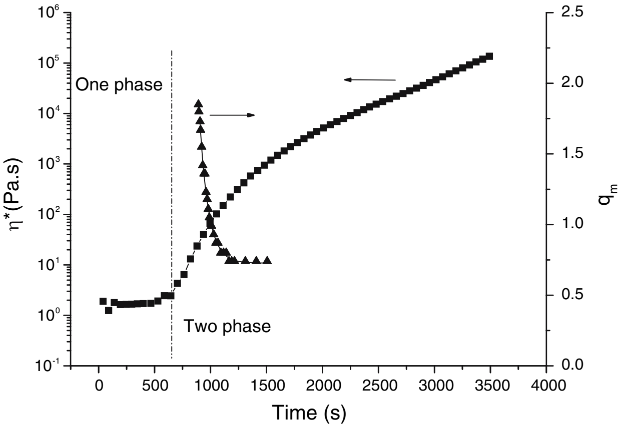

Fig. 2 Evolution of q_m and complex viscosity of BMI-12 cured in 160 °C

The fully cured blends display different morphologies are shown in Fig. 3. The cured BMI-5 and BMI-7 have spherical domains of PES dispersed in the BDM/DBA-rich matrix, while the cured BMI-12 shows complete phase inversion, in which spherical BDM/DBA-rich particles of regular diameter around 10 μm dispersed in the PES-rich matrix. The morphology of cured BMI-15 is similar to that of cured BMI-12 but with smaller average size of the BDM/DBA-rich particle. Combined with Figs. 1 and 3, when phase separation occurs, the complex viscosity drops rapidly in blends with PES dispersed phase structures because of initially dissolved highly viscous PES component separating from the BDM/DBA-rich matrix (as shown in Fig. 3c, d). When the content of PES is high enough to form continuous PES-rich phase up to the end of phase separation (as shown in Fig. 3c, d), the

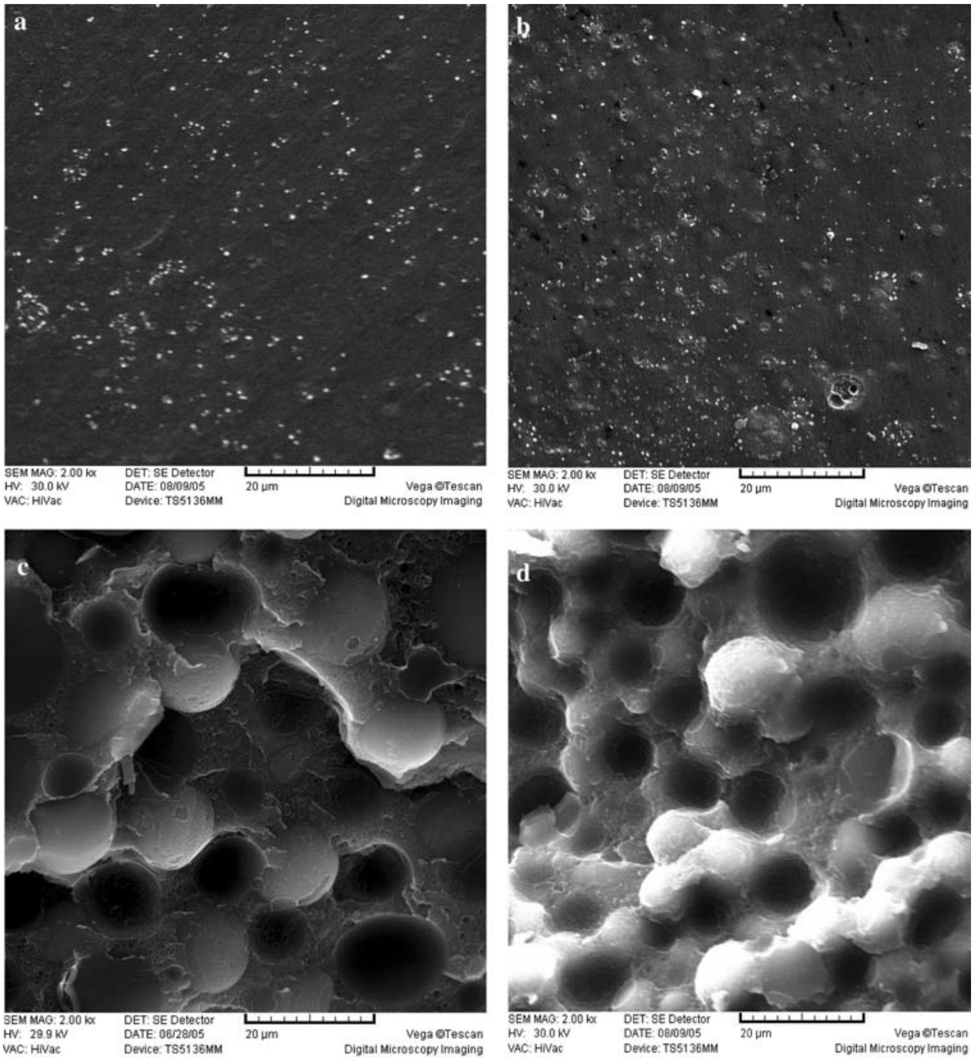

Fig. 3 Morphologies of PES/BDM/DBA blends cured at 160 °C. (**a**) BMI-5 (×2,000), (**b**) BMI-7 (×2,000), (**c**) BMI-12 (×2,000), (**d**) BMI-15 (×2,000)

occurrence of phase separation results in a quickly increase in the complex viscosity. Actually, similar phenomena also have been reported in the thermoplastic modified epoxy resin system [15, 16, 20].

After the occurrence of phase separation, complex viscosities of all blends increase gradually with curing time. Although the initial complex viscosities of all blends increase with the increase of PES contents, the complex viscosities of BMI-5 and BMI-7 increase faster than those of BMI-12 and BMI-15 in the early stage of isothermal curing reaction. This could be attributed to the dilutedness effect of PES, which causes the higher rate of cure reaction for the blends with lower PES content.

Effect of curing temperature

The effect of curing temperature on the complex viscosity was examined at 150 and 170 °C, respectively. In Fig. 4, it is found that at higher curing temperature, the phase separation occurs earlier and the complex viscosity of blends increases faster.

In thermoplastic modified thermoset systems, reaction-induced phase separation takes place under chemical quench [21] with progressive changed depth that relates to the curing conversion of the thermoset. For further analyzing, curves of the reaction conversion versus time were shown in Fig. 5, and curves of the complex viscosity versus conversion were plotted in Fig. 6.

Figure 6 shows that the phase separation occurs almost at the same conversion for each blend despite of different cure temperature. Furthermore it is clearly to see that, at the same conversion, the complex viscosity of BMI-5 cured at 170 °C is higher than that cured at 150 °C, while the complex viscosities of BMI-15 cured at two temperatures are very close throughout the curing process.

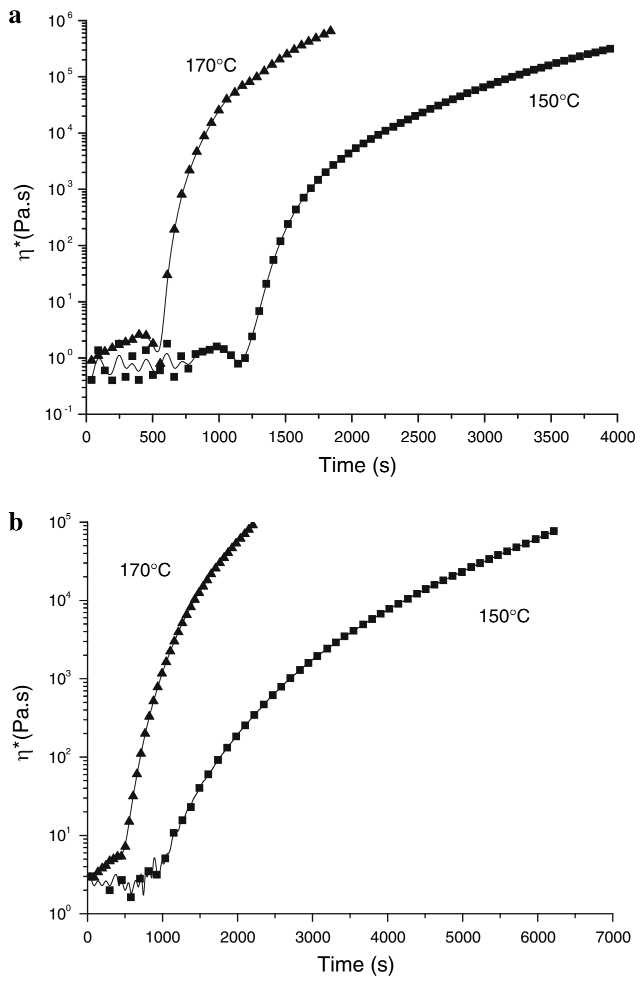

Fig. 4 Influence of curing temperature on complex viscosity: (**a**) BMI-5, (**b**) BMI-15

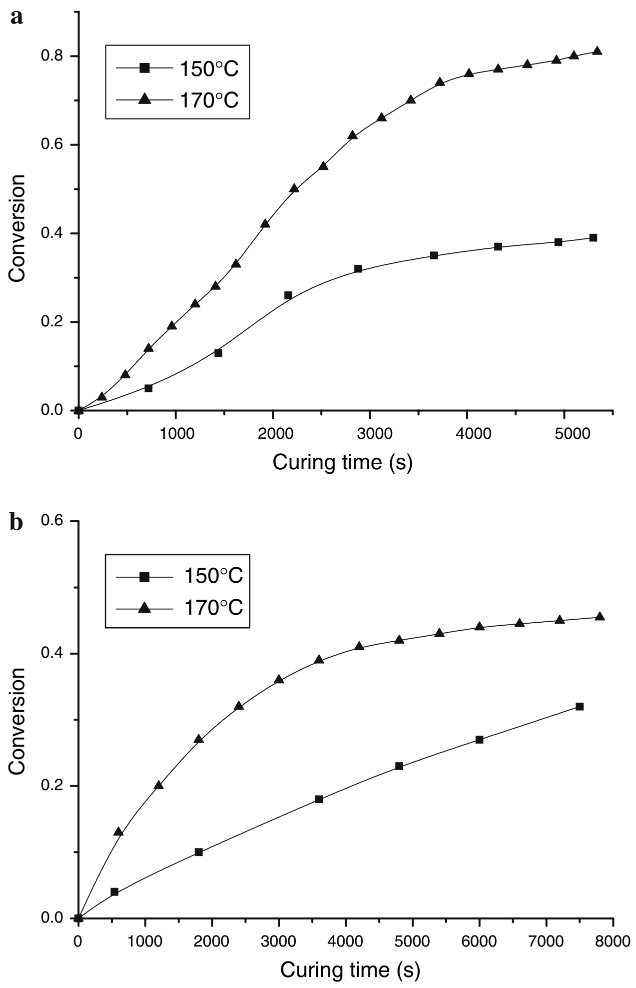

Fig. 5 Conversion versus curing time of blends isothermally curing at 150 and 170 °C: (**a**) BMI-5, (**b**) BMI-15

Einstein equation [22] could help us to understand this phenomenon even it did not consider viscoelastic effects of thermoplastic [15]. According to Einstein equation, the suspension viscosity is mainly governed by the matrix viscosity evolution and the quantity of dispersed phase:

$$\eta_{\alpha,\beta(t)} = \eta_{\beta(t)}\left[1 + 2.5k\phi_{\alpha(t)}\right],$$

where $k = (\eta_{\alpha(t)} + 0.4\eta_{\beta(t)})/(\eta_{\alpha(t)}) + 0.4\eta_{\beta(t)})$, $\varphi_{\alpha(t)}$ is the volume fraction of the dispersed α phase, $\eta_{\alpha,\beta(t)}$ is the viscosity of blends, $\eta_{\alpha(t)}$ and $\eta_{\beta(t)}$ are the viscosities of the dispersed α phase and the matrix β phase, respectively. All the parameters changes with cure reaction.

After the occurrence of phase separation, in BMI-15 the β phase was continuous PES-rich phase. The *K* is almost a constant as the viscosity of PES-rich phase (β phase) is far higher than that of BDM/DBA-rich phase (α phase) at curing temperature that was below the glass transition temperature of PES. Under this circumstance, according to Einstein equation, the complex viscosity of blends mainly depends on the viscosity of PES-rich phase. On the contrary, In BMI-5, the β phase is continuous BDM/DBA-rich phase, in which the increase of the complex viscosity is sensitive to the increase of curing reaction conversion. Therefore, it is reasonable that the complex viscosity of blends with lower PES content is relatively more sensitive to curing temperature.

In brief, the phenomenon shown in Fig. 6 could be well explained by the phase morphologies in phase separation: the continuous BDM/DBA-rich phase in BMI-5 and the continuous PES-rich phase in BMI-15.

Effect of the molecular weight of PES

The effect of the molecular weight of PES on the complex viscosity was also investigated. As shown in

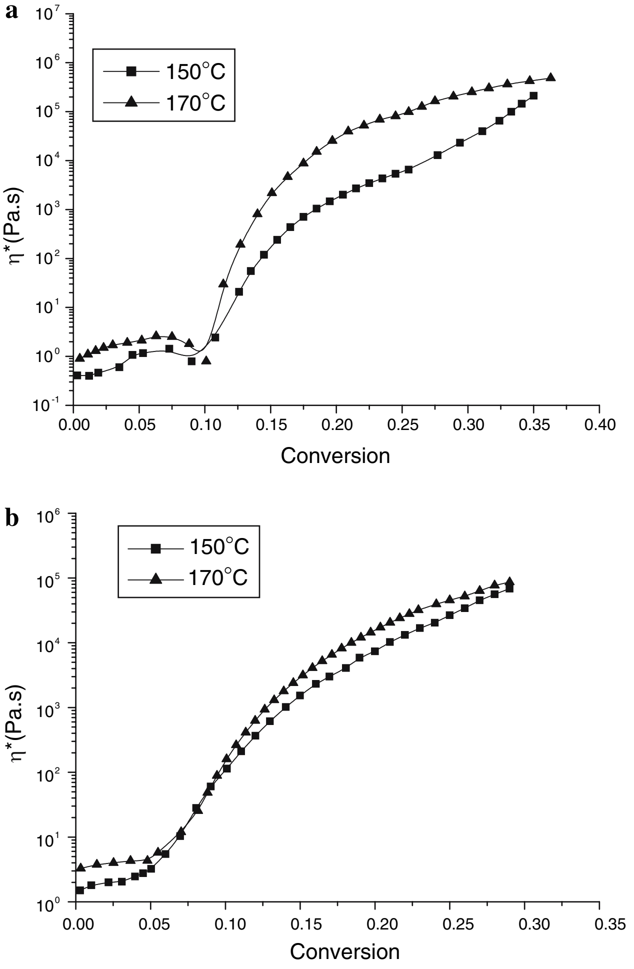

Fig. 6 Complex viscosities versus conversion of blends: (**a**) BMI-5, (**b**) BMI-15

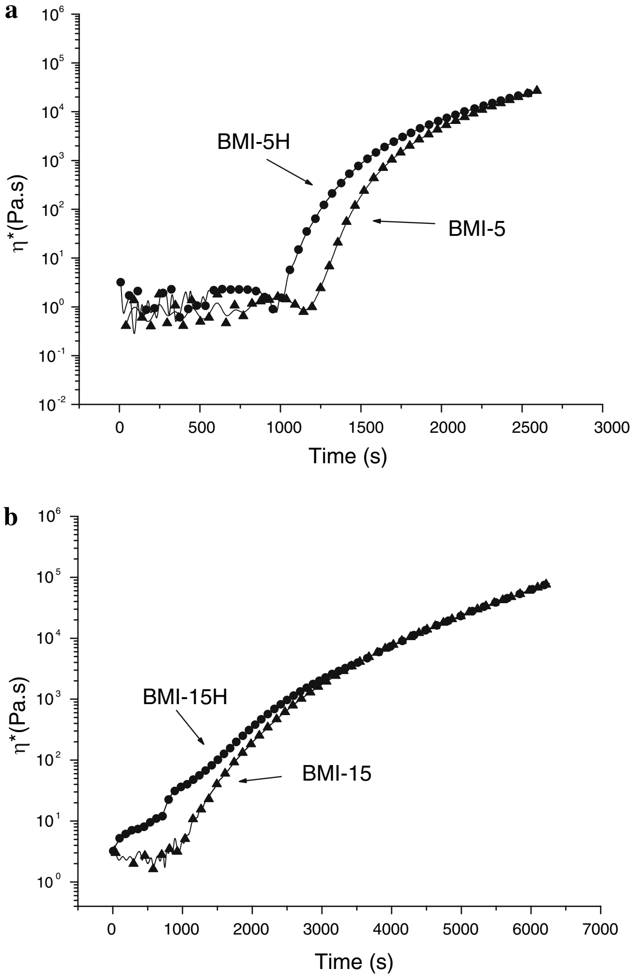

Fig. 7 Influence of PES molecular weight on the complex viscosity during curing at 150 °C. (**a**) 5 wt% PES, (**b**) 15 wt% PES

Fig. 7, at the beginning of curing reaction, the blends with high molecular weight PES (BMI-5H and BMI-15H) have high initial complex viscosities. Furthermore, the onset of phase separation delays for the blends with low molecular weight PES (BMI-5 and BMI-15). It is coincident with the results obtained from TRLS that the addition of high molecular weight PES can enhance the initial chemical quench depth, which facilitates the evolution of phase separation [23]. In addition, it is also shown in Fig. 7 that, after the occurrence of phase separation, the complex viscosities of blends with the same content of PES are somewhat close despite of the molecular weight of PES, which suggests that the effect of the molecular weight of PES on complex viscosity could be neglected after the occurrence of phase separation. In our previous work [24], it was found that the molecular weight of PES affected obviously the evolution of phase structure and the evolution of viscosity of the system. However, in this work, PES molecular weight mainly affected the onset time of phase separation of the blends, but has fewer effects on the evolution of complex viscosity in the succedent curing process.

Conclusion

The influences of the PES content, the molecular weight of PES and curing temperatures on the rheological behavior of PES modified bismaleimide resin were studied during isothermal curing. At the beginning of phase separation, the complex viscosity abruptly dropped in blends with PES dispersed phase structure, while quickly increased in blends with PES phase inversion structure. In addition, the complex viscosity of the blends with lower PES content increased faster than the blends with high PES content owing to the diluteness effect of PES. Moreover, the evolution of the complex viscosity of blends with high

PES content was relatively less sensitive to the curing temperature due to the formation of the continuous PES-rich phase. The PES molecular weight mainly influenced the onset of phase separation but was relatively less influential on the evolution of the complex viscosity in the succedent curing process. The results indicated that phase morphology as well as the composition of continuous phase played an important role in the rheological behavior of PES modified bismaleimide resin during isothermal curing.

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