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SHORT COMMUNICATION

Rheological behaviors and structural transitions in a polyethersulfone-modified epoxy system during phase separation

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Abstract The rheological behaviors and gelation transitions in a polyethersulfone (PES)-modified epoxy system during phase separation were studied by rheometry, time-resolved light scattering, and differential scanning calorimetry. Two separate structural transitions in the curing process of the blend were identified as the first one because of phase separation and the second one related to cross-linking reaction of epoxy resin. Both the times of the two structural transition at different temperatures could be described well by the Arrhenius type equation. The complex viscosity exhibits an exponential growing process during phase separation at various temperatures, correlating to the light-scattering results. The exponential behavior of complex viscosity could be attributed to the viscoelastic flow of epoxy-rich escaping from PES-rich during phase separation process.

Keywords Rheological behaviors · Gelation · Phase separation

Introduction

Traditionally, to improve the fracture toughness of thermosets using rubber modification is invariably accompanied by significant drops in heat resistance and rigidity. Therefore, much work has been made to toughen highly cross-linked thermosetting polymers with high modulus, high Tg thermoplastics, such as polyethersulfone (PES) [1, 2], polysulfone [3], poly (ether ether ketone) [4], and polyetherimide [5]. In these thermoplastic/ thermoset blends, the phase separation in curing process has been reported [6].

The polymerization-induced phase separation affects the rheological behaviors in great deal. In the blends with thermoplastic-dispersed structure, Kim and Char [7] noted that there is a fluctuation in viscosity just before the abrupt viscosity increase, which is believed to be due to the phase separation of thermoplastic from the thermoset matrix. Bonnet et al. [8] showed large interdependence between morphology and viscosity, a gradual increase in viscosity was observed in inversed phase structure systems at higher thermoplastic concentrations. Tercjak et al. [9] investigated the influence of the syndiotactic polystyrene concentration on the dynamic rheological properties of the samples. Meanwhile, the interplay between phase separation and gelation is an important parameter controlling the final morphology and material performance [10–12].

In our previous works [13–15], the phase separation of thermoplastic-modified epoxy resin systems was studied systemically, and it was also found that phase separation has an important effect on their rheological behaviors [14, 15]. In the present work, the rheological behaviors and gelation transitions in a PES-modified epoxy system during phase separation were studied in details by using rheological

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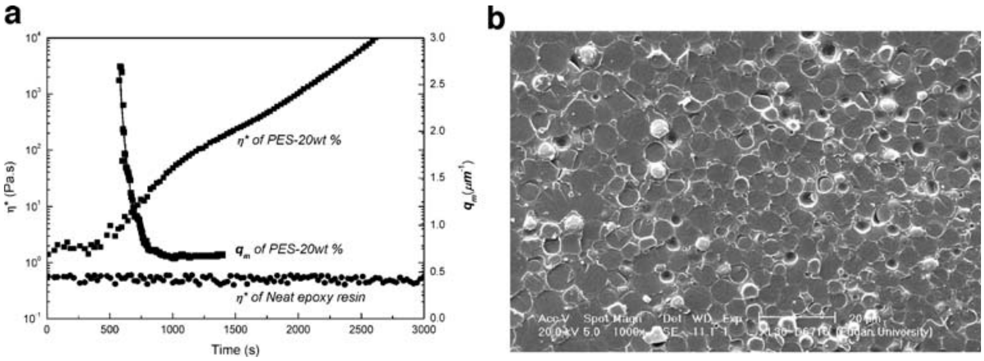

Fig. 1 Variation of η^* and $\boldsymbol{q}_{\mathrm{m}}$ vs time and the final morphology in the PES-20wt% cured at 130 °C. **a** Variation of η^* and $\boldsymbol{q}_{\mathrm{m}}$ vs time of PES-20wt % and neat epoxy resin cured at 130 °C. **b** Morphology of PES-20wt% cured at 130 °C for 5 h

measurements combined with time-resolved light scattering (TRLS) and differential scanning calorimetry (DSC).

Experimental

Materials and samples preparation The epoxy resin DER 331 was provided by Dow Chemical and is a low-molecular-weight liquid diglycidyl ether of bisphenol A (DGEBA) with an epoxide equivalent of 182–192. PES was supplied by Jilin University, China, which has an intrinsic viscosity of 0.36 dL/g. The curing agent is methyl tetrahydrophthalic anhydride (MTHPA), LHY 908, Ciba-Geigy.

The homogeneous mixture of PES/DGEBA was prepared by adding PES to the stirring epoxy monomer at 150 °C under nitrogen gas; after the mixture had cooled to 80 °C, MTHPA was added and stirred vigorously for 2 min till MTHPA was completely dissolved. The samples were degassed under vacuum for a few minutes. The weight composition of the blend is PES/DGEBA/MTHPA=45:100:80. The code name of the blend in this paper is *PES-20wt%.*

Measurements Philip XL 30 scanning electronic microscopy (SEM) was employed to examine morphologies of the fracture surfaces of cured specimens. A Setaram DSC92 instrument was used for cure reaction. The melt viscosity variations of the blends during cure reaction were recorded on ARES-4A rheometers by TA Instruments: About 1 g of the blend was sandwiched between two round plates and softened at 80 °C for 2 min. The plate distance was then adjusted to about 1 mm, and the temperature was raised quickly at a rate of 100 °C/min to the preset curing temperature. All the blends were tested under a parallel plate mode with a controlled strain of 1% to ensure that measurements were performed under linear viscoelastic conditions. The test multifrequencies are set at 1, 2, 5, 10, and 20 rad/s. The phase separation process during isothermal curing reaction was observed in situ on the self-made TRLS with a controllable hot chamber. The change of the light-scattering profiles was recorded at appropriate time intervals during isothermal curing. The blend of epoxy monomer with PES for TRLS observation was prepared by the melt-pressing film.

Table 1 t_{onset} and t_{offset} obtained by ARES and TRLS at different cure temperature during phase separation and relaxation times obtained by simulation of the results of ARES ($\tau\eta$) and TRLS (τ_{qm})

		110 °C	120 °C	130 °C	140 °C	150 °C
t_{onset} (s)	ARES	1,100	700	500	220	150
	TRLS	1,510	960	570	420	260
t_{offset} (s)	ARES	2,600	1,750	1,020	680	480
	TRLS	3,100	2,100	1,050	870	600
t (s)	ARES	522	361	219	154	114
	TRLS	332	224	80.5	69.3	42.6

Results and discussion

Rheological behaviors and phase separation

The rheological behaviors of thermoplastic-modified thermosetting systems are closely connected to their morpho-

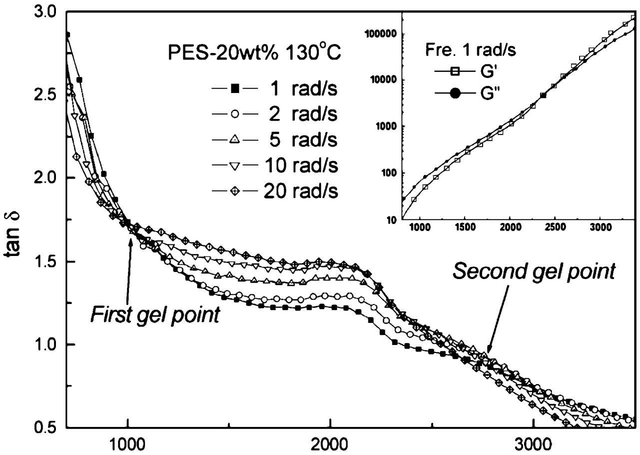

Fig. 2 Evolution of G' and G'' at 1 rad/s and tan δ of PES-20wt% cured at 130 °C isothermally at different frequencies

Table 2 The gel time and the critical exponent *n* of PES-20wt% at different temperatures

Temperature (°C)	t_{gel1} (t_{offset}) (s)	n_1	t_{gel2} (s)	n_2
110	2,600	0.66	5,600	0.56
120	1,750	0.67	3,600	0.55
130	1,020	0.69	2,800	0.52
140	680	0.70	2,080	0.44
150	480	0.68	1,200	0.48

logical evolution. The profile of complex viscosity $\eta^*$of PES-20wt% and neat epoxy resin cured at 130 °C is shown in Fig. 1. As we have reported previously [14, 15], the addition of PES would increase the curing rate of modified epoxy systems because of the catalyst effect of the hydroxy group in PES. Compared with the PES-20wt% system, the neat epoxy resin cured little at this time scale, and the viscosity was kept almost unchanged during this period because of the low curing rate of neat epoxy/anhydride at 130 °C.

At the beginning of cure reaction, the PES-20wt% blends behaved as semidilute polymer solutions having viscosities about 2 Pa s. Then, η^* increased quickly at about 500 s; the reason is because that the onset of phase separation caused the formation of a continuous thermoplastic-rich phase, which was also founded in our previous works [14, 15]. The morphology of the fully cured blend was observed under SEM (in Fig. 1b); phase inversion was founded from the beginning of phase separation and kept to the end of curing process. After approx. 2,000 s, the gradual increase in η^* caused by the network of the epoxy reins was observed. This phenomenon was reported in previous studies [9, 14, 15].

The corresponding TRLS results are also shown in Fig. 1. After the onset of phase separation, the scattering vector with maximum scattering intensity, $\boldsymbol{q}_{\mathrm{m}}$, appeared at 570 s and then decreased with time; finally, $\boldsymbol{q}_{\mathrm{m}}$ is approaching constant.

Both t_{onset} and t_{offset} obtained by ARES and TRLS at different curing temperatures are shown in Table 1. t_{onset} obtained by ARES is according to the jumping-off point of first rise in η^* and that obtained by TRLS is according to the time when light-scattering profiles appeared. t_{offset} obtained by ARES is according to the first critical gel point in rheology (which will be discussed in details later) and t_{offset} obtained by TRLS is according to the time when $\boldsymbol{q}_{\mathrm{m}}$ is approaching constant. The results show that both t_{onset} and t_{offset} obtained by ARES and TRLS correspond well with each other, although a little earlier for that of ARES. It is reasonable that the rheological change corresponds to the earlier stage of phase separation. It is also worthwhile to note that the onset (t_{onset}) and the offset (t_{offset}) of the phase separation obtained by TRLS are comparable to the first growth in complex viscosity profiles.

Discussion on two gel points

The polymer at the gel point is in a critical state. A general method to determine gel points from dynamic viscoelastic data is based on the observation that tan δ is independent of frequency at the gel point; that is, the tan δ curves as a function of reaction time at different frequencies pass through a single point [16–19].

Figure 2 displays a representative tan δ curve as a function of reaction time at five frequencies for the PES-20wt% cured at 130 C and the corresponding curves of G' and G'' at 1 rad/s are also attached. There are two points of intersection in the curves of tan δ vs cure time, which means that there are two critical state (structural transitions) in the PES-20wt% system, and these transition times at various temperatures are listed in Table 2. As shown in Table 2, both t_1 and t_2 decrease with increase of cure temperature; it can be attributed to the effect of cure rate, where the higher cure temperature will lead the higher cure rate.

For a critical gel, the self-similar relaxation governs the rheological behaviors; the characteristics of shear moduli

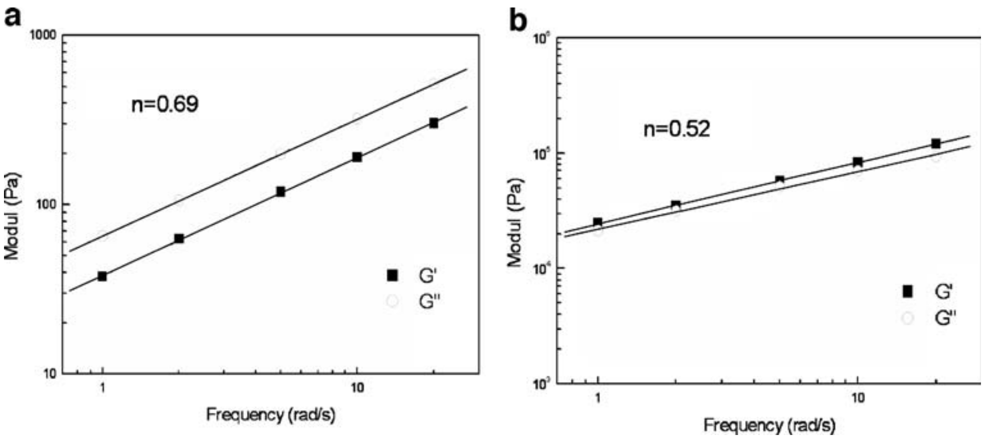

Fig. 3 Plots of dynamic moduli (G' and G'') vs frequency at the gel point in PES-20wt% cured at 130 °C. **a** at the first structural transition point; **b** at the second structural transition point

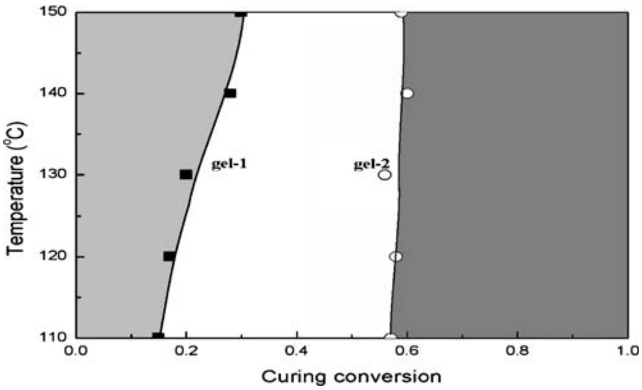

Fig. 4 Cure conversions of the two gel points at different cure temperature

(G' and G″) are predicted by power law expressions: $G' \propto G'' \propto \omega^n$ [16–20]. The critical relaxation exponent, n, is determined from plots of the dynamic moduli at the gel point vs the applied frequency, as shown in Fig. 3. The values of n at different temperature are also listed in Table 2.

As shown in Table 2, it is seen that both n_1 and n_2 of this system obey the universal power law independent on temperature. For a homogeneous system, this exponent reflects the strength of the critical gel; the higher n value means lower strength or loose networking at gel point. There are various theories to explain the value of the critical exponent [21–24], The critical exponent could be predicted by the Rouse model and the Zimm model. In the Zimm case [25], the system is dominated by hydrodynamic interactions between segments of polymer at $n \approx 2/3$, which is very close to the n value near the first gel points of this system. In contrast, the Rouse model [26] can be applied to concentrated polymer systems in which hydrodynamic interactions are completely screened out by polymer coil at $n \approx 1/2$, which is very close to the n value near the second gel points of this system.

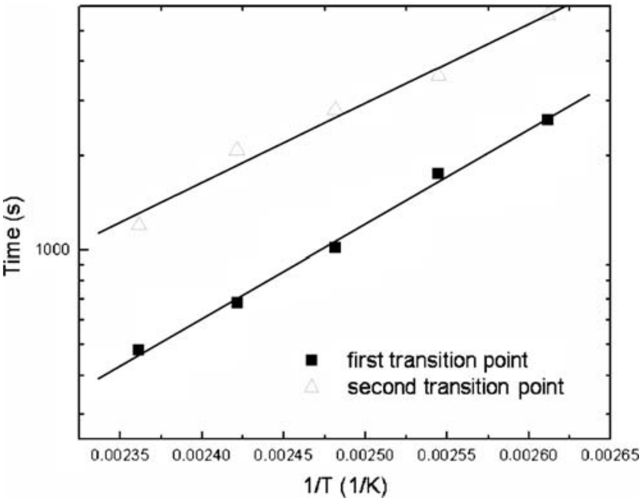

Fig. 5 An Arrhenius plot obtained by both t_{gel1} and t_{gel2}

To our studied blend systems, a heterogonous structure is formed because of the phase separation. It is not quite feasible to use the exponents; the above results can only be related to an aspect of the changes during phase separation and curing. Thus, the results above suggest that the first critical gel point may be related to phase separation with hydrodynamic interaction from small epoxy molecules, while the second one may be corresponded to the network of epoxy resin, and hydrodynamic interaction was screened by cross-linking molecular groups.

This physical scheme is also supported by DSC results as shown in Fig. 4, where the cure conversions of the two critical gel points at different temperatures are clearly separated. The cure conversion of the first gel point is quite low and vary with cure temperature in the range of 0.15 to 0.3. This is compatible with the scheme that the first gel point is related to phase separation.

However, the second gel points are independent of cure temperature and locate at about 0.58, which agree with the theoretical conversion of gelation of epoxy resin. This justifies the second gel point caused by the cross-link reaction.

It has been known that the dependence of gel time on temperature can be described using Arrhenius expression [27]:

$$t_{\mathrm{gel}} = Ae^{E_{\mathrm{a}}/RT} \tag{1}$$

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 by both t_{gel1} and t_{gel2} using Eq. 1, and based on the slopes, we can calculate the activation energy: E_{a1}=57.6 kJ mol^{-1}, E_{a2}=48.3 kJ mol^{-1}. In our previous works [13–15], we have found that

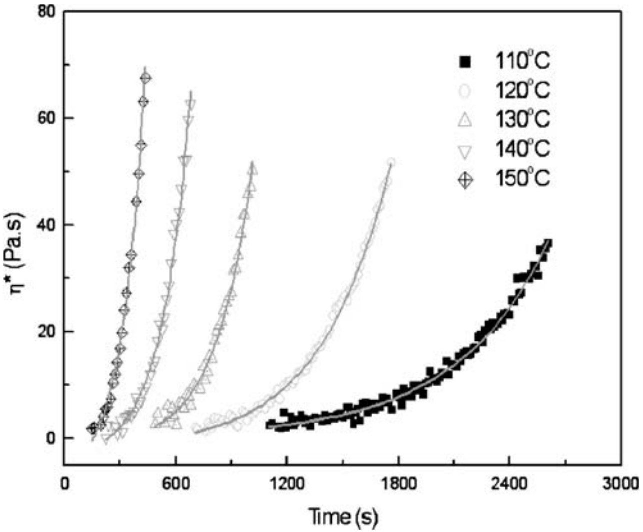

Fig. 6 η^* evolution during phase separation process in the PES-20wt % system at different temperatures. *Dot* corresponding to the experiment data and *line* corresponding to the result simulated by $\eta^*(t) = \eta_0^* + A_\eta \exp\left(t/\tau_\eta\right)$

the phase separation in our systems was controlled by diffusion. Therefore, E_{a1} may be related to diffusion activation energy to affect phase separation, whereas the E_{a2} is related to cure activation energy.

Exponential growth of complex viscosity during phase separation

As found in our previous works [13–15], the evolution of the light-scattering vector $\boldsymbol{q}_{\mathrm{m}}$ in the phase separation follows the equation:

$$q_{\mathrm{m}}(t) = q_0 + A_q \exp\left(-t/\tau_{q_m}\right) \tag{2}$$

Figure 6 is the η^* evolution plot during the phase separation process of PES-20wt% system cured at different temperatures (in the range of t_{onset} to t_{offset}) The experimental results of η^* gave a fairly well fitting to an exponential grow process as Eq. 3:

$$\eta^*(t) = \eta_0^* + A_\eta \exp\left(t/\tau_\eta\right) \tag{3}$$

Usually, time dependence of diffusion processes is related to power laws rather than to exponentials. In our case, the evolution of $\boldsymbol{q}_{\mathrm{m}}$ show an exponential decay with cure time because of the diffusion of epoxy escaping from thermoplastic-rich media [13–15]; therefore, it may be referred that exponential evolution of η^* may be also related to the diffusion of epoxy molecules.

Because the cure conversion was still low (<0.3) at t_{offset} and only had a little increase in molecular weight of epoxy resin during phase separation, the viscosity growth was caused by an increase in the thermoplastics concentration of the thermoplastics-rich phase in phase separation.

The characteristic relaxation times of rheological change ($\tau\eta$) obtained by Eq. 3 were listed in Table 1. Compared with those obtained by TRLS ($\tau_{q\mathrm{m}}$), it should be indicated that the relaxation times obtained by rheological behavior are higher than the relaxation times obtained by TRLS. The possible explanation could be related to the fact that $\boldsymbol{q}_{\mathrm{m}}$ reflects average domain size and η^* reflects the longer relaxation modes of macromolecular deformation of inter/intradomains.

Conclusions

The characteristic rheological behavior of thermoplastic-modified thermosetting systems is connected closely to both phase separation and gelation. There are two separate gel points identified: The first one is attributed to phase separation, and the second is attributed to the cross-link reaction of epoxy. The complex viscosity evolution corresponds well with the TRLS result, and it showed an exponential grow procedure during the phase separation process, which is influenced by the viscoelastic effect.

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