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SHORT COMMUNICATION

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Phase separation and rheological behavior in thermoplastic modified epoxy systems

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Abstract The relationship between rheological behavior and phase separation in polyesterimide modified epoxy systems was studied by rheometry, time-resolved light scattering (TRLS), and Differential Scanning Calorimetry (DSC). The rheological behaviors of blends during phase separation showed an exponential grow of complex viscosity, while the phase separation was inhibited by the vitrification of the polyesterimide-rich matrix phase rather than gelation of dispersed epoxy-rich particles. The characteristic relaxation time obtained by the simulation of complex viscosity could be described well by the Williams–Landel–Ferry equation, which corresponded well with the light scattering results. Therefore, this work would further provide the experimental proofs that the exponential relaxation behavior of complex viscosity could be attributed to the viscoelastic flow of epoxy-rich escaping from polyesterimide-rich matrix during phase separation.

Keywords Phase separation · Rheological behavior · Exponential relaxation

Introduction

Thermosets tend to have a characteristic low resistance to brittle fracture; thus, rubbers or thermoplastics are invariably blended to improve their fracture toughness[1–5]. It is well-known that the mechanical properties of the materials are determined by their final morphologies. With the increase of thermoplastics amount in the modified thermoset systems, three kinds of morphologies have been observed, namely, thermoplastics particle structure, bicontinuous (a co-continuous, double-phase structure which consists of a dispersion of macroscopic irregular domains showing a phase-inverted structure in a thermoset-rich matrix exhibiting a dispersion of thermoplastic-rich particles) and phase inversion (or sponge-like, network-like for a dispersion of thermoset-rich in a thermoplastic-rich matrix) structure.

In thermoplastic/thermoset blends, the whole curing process combining phase transformation has been reported, [6] which involves the onset of phase separation, gelation, fixation of the dimension of the phase structure, offset of phase separation, and vitrification. When the system is fully gelled, the spacing ceases to increase, but the concentration fluctuation continues to grow further, and the whole system is finally vitrified by the increase in T_g of the epoxy-rich phase.

However, it should be noted that spontaneous pinning of phase structure was also observed due to the vitrification

(plasticization) of thermoplastic-rich phase, i.e., the offset of phase separation was earlier than gelation of thermoset [7]. Thus, the morphology of a blend is determined by the competition of the rates between phase separation and gelation [8].

During isothermal polymerization, a thermosetting polymer exhibits profound rheological changes; in particular, the steady shear viscosity increases steadily and then diverges at the gel point, whereupon the equilibrium modulus becomes finite [9]. Whereas, the modification of thermoset with thermoplastic changed their rheological behaviors completely. It has been reported that the initially low complex viscosity increases abruptly during curing, which is the typical viscosity profile during the curing of toughened epoxy systems [10]. While in the blends with thermoplastic-dispersed structure, Kim et al. [11] also 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. Other experimental results [3] showed that a large interdependence between morphology and initial composition was exhibited; when thermoplastic concentration was higher, a gradual increase in viscosity was observed in phase inversion structure.

Although different types of models describing the viscosity evolution of immiscible thermoplastic–thermoplastic blends [12] exist in literature, very few describe that of thermoplastic–thermoset blends. Unlike the thermoplastics, in which the isochronal complex viscosity is an extremely degenerated parameter and is adequate only for a linear viscoelastic body, thermosets and their blends with thermoplastics have shown an interesting rheological behavior during isothermal study [3]. As a result, any one is interested in a suspension like a thermoplastic in a reactive thermoset precursor, where the coexisting phases are changing continuously in composition with reaction time.

In our previous works, it has been found that the evolution of the light-scattering vector q_m during the late stage of spinodal decomposition follows the time–temperature superposition principle (WLF-like function) [13], and phase inversion structure was observed in the early stage of phase separation in polyetherimide and polyethersulfone-modified thermoset systems [14]. The aim of the present work is to propose an analysis of the relationship between the rheological behavior and the phase separation by using rheological measurements combined with time-resolved light scattering (TRLS), differential scanning calorimetry (DSC), and scanning electronic microscopes (SEM).

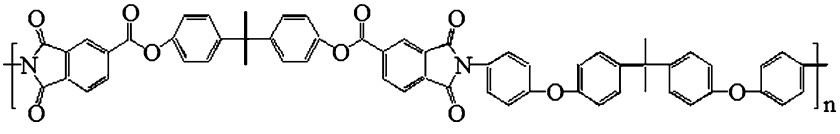
Experimental

Materials and preparation of samples The epoxy oligomer DER 331 (182-192 g/eq, Dow Chemical) is a liquid diglycidyl ether of bisphenol A (DGEBA). The curing agent is methyl tetrahydrophthalic anhydride (MTHPA), HY 918, Ciba-Geigy. The initiator is benzyldimethylamine (BDMA) from Shanghai Third Reagent Factory. Polyesterimide (PEtI), (Scheme 1) which has an inherent viscosity of η_{inh}=0.69 dl/g and a weight-average molecular weight of 4.9×10^4 g/mol, was synthesized by the two-step route as described elsewhere [15].

The homogeneous mixture of thermoplastics/DGEBA was prepared by adding 45 phr (per hundred weight of epoxy resin) PEtI to the stirring epoxy monomer at 150 °C under nitrogen gas, after the mixture had cooled to 80 °C; 80 phr MTHPA and 0.2 phr BDMA were added and the mixture was stirred vigorously for 2 min until MTHPA and BDMA were completely dissolved. The samples were degassed and then used immediately. In our studied PEtI-20 system, PEtI has a weight percent of 19.98.

Measurements A Setaram Differential Scanning Calorimetry (DSC92) instrument was used for cure reaction and Tg detection. The total reaction heat of samples was obtained by the summation of the heat of reaction generated during the isothermal run and the residual heat of reaction generated during the second scanning run using a 5 °C/min heating rate from room temperature to 300 °C. Philip XL 39 scanning electronic microscopes (SEM) were used to examine morphologies of the fracture surfaces of cured specimens. The melt viscosity variations of the blends during cure reaction were recorded on an Ares-9A rheometry instrument: about 1 g of the blend was sandwiched between two round fixtures and softened at 60 °C for 2 min. The plate distance was then adjusted to about 1.5 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% and test frequency of 1 Hz to ensure that measurements were performed under dynamic equilibrium conditions. The phase-separation process during the isothermal curing reaction was observed at real time and in situ on the self-made time-resolved light scattering (TRLS) instrument with controllable hot chamber and with the TRLS technique described elsewhere [4].

Scheme 1 Structure of polyesterimide



Results and discussion

Rheological behavior of the blend during curing

As different morphologies have complicated the rheological behaviors, PEtI-20 system, a blend with phase inversion structure at all curing temperatures, was selected and would help to understand the connections between evolutions of complex viscosity and phase separation. The starting PEtI-20 system is a homogeneous mixture of epoxy monomer, a curing agent, and an initiator mixed thoroughly with a PEtI sample that amounts to 20 wt% of total mixture. The mixture was then cured at different temperatures. Eventually epoxy-rich particles emerge in the PEtI-rich matrix and form the phase separation structure. Previous studies [13, 14] have shown that the morphology at the initial phase separation stage is the PEtI-rich matrix with dispersed epoxy monomer (oligomer)-rich particles, which is formed due to the viscoelastic effects.

As shown in Fig. 1a, as an example, PEtI-20 shows a phase inversion structure, in which about 3–5 um diameter of epoxy-rich particles dispersed in the PEtI-rich matrix after cured at 150 °C for 5 h. Fig. 1b. shows the change of complex viscosity with the curing time at all isothermal curing temperatures. All the complex viscosities manifest a similar pattern at different temperatures.

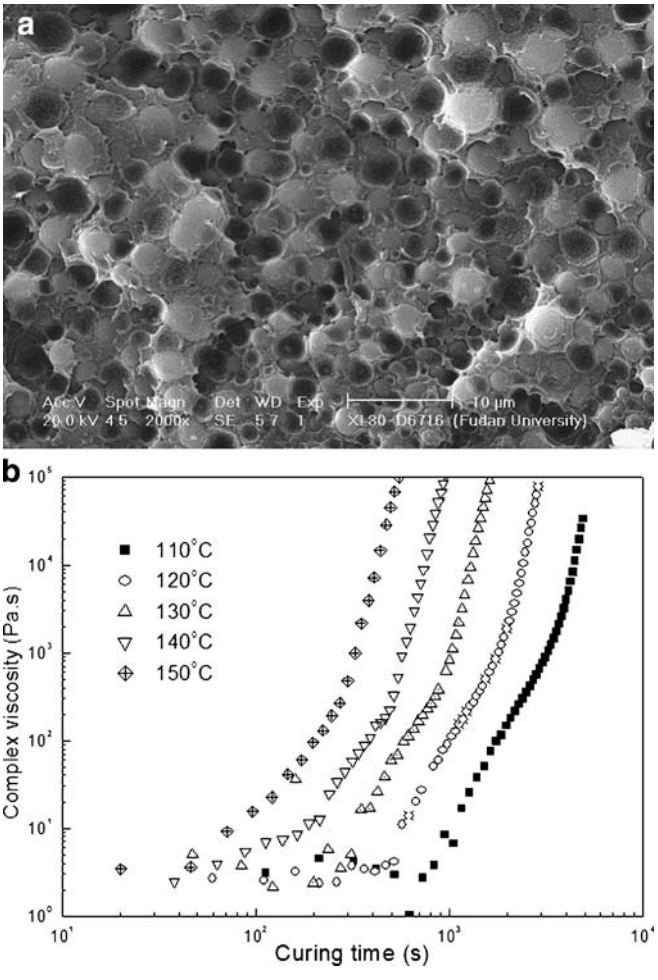


Fig. 1 **a** SEM of PEtI-2-cured at 150 °C; **b** complex viscosity evolution in PEtI-20-cured at different temperatures

Nevertheless, the rheological behavior could not be understood until determination of the curing conversion and time interval between the onset and offset of phase separation. Table 1 shows the phase separation time and curing conversion interval at different temperatures observed by TRLS and DSC, in which the onset of phase separation was defined as the appearance of light-scattering profiles and the offset of phase separation as fixedness of scattering vector $\boldsymbol{q}_m$ and light intensity I_m. The curing conversions were quite low at the onset of phase separation, and most of the epoxy monomers are unchanged (x-Onset at about 0.1 and x-Offset at about 0.2) during the phase separation process.

Therefore, it is quite clear that before phase separation, complex viscosity almost keeps unchanged, and then increases suddenly when the homogeneous mixture decomposed into a phase inversion structure. It is also worthwhile to note that the onset and the offset of the phase separation are comparable to the first fluctuations in complex viscosity profiles [3, 5, 16]. After the offset of phase separation caused by vitrification (plasticization) of PEtI-rich phase, another abrupt increase of complex viscosity was then observed because of the extensive network formation of the epoxy matrix (gelation) [3, 16].

Exponential relaxation of complex viscosity

Furthermore, the evolutions of the complex viscosity of the PEtI-rich phase during phase separation was plotted as

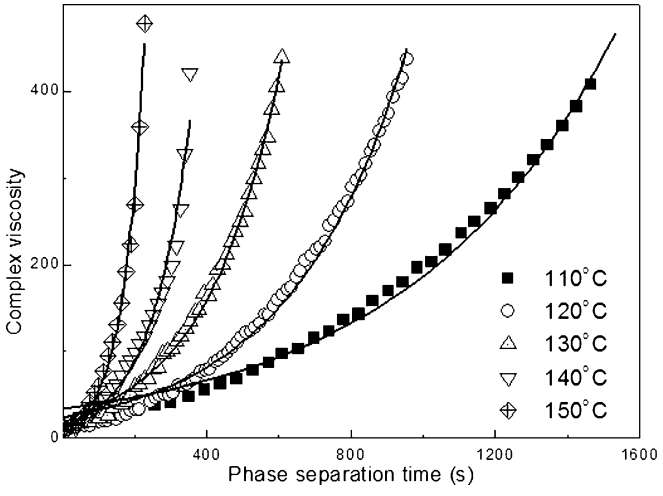


Fig. 2 Complex viscosity evolution during phase separation in PEtI-20-cured at different temperatures. *Dot* corresponds to the experimental data and *line* corresponds to the result simulated by Eq. 1

Table 1 Phase separation time vs curing conversion obtained by TRLS and DSC for PEtI-20

Temp. (°C)	*t*-Onset(s)[a]	*x*-Onset[a]	*t*-Offset[b]	*x*-Offset[b]
150	270±10	0.19±0.005	440±20	0.33±0.01
140	300±10	0.11±0.002	630±20	0.27±0.01
130	360±10	0.09±0.002	780±20	0.20±0.01
120	730±20	0.09±0.002	1210±40	0.20±0.01
110	840±20	0.08±0.002	2750±50	0.20±0.01

[a] *t*-Onset, *x*-Onset: the time and curing conversion of onset of phase separation observed by TRLS and DSC
[b] *t*-Offset, *x*-Offset: the time and curing conversion at the fixedness of $\boldsymbol{q}_m$ and I_m

shown in Fig. 2, in which they showed an exponential growth of the complex viscosity as

$$\eta*(t) = \eta*_0 + A_0 \exp(t/\tau), \tag{1}$$

where A_0 is magnifier, and τ is the relaxation time. The characteristic relaxation times of rheological behavior were obtained by simulation of all complex viscosity patterns from Eq. (1) (Table 2), and the results indicate that the complex viscosity development fitted exponential growth quite well.

To study the exponential growth of complex viscosity, light-scattering profiles were also recorded at appropriate time intervals during isothermal curing. As an example, Fig. 3 shows profiles for the PEtI-20 system cured at 150 °C isothermally. The appearance of the maximum of scattered light intensity is an indication for the phase separation, and the decrease of $\boldsymbol{q}_m$ and the increase of I_m corresponded to the phase structure size and concentration growth, respectively.

As shown in Fig. 3b, PEtI-20 system at 150 °C, as an example, typical exponential decays of both scattering vector $\boldsymbol{q}_m$ and light intensity I_m were found by simulation of TRLS results to Eq. (2).

$$q_m(t) = q_0 + A_1 \exp(-t/\tau);\ I_m(t) = I_0 + A_2 \exp(-t/\tau). \tag{2}$$

Here A1 and A2 are magnifiers and τ is the relaxation time and could indicate the coarsening capability of epoxy droplets. Furthermore, the relaxation time τ, obtained by simulation of results of both TRLS and complex viscosity vs temperature T listed in Table 2, were simulated by the Williams–Landel–Ferry (WLF) equation

$$\log\frac{\tau}{\tau_s} = \frac{-C_1(T - T_s)}{C_2 + (T - T_s)}, \tag{3}$$

where the C1 and C2 values are the empirical constants of 8.86 and 101.6 in the universal WLF function for polymer melts viscosity, and the reference temperature T_s is usually selected about 50 °C higher than T_g. As shown in Fig. 4, the simulation results give a good fit to the experimental data. The T_s values obtained from the simulation of scattering vector $\boldsymbol{q}_m$, light intensity I_m, and complex viscosity are 269+7, 282+8, and 284+7 K for PEtI-20 systems, respectively. It means that the relaxation times of both TRLS and rheological results obey the time–temperature superposition (TTS) principle and can be described by the WLF equation [13, 14].

As T_g (248.2 K) of the epoxy-anhydride, without PEtI being measured by DSC previously, the result implies that the coarsening process at the late stage SD is mainly controlled by the viscoelastic flow of epoxy monomers [13, 14]. It is interesting to note that the parameter τ obtained by simulation has a reasonable agreement between the TRLS and rheological results (Table 2 and Fig. 4).

Table 2 Relaxation times obtained in evolution of complex viscosity and TRLS profiles for PEtI-20

Temp. (°C)	$\tau(\eta^*)$[a]	R^2	$\tau(q_m)$[b]	R^2	$\tau(I_m)$[c]	R^2
150	59±2	0.993	40±0.7	0.996	54±0.8	0.998
140	108±3	0.992	63±1	0.996	94±6	0.996
130	204±3	0.995	102±1	0.997	165±15	0.996
120	333±4	0.995	133±2	0.997	217±19	0.995
110	592±6	0.993	209±3	0.995	363±20	0.997

R^2 Correlation coefficient
[a] Relaxation time related to viscosity
[b] Relaxation time related to $\boldsymbol{q}_m$
[c] Relaxation time related to I_m

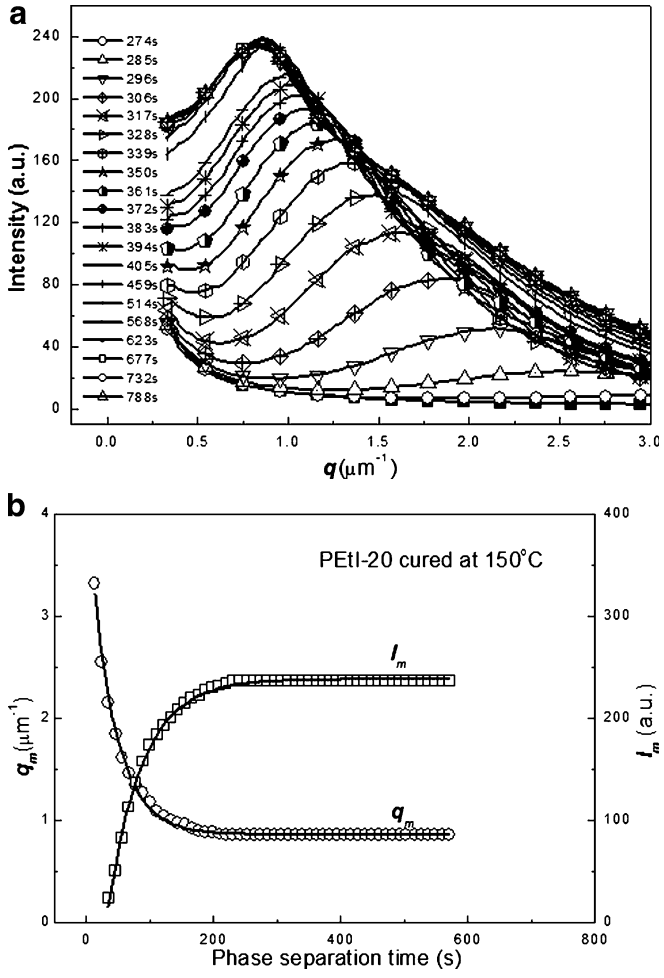


Fig. 3 TRLS profiles for PEtI-20-cured at 15-°C. **a** q_m vs I_m at different curing times; **b** q_m and I_m vs phase separation time. *Dot* corresponds to the experimental data and *line* corresponds to the result simulated by Eq. 2

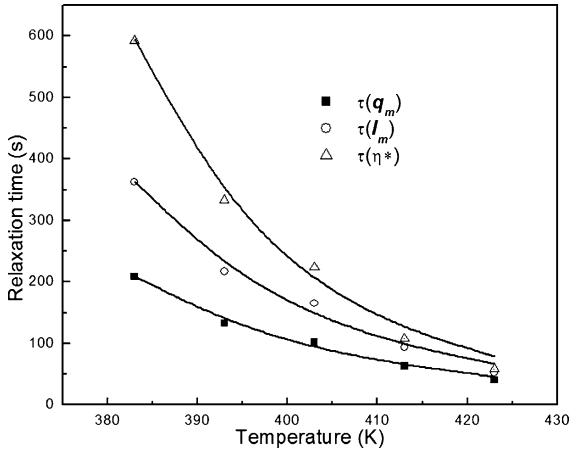


Fig. 4 The plots of the relaxation time τ vs temperature for PEtI-20. *Dot* corresponds to experimental data and *line* corresponds to the result simulated by Eq. 3

Therefore, the relaxation behavior of both TRLS and rheological behavior could be attributed to the diffusion (viscoelastic flow) of epoxy monomers/growing chains during phase separation, in which the relaxation behavior of q_m and I_m resulted from the decrease of diffusion rate of epoxy monomers (viscoelastic flow) escaping from PEtI-rich matrix phase. As it is well-known that I_m and q_m are expectedly comparable as

$$I_m \sim c/q_m^3 \tag{4}$$

where c is the concentration of the droplets of size $1/q_m$, i.e., the concentration also has an exponential decay process during phase separation, which transferred PEtI-rich from viscous flow to elastic state and vitrified finally.

As the complex viscosity was a control factor in phase separation process, the reason of complex viscosity exponent growth also needed to be explored. The complex viscosity of blend system could be described by the Einstein equation: [3, 17]

$$\eta(t) = \eta_{TP(t)}\left(1 + 2.5K_{e(t)}\phi_{TS(t)}\right), \tag{5}$$

where $\eta(t)$ is the viscosity of blend system and $\eta_{\mathrm{TP(t)}}$ is that of the thermoplastic-rich continues phase, $\phi_{TS(t)}$ *is the volume fraction of thermoset-rich dispersed phase in phase inversion structure, and* $K_{e(t)}$ *is the Einstein coefficient.*

During phase separation, the change of curing conversion is quite low and the viscosity difference between thermoplastics-rich matrix and dispersed thermoset-rich (low conversion and molecular weight) is very large and increases with the phase separation process; at the extreme of negligible dispersed phase viscosity of thermoset-rich, Eq. (5) reduced to

$$\eta(t) \sim \eta_{TP}(t) \tag{6}$$

as thermoplastics-rich phase could be taken as a polymer solution and its viscosity is determined by the free volume, which has been employed by Kelley and Bueche [18] to predict the viscosity of concentrated (entangled) polymer solution using the neat polymer (thermoplastics) as the reference. The final equations are:

$$\frac{\eta}{\eta_p} = \phi_p^4 \exp\left(\frac{1}{\phi_p + f_p + \phi_L f_L} - \frac{1}{f_p}\right) \tag{7}$$

The free volumes of the polymer and liquid (thermosets) are $f_p\left(f_p^{=0.025+4.8\times10^{-4}\left(T-T_{gp}\right)}\right)$ and $f_L\left(f_L^{=0.025+\alpha_L\left(T-T_{gL}\right)}\right)$, respectively. The α_{L} is the difference between the expansion coefficient of the liquid above and that of below T_{g}. The glass transition temperatures of the polymer and the solvent

are T_{gp} and T_{gL}, respectively. By substituting exponent decay of phase separation and concentration as Eqs. (4 and 6) into Eq. (7), we could get the exponent growth of viscosity as $\eta \propto e^{t/\tau}$. Thus, it means that the viscosity would be related to the relaxation time τ, i.e., diffusion of epoxy monomers/growing chains from thermoplastic-rich results in an exponent decay of thermoplastic concentration during phase separation, which give an exponent growth of complex viscosity.

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