



Rheological behavior of the epoxy/thermoplastic blends during the reaction induced phase separation



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ABSTRACT

The correlation between rheological behavior and time evolution of the phase separation patterns was investigated in the epoxy/thermoplastic blends. Before and during the induction period of phase separation, the storage and loss modulus initially increased with epoxy curing reaction and the concentration fluctuation. At the late stage of phase separation, the modulus values also increased and showed a sharp enhancement around the epoxy gel point. However, the time evolution during the reaction induced phase separation process differed a lot at various thermoplastic (TP) concentrations. At the low TP concentrations, the rheological parameters decreased with the coarsening of sea-island structure. At the high TP concentrations, the TP-rich continuous structures initially formed and maintained until the end, resulting in a continuous increase for the rheological characters. At middle TP concentrations, formation and evolution of the three-layered structure displayed a complicated rheological behavior. It was found that the storage modulus quickly increased, reached a vertex, then rapidly decreased, reached a minimum, and increased again afterwards. Although the rheological behaviors were almost phenomenologically similar as that in the normal dynamically symmetric system, driving force for the variation was fundamentally different. Especially for the case of middle TP concentrations, the behavior of the holistic volume shrinking of the slow dynamic TP-rich network and the flowing out of the fast dynamic epoxy-rich phase from the network during this period, as radically transformed the nature of the matrix from an elastic network to a macro-phase separated layer structure and caused the dramatic change of the rheological behaviors.

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1. Introduction

Reaction induced phase separation of the epoxy/thermoplastic blends has been extensively investigated from both fundamental and industrial viewpoints [1–6]. Morphology is one of the most interesting topics, since it directly dominates the final performance of the material. After the samples are cured, various morphological structures can be obtained: sea-island structure formed with low thermoplastic (TP) loadings, nodular structure formed at high TP concentrations, and bicontinuous, salami or layered structure formed in the middle TP concentration range [7–10]. There are several factors for the various morphology formation, i.e.,

compatibility between the components, process and competition of the reaction and phase separation, gelation time, etc. In the epoxy/TP blends, phase separation will be induced by the reaction as the molecular weight of epoxy increases, but slowed down and finally stopped due to the epoxy gelation. Thus, competition between the curing reaction and phase separation is a crucial point on the morphology and structure development [1,2,11–16].

Rheological response during this process may directly reflect the morphological transformation on different length scales, as will greatly benefit the understanding on the reaction and phase separation mechanism in such systems [17–24]. During the curing reaction of the neat epoxy/curing agent system, the storage (G') and loss modulus (G'') gradually increase with curing time and then abruptly increase at gelation [25–28], where G' and G'' will typically intersect [29–31]. However, for the epoxy/TP blends, the rheological behavior will be significantly affected by the reaction-

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induced phase separation and thus becomes complicated. Before phase separation starts, the modulus increases similarly as that of the neat epoxy system. With the phase separation proceeding, various patterns of rheological information may be obtained due to the competition between reaction and phase separation [12,19,24]. In the epoxy/polyetherimide (PEI) blends, Bonnet et al. [12] found a large interdependence between the rheological behavior and phase separation. When PEI concentration was low, phase separation induced a rapid decrease of the viscosity. While when PEI concentration was high, phase separation led to a gradual increase in the viscosity. The viscosity fluctuation dependence on phase separation process was also noticed by Kim et al. [19]. In the recent work on epoxy/Acrylonitrile Butadiene Styrene (ABS) blends, Thomas et al. [24] found that the modulus varied together with the evolution of complex phase separation, and complex viscosity profiles showed an exponential growth with curing reaction. Besides the present understandings, rheological behavior may remarkably differ for the individual systems. However, the phenomenological response must consistently reflect the essential features of the morphological transformation and phase separation process, which need more in-depth and systematic investigations, especially in the reaction-induced phase separation study of the epoxy/TP blends [32–34].

In our previous work, a typical but not traditional three-layered structure was observed and this ubiquitous nature has been discussed in the epoxy/TP blends [35–39]. Similar three-layered structure phenomenon has also been reported in the photopolymerization-induced phase separation of a polystyrene derivative (PSAF) and methyl methacrylate (MMA) system [40]. It should be noted that the three-layered structure in our case was not originated from the wetting phenomena [36] but caused by the dynamically asymmetric phase separation process [37]. Volume shrinking of the slow dynamic TP component and hydrodynamic flow of the fast epoxy component during the three-layered structure formation process must have a significant effect on the corresponding rheological behavior. This is a very important topic related to the polymer entanglement, modulus and engineering properties of this type of materials. Some recent investigations on viscoelastic properties related to the morphology evolution also give a clue for our further discussion of epoxy/TP blends in this paper [41–43].

2. Experimental section

The epoxy resin used was a low molar mass liquid diglycidyl ether of bisphenol A (DGEBA), supplied by Shell Chemical Co. (product No. Epon 828). The curing agent used was 4,4'-diaminodiphenyl sulfone (DDS), purchased from Sigma–Aldrich Chem. Co. Three kinds of amorphous TP were used to blend with the epoxy resin system: poly(vinyl acetate) (PVAc) (Alfa Aesar, $M_n = 24,000$ g/mol, $M_w = 45,000$ g/mol, $T_g = 40$ °C), polysulfone (PSF) (Solvay Co. Udel P1700, $M_n = 38,000$ g/mol, $M_w = 62,000$ g/mol, $T_g = 183$ °C) and poly(ether imide) (PEI) (General Electric Ultem 1000, $M_n = 26,000$ g/mol, $M_w = 50,000$ g/mol, $T_g = 210$ °C). DDS was dried at 100 °C for 2 h under vacuum before use. The other chemicals were used as received.

The mixture of epoxy and TP was mechanically stirred at 150 °C for about 3 h to sufficiently blend the components, cooled to 100 °C for the addition of DDS, and stirred vigorously for about 30 min. Homogeneous samples with different TP concentrations were thus obtained, as was proved through the transparency of the sample and phase contrast optical microscope observation. The ratio of DGEBA/DDS was fixed at 1:0.27 w/w, i.e., 0.8 hydrogens of amino groups per epoxide group. All samples were degassed under vacuum at 130 °C for about 25 min to completely remove the air bubbles before the subsequent measurements.

Rheological properties were measured with an Advanced Rheometric Expansion System (ARES, Rheometric Scientific, Piscataway, NJ), which was a strain rate controlled rheometer. A stress-controlled rheometer (Anton Paar MCR 501) was also used to confirm the experimental results. The sample (about 0.5 g) was first sandwiched between two parallel plates (diameter: 25 mm) at room temperature. Then, the temperature was raised quickly to the preset curing temperature. After the sample was softened for about 1 min, the gap was gradually adjusted to 1 mm. The dynamic strain sweep measurements at the frequency of 1 rad/s were conducted for the initially homogeneous sample. The linear viscoelastic region was found at 30% strain and less. The samples were also measured at different frequencies with the strain of 1% to obtain the gel point. In order to avoid disturbing the phase separation process and the morphological structure formation, the oscillatory conditions were controlled at strain of 1% and frequency of 1 rad/s for the time sweep experiments. Morphological study with transmission electron microscope (TEM) and scanning electron microscope (SEM) at the same conditions have been studied and reported earlier [10,37].

3. Results and discussion

3.1. Rheological behavior of the epoxy/PSF blends

For the epoxy/thermoplastic systems, the crosslinking reaction may be slightly depressed by the addition of the thermoplastic [44–46], which will not change our discussion on the morphology evolution, since only epoxy species are active to form the chemical network and phase separation is almost complete before this stage. Fig. 1 shows the variation of storage (G') and loss modulus (G'') at different frequencies, with the epoxy/PSF blends at the PSF weight fraction $w = 0.15$. Small amplitude oscillatory shear was conducted at different time during the isothermal curing process at 130 °C. It was observed that the storage modulus generally increased during the reaction process. In the low frequency region, from 0.1 to 1 rad/s, the data initially fluctuated vibrantly, which was caused by the insensitive response of the rheometer at the very low viscosity [47]. After the sample was cured for about 130 min, the slope at low angular frequency (ω) was found to become smaller in the terminal region, which implied the formation of a network structure. This phenomenon was very clear in the following sweeps from 135 to 159 min, with the terminal region shifting to even lower frequencies. This period may correspond to the development of the bicontinuous structure, as will be discussed later. However, G' in the low ω range at about 168 min was smaller than before, and the plateau phenomenon disappeared. Usually G' should increase with the epoxy reaction. It indicated that this decrease phenomenon must correspond to the phase structure variation. It continued for about 50 min in the subsequent scans. G' at about 219 min was larger than that at 159 min and kept increasing in the following reaction and phase separation process. The question is why the G' decreased for a while instead of continuously increase with the reaction of epoxy? To answer this point, time evolution of the morphology will be discussed in the following section.

It was found that $G' < G''$ during the reaction and phase separation process, which indicated that the sample generally exhibited as a complex liquid. Molecule size of epoxy gradually increased with the reaction continuing, and phase separation proceeded. Phase structure coarsened and the characteristic length of the phase domains increased, as caused the plateau region shifting to lower frequencies, where the micro-sized domains may be detected. The conformational relaxation of the crosslinked clusters became slower and slower. Especially when the percolation limit was reached, gelation can be firstly detected at high frequencies, which probes a smaller dimension. Thus, the gelation information

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