Notes

Nucleation/Growth in the Metastable and Unstable Phase Separation Regions under Oscillatory Shear Flow for an Off-critical Polymer Blend

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Introduction

After some important advancement[1−7] were obtained in the phase separation of polymer blends in static conditions, researchers gradually turned their attention toward the area of phase transitions under shear field in recent years.[8−12] Light scattering and neutron scattering were frequently used to investigate the shear induced mixing phenomenon.[8,12] However, most of these studies[8−12] were focused on the steady state of the phase boundary shift, either at critical or off-critical compositions, under simple or oscillatory shear field. There were few studies reporting the kinetics of phase transitions under a shear field.[13]

On the other hand, based on some excellent work of Fredrickson and Larson[14] as well as Ajji and Choplin,[15] rheological theory has been introduced into the phase transitions near the critical point. In these theories the essential ingredient is the dominance of concentration fluctuations in the viscoelastic measurements. The general functions of fluctuation dependent storage modulus and loss modulus are[14] shown as follows:

$$G'(\omega) = \frac{k_B T \omega^2}{15\pi^2} \int_0^{k_c} \frac{k^6 S_0^{\,2}(k)}{\omega^2 4\varpi^{-2}(k)} \left[\frac{\partial S_0^{\,-1}(k)}{\partial(k^2)}\right]^2 \mathrm{d}k \qquad (1)$$

$$G''(\omega) = \frac{2k_B T \omega}{15\pi^2} \int_0^{k_c} \frac{k^6 S_0^{\,2}(k)\varpi(k)}{\omega^2 4\varpi^{-2}(k)} \left[\frac{\partial S_0^{\,-1}(k)}{\partial(k^2)}\right]^2 \mathrm{d}k \qquad (2)$$

where $\varpi(k) = k^2 S_0^{\,-1}(k)\lambda(k)$ and $S_0(k)$ is the static structure factor, $\lambda(k)$ the Onsager coefficient, and k the wave vector. These general equations are suitable for both block copolymers and binary homopolymer blends. Ajji and Choplin applied these equations to a binary homopolymer blend near the critical point.[15] Using the structure factor from the random phase approximation (RPA) and the scaling concept, they obtained two detailed expressions of G' and G''. The ratio of $G'(\omega)/G''^2(\omega)$ in their results is[15] shown in Equation (3).

$$\frac{G'(\omega)}{G''^2(\omega)} = \frac{30\pi}{k_B T}\left\{\frac{a_1^{\,2}}{36\varphi} + \frac{a_2^{\,2}}{36(1-\varphi)}\right\}(\chi_s - \chi)^{-3/2} \qquad (3)$$

where χ_s designates the interaction parameter in the spinodal point, χ is the interaction parameter, and a_i is the statistical segment length of repeating unit for species i.

Vlassopoulos et al.[9,10] extended this method to analyze off-critical blends system, and obtained the "spinodal points". They assumed a simple form of χ to be $\chi = A + B/T$, and then a linear relation could be obtained through $\{G''^2(\omega)/[G'(\omega)T]\}^{2/3}$ versus $1/T$, which led to an intercept at $1/T$ axis denoting the "spinodal" temperature, T_s.[9,10] In fact the phase transition under shear field has changed the system from the equilibrium condition to a nonequilibrium one. Also this kind of generalization depends mainly on the hypothesis that the fluctuations in off-critical compositions are very similar or identical with the critical ones, and the correlation length may diverge at the "spinodal point". But until now there was no experimental evidence reported on verification of this theory.

Many studies have been reported in the literature[15,16] which used the oscillatory rheological measurements to probe the phase boundaries and the phase separation dynamics without discussing the details of the shear mixing (shift of the phase boundary) due to the flow field. Also, the question of shear rate change at any given frequency has not been discussed. On the other hand the use of Fredrickson−Larson−Ajji−Choplin viscoelastic model has also neglected the shear distortion of the structure factor $S(q)$ of the concentration fluctuations. The equilibrium mean field structure factor is always assumed without looking into its change beyond mean field and/or the distortion due to shear field. However, in any experimental study using this theory, a ratio of $\{G''^2(\omega)/[G'(\omega)T]\}^{2/3}$ is necessary, so presumably the frequency effect can be minimized. Whether the above-mentioned approximations can be used or the question of how to obtain better results if these approximations were assumed has not been reported before.

In this note we will present our recent results from the shear quench experiments from a set of frequency dependent measurements to evaluate the physical basis of obtaining the extrapolated binodal and spinodal points. And also we will propose an additional implementation of this theory to obtain the nucleation rate in metastable region under oscillatory shear flow.

Experimental Part

The two polymers used in this study, polybutadiene (PB) and low vinyl content polyisoprene (LPI), were both anionically polymerized in Beijing Yanshan petrochemical Co., Ltd., with mass-average molecular weight of 5.5×10^4 and 3.3×10^4, and polydispersity of 1.1 and 1.5 respectively. In this work an off-critical

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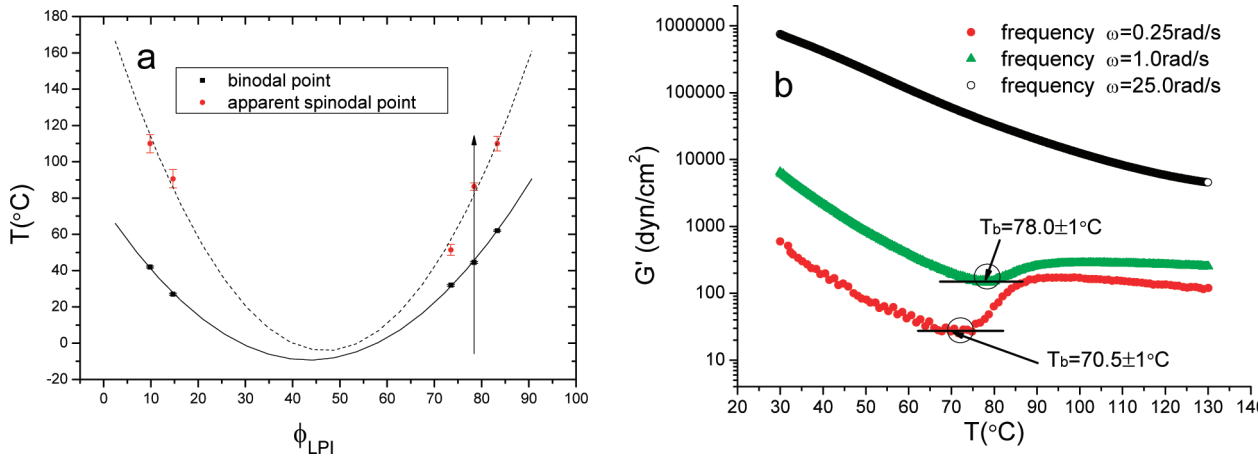

Figure 1. (a) Solid line and the dashed line are the polynomial fitted binodal line spinodal line respectively in static condition. The vertical line with arrow indicates the experiments considered in this paper. (b) Storage modulus of LPI80 as a function of temperature during heating from one phase region to the phase separation region under frequencies of 0.25 and 1.0 rad/s, and the apparent binodal points are 70.5 ± 1.0 and 78.0 ± 1.0 °C, respectively. At the frequency of 25 rad/s, there is no sign of phase separation in our temperature region.

sample of *LPI*80 was used in which LPI content is 80% in weight fraction of this blend sample. We started with a dilute solution of 2% polymer mass fraction, which also contains antioxidant BHT with mass fraction 2.5% of the total polymer mass, in a solvent of methylenechloride. Then the solution was filtered through a 1 μm Millipore filter and the solvent was evaporated at35 °C. Samples were further dried in vacuum oven at 25 °C for a week to eliminate the rest of methylenechloride.

The viscoelastic properties of samples were measured with an Advanced Rheometric Expansion System (ARES, Rheometric Scientific, Piscataway, NJ), which was a strain-controlled rheometer with a parallel plate-plate fixture (25 mm diameter) and a testing gap value of 0.5 mm between two plates was used. All measurements were carried out under the protection of nitrogen to prevent the degradation of the thermal sensitive elastomers. The precision of the temperature control in the rheometer is ±0.1 °C. The shear quench experiments were carried out with the following procedure: first the temperature ramp test with oscillatory shear mode with frequency of 25 rad/s and strain amplitude of 10% were conducted to reach at certain temperature without apparent phase separation. Then the temperature was holding at the specified value and the test mode was switched to a time sweep mode with a constant frequency of 1 rad/s and a strain amplitude of 10%. A strain amplitude of 10% was chosen to keep our sample in an apparent Newtonian region, as was reported in the previous paper.[17]

Results and Discussion

For the purpose of expedient experimental analysis, the static phase diagram of the PB/LPI system was shown in Figure 1a, which is a typical low critical solution temperature (LCST) type and was reported in our previous paper.[17] The binodal points were measured through optical microscopy while the apparent "spinodal points" were extrapolated through the method described in our previous paper.[17] The static binodal point of LPI80 is 44.5 ± 0.5 °C. In the rheological temperature ramping measurement, we define the point at which the derivative of G' on T equals to 0 as the apparent binodal point. This method is based on the knowledge that phase separation will increase the storage modulus G',[9−11] which should be decreasing with further increasing of temperature. In Figure 1b we can see that with the same strain amplitude of 10% and the same ramp rate at 1.0 °C/min, the apparent binodal point moved to higher temperatures with higher frequencies. For example, under the frequency of 1.0 rad/s (with peak shear rate of 0.1 s^{-1}) the

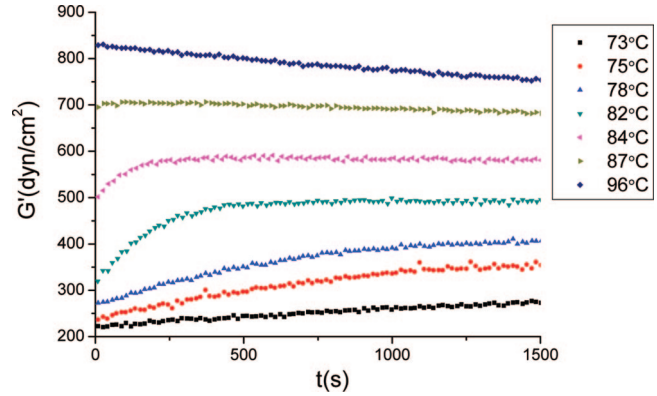

Figure 2. Time evolution of the storage modulus of LPI80 under 1.0 rad/s with strain amplitude of 10% after the shear quench from 25 rad/s at 73.0, 75.0, 78.0, 82.0, 84.0, 87.0, and 96.0 °C. Data are shifted vertically to avoid crossover.

apparent binodal point was elevated to 78.0 ± 1.0 °C. The shear induced mixing phenomenon was very prominent even under such "weak" oscillatory shear fields. Thus the time sweep tests under shear field of 1.0 rad/s were selected to study the nonequilibrium contribution to the phase separation process. At the frequency of 25 rad/s, the "binodal point" normally characterized by the upturn of storage modulus was not observed. The reason is that when we carried out temperature ramp test under 25 rad/s in our experimental temperature region, 30.0−130.0 °C, our sample always stayed in the shear induced homogeneous state.

After that, the temperature was kept at what it is and the frequency quenched from 25 to 1.0 rad/s, and at the same time the temperature ramp test was switched to time sweep mode. Figure 2 shows the time evolution of the storage modulus at different temperatures after the shear quench. The storage modulus G' increases linearly with phase separation time t in the early stage of phase separation from 73 °C to 84 °C. We concluded from these experimental results that, below 84 °C, the linear increase of G' with time t were clear. However, once the temperature was above 87 °C, we could not find such a distinct increasing process. The interesting linear increase of G' with t is interpreted through the following argument.

The nucleation phase separation in metastable region of polymer blend has been investigated by Balsara et al.[5,6] They

reported that the nucleation process in the static metastable region was very different from what people used to believe.[18] The newly discovered results indicated that the nascent nuclei was just a tiny region with diffused structure, and they had no clear interface. Also the existence of the mean field spinodal point should only be a limiting case,[19,20] and the difference in phase separation mechanisms between metastable and unstable regions was ambiguous. Based on such a discovery, we attribute the viscoelastic effects in a multicomponent polymer blends to three major contributions, the bulk part from the polymer chain dynamics and entanglements, the concentration fluctuations from thermal noise, and the interfacial tension due to the phase domains. If we assume a linear additivity of these contributions, then:

$$G' = G'_{\text{bulk}} + G'_{\text{fluctuation}} + G'_{\text{interface}} \tag{4}$$

Such a phenomenological treatment is similar to the Palierne model in linear additivity.[21,22] In this case, we assumed that the early stage of phase separation process through the nucleation mechanism can not form a sharp interface, just like the static case. Then the storage modulus is dominated by bulk storage modulus and the fluctuation contribution. Intuitively, we have separated the fluctuations into two parts. The first one is the fluctuations which form the nuclei, and the second one is the fluctuations due to the already formed nuclei which are going through the initial stage of growth and dimensional increase. These two kinds of fluctuations are corresponding to the nucleation and growth processes respectively, as mentioned in our previous paper.[17] We have made assumptions that the first kind of fluctuations is similar to the critical fluctuations in concentration and the second one is the fluctuation in nuclei dimensions at different wavelength. The structure factor may be still represented by the random phase approximation (RPA) structure factor, even under the shear field,[12] on the assumption that the number of nuclei in the sample volume is still small. Then the fluctuations based storage modulus can be expressed as

$$G'_{\text{fluctuation}}(\omega,t) = \frac{k_B T\omega^2}{15\pi^2}\left[\int_0^{k_c} \frac{k^6 {S_0}^2(k)}{\omega^2 4\varpi^{-2}(k)}\left[\frac{\partial {S_0}^{-1}(k)}{\partial(k^2)}\right]^2 \mathrm{d}k + N\int_{k_a}^{k_b} \frac{k^6 {S_n}^2(k)}{\omega^2 4\varpi^{-2}(k)}\left[\frac{\partial {S_n}^{-1}(k)}{\partial(k^2)}\right]^2 \mathrm{d}k\right] \tag{5}$$

where, $\varpi(k)$, $S_0(k)$, $\lambda(k)$, and k are the same with which in eq 1, $S_n(k)$ is the nucleus structure factor, and N is the number of the nuclei. At the beginning of phase separation the nucleation rate remains constant, because the density of the first type of fluctuation remains nearly unchanged. The number N can be written as

$$N = R \times t \tag{6}$$

where R is the nucleation rate, and t is the phase separation time. Thus the nucleation rate has the following relationship with the increment of storage modulus as a function of time

$$\Delta G' = G'(\omega,t) - G'(\omega,0) = N\frac{k_B T\omega^2}{15\pi^2}\int_{k_a}^{k_b} \frac{k^6 {S_n}^2(k)}{\omega^2 4\varpi^{-2}(k)}\left[\frac{\partial {S_n}^{-1}(k)}{\partial k^2}\right]^2 \mathrm{d}k \tag{7}$$

If we assume that the $(k_B\omega^2)/(15\pi^2)\int_{k_a}^{k_b}(k^6 {S_n}^2(k))/(\omega^2 4\varpi^{-2(k)}[(\partial {S_n}^{-1}(k))/(\partial k^2)]^2\,\mathrm{d}k = C$ is a constant at any given temperature in one measurement, that is to say it is only a function of the temperature or the interaction parameter. Then we can compare the relative nucleation rate at any temperature given as eq 8.

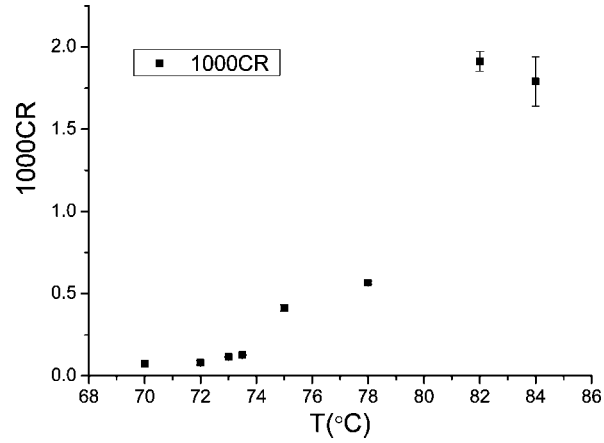

Figure 3. The relative nucleation rates 1000*CR* were ploted versus temperature *T*.

$$CR = \frac{\Delta G'}{T \times t} \tag{8}$$

The linear time evolution of loss modulus G'' can also be obtained through a similar analysis. The assumption of the constant C implies that both the size distribution and the growth kinetics of nuclei remain the same for a given quench depth in the early stage of phase separation. At last, it was found that $\{G''^2(\omega,0)/[G'(\omega,0)T]\}^{2/3}$ should have a linear relationship with respect to $1/T$ as proposed by Vlassopoulos et al.[9,10] at the region where the first kind of fluctuations dominant the viscoelastic properties.

Thus there are two reasons that could explain why the increasing of G' with time was not observed at 87 and 96 °C in the Figure 2. The first one is that the nucleation process is too fast to be detected by the rheological measurements. And the second reason is that the phase separation mechanisms might have been changed when the quench temperature is too deep (too high in this LCST case) and may be already in the unstable region.

Figure 3 shows the calculated relative nucleation rates 1000*CR* versus the phase separation temperature *T*. The quick growth of the relative nucleation rate with the quench depth is probably caused by the exponential decrease of the nucleation energy barrier.[18] Through the time sweep measurements, we also found that phase separation have already started at 70.0 °C, which is lower than the apparent binodal point measured from the temperature ramp test, but still higher than the static binodal point of 44.5 °C.

In Figure 4 $\{G''^2(\omega,0)/[G'(\omega,0)T]\}^{2/3}$ versus $1000/T$ are displayed, and the extrapolated "spinodal point" is 88.0 ± 2.0 °C. The "spinodal points" obtained by temperature ramp experiments were 105.5 ± 2.0 and 94.5 ± 2.0 °C, corresponding to temperature ramp rates of 0.2 and 1.0 °C/min respectively.[17] Such difference is probably caused by the interference of the second type of fluctuations and the interfacial tension by the shear field in the temperature ramp experiments.[17] Although the extrapolation procedure is qualitatively and has a large uncertainty due to the short-range of data in the linear region, we can still conclude that the faster the ramp rate, the lower the "spinodal point" we obtained. And also the result in quench experiment clearly shows that before we reach the extrapolated "spinodal point" at 88.0 ± 2 °C the behavior of $\{G''^2(\omega,0)/[G'(\omega,0)T]\}^{2/3}$ versus $1000/T$ have already changed. This phenomenon may imply that either the determination of the

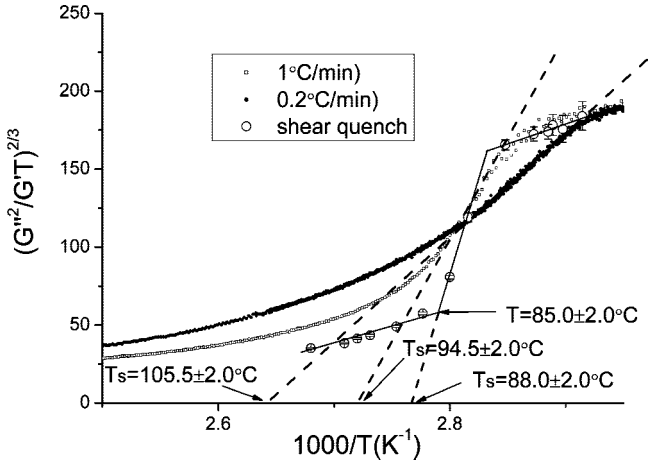

Figure 4. The calculated $\{G''^2(\omega,0)/[G'(\omega,0)T]\}^{2/3}$ versus $1000/T$ from the quench experiments. Results of $\{G''^2/[G'T]\}^{2/3}$ from the temperature ramp tests with ramp rates of 0.2 and 1.0 °C/min are also plotted. The dashed lines are the linear extrapolations.

"spinodal point" by rheology should be further improved or the physical meaning of the "spinodal point" obtained by rheology is different from the traditional thermodynamic definition.

Conclusion

We have attempted to use the shear quench experiments to analyze the phase separation mechanism. Based on the theoretical analysis, we deduced an expression to evaluate the relative nucleation rate under the oscillatory shear flow. The model deduced in this work can explain the time dependent data of G' or G'' at the beginning of the nucleation phase separation. It was found that the relative nucleation rate increased rapidly with the increasing of quench depth of the shear frequency. The differences in the extrapolated "spinodal points" between the temperature ramp measurements and the shear quench experiments are obvious. The influence of the second type of fluctuations and the interfacial tension effect may have caused such difference. And the physics of the extrapolated "spinodal point" by shear quench experiments is still qualitatively plausible.

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