

Phase Behavior Actuating Morphology and Rheological Response of Polybutadiene/Polyisoprene Blends under Small Amplitude Oscillatory Shear*

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Abstract The morphology evolution and the corresponding linear viscoelastic behavior of the phase-separating polybutadiene (PB)/low vinyl content polyisoprene (LPI) blend have been investigated by phase contrast optical microscopy (PCOM), small-angle light scattering (SALS) and rheometry. Two kinds of structure evolutions and rheological responses have been observed. It is found that the co-continuous structure generally gives a power law behavior of the dynamic storage modulus versus frequency and the coarsening of co-continuous structure leads to a decrease of the storage modulus. For the droplet-matrix structure, a platform modulus is observed at the mediate frequencies, followed by the typical terminal relaxation behavior of storage modulus at the extremely low frequencies. The decreasing platform modulus and increasing terminal modulus with the growth of droplets are observed and can be well interpreted by the simplified Palierne model. The platform modulus and terminal modulus at a given frequency are found to be scalable with the phase separation time. Besides, the characteristic relaxation time and domain size of the droplets have been obtained by rheology. And it seems that the rheologically determined droplet dimensions are consistent with the ones determined by PCOM and SALS.

Keywords: Phase separation; Structure evolution; Rheology.

INTRODUCTION

The rheological properties of two-phase polymer blends generally depend strongly on their internal structure, *i.e.*, their morphology. Thus, the relationship between rheology and morphology of the multi-phase polymer blend has attracted much attention in recent years^[1–18]. For immiscible polymer blends, on one hand, the rheological measurements such as the dynamic frequency sweep test can be used to distinguish two kinds of multi-phase structure, like the droplet-matrix structure and the co-continuous structure^[5, 18–20]. On the other hand, combining several emulsion models which were independently developed by Palierne^[12], Gramespacher-Meissner^[21] and Bousmina^[22], the linear dynamic measurements are widely used to obtain either the interfacial tension or structure information (domain size and distribution) for the droplet-matrix structure^[8, 14, 16]. Although these emulsion models are originally proposed for immiscible polymer blends, they are believed to be also suitable for the phase-separated blend after the partially miscible polymer blend enters into the two-phase region. However, it is necessary to assume that the interfacial tension and the variation of the interface is independent of local shear at low frequency since the coupling between the thermodynamics and the oscillatory shear may be no longer negligible when the applied strain or stress is not small enough^[7, 13].

* This work was financially supported by the National Natural Science Foundation of China (Nos. 51173195 and 50930002).

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Received August 23, 2013; Revised October 5, 2013; Accepted October 9, 2013

doi: 10.1007/s10118-014-1443-8

Recently, an important subject exists in the rheological responses to the dynamics of the phase separation process. There have been arguments dealing with the relationship between the resulted phase-separated morphology and viscoelastic properties of various polymer blend systems^[2, 5–9, 23–26]. Different observations and explanations were made from temporal evolutions of dynamic moduli in the metastable and unstable regions. With phase separation progressing, dynamic moduli could show monotonic increase^[3, 5, 7] or decrease^[5, 6, 8, 9, 25] essentially depending on the resulted morphologies. Xie *et al.*^[26] for the first time investigated the dynamic moduli of the unstable polystyrene/polyvinyl methyl ether (PS/PVME) blend and found that the dynamic moduli increased with time in the early and intermediate stages of spinodal decomposition (SD), and decreased in the late stage. However, they didn't give any information on the resulting morphologies during the measurements. A few years later, Polios *et al.*^[6] investigated the relation between rheology and the time dependent morphology of the same binary blend, and demonstrated that the initial increase of the dynamic moduli should be attributed to the formation of highly interconnected PS-rich and PVME-rich phases during SD, while the subsequent decrease is due to the loss of the interconnectivity between the two phases. Vinckier *et al.*^[5] have investigated the linear viscoelastic properties of the poly- α -methylstyrene-*co*-acrylonitrile/polymethylmethacrylate (P α MSAN/PMMA) bend during the process of phase separation, and observed different rheological responses to the different resulting morphologies. Thus it is confirmed that the linear dynamic measurements can be used for probing phase separation and subsequent coarsening of the morphology. Zhang *et al.*^[7] have also studied the viscoelastic properties of the phase-separating polymer blend and observed both the increase and decrease of the storage modulus with time during the nucleation phase separation.

In the present work, we want to investigate how the phase-separating structure influences its dynamic moduli and try to establish the probable quantitative correlations between domain structure and dynamic moduli, especially for the storage modulus of the sea and island structure. For co-continuous structure, the relationship of the storage modulus and the evolution time is fitting the power law regulation which model was reported by Yu *et al.*^[10]. However, as we know, the rheologically measured storage modulus usually includes two kinds of contribution, namely the interfacial contribution coming from the phase-separating domain and the bulk contribution coming from the polymer chain dynamics and entanglement^[21, 27]. From this point of view, if we try to investigate the quantitative influence of the domain size on the storage modulus, it is desirable to choose the low molecular weight polymer blend whose terminal relaxation times are short enough and then supply the situation that the storage modulus coming from the bulk contribution is much smaller than that coming from the interfacial contribution^[13]. Here, we chose a low molecular weight polymer blend of polybutadiene and polyisoprene as our research object. As will be shown in the next text, such a polymer blend gives us a chance to quantitatively describe the interfacial contribution to the storage modulus during the phase separation process. And through our experiments it is found that the temporal evolution of the storage modulus can be quite different for the same phase separation process, depending on the applied angular frequency. Besides, it is for the first time to observe that the storage modulus coming from the interfacial contribution can be scalable with the phase separation time. It is believed that this study can clear some arguments on the relationship between the resulted phase-separated morphologies and viscoelastic properties of polymer blends.

Theoretical Background

For a multi-phase polymer blend, its storage modulus generally can be ascribed by two parts, the component part, G'_{comp} , and the interface part, G'_{inter} . G'_{inter} can generally be calculated by the Palierne model assuming the interfacial tension equal to zero^[10]. However, it is also reported that the component part can be described by the log-additive mixing rule^[16]. By contrast, the calculation of the interfacial part is more complex and found to be dependent on the detailed morphology. As for the droplet-matrix structure, Palierne^[12], Gramespacher and Meissner (G-M)^[21], and Bousima^[22] have independently proposed several emulsion models to quantitatively describe its linear viscoelastic behavior. Here we used the Palierne model to analysis the effect of the droplet size on the rheological behavior.

Once we use the Palierne model to interpret the dynamic frequency sweep curves, it is necessary to assume that the interfacial tension and the variation of the interface is independent of local shear at low angular frequency. In a simplified version of Palierne model, the complex modulus could be obtained as

$$G'_{\text{blend}} = \phi_A G'_A + \phi_B G'_B + \frac{\omega^2 \eta_0 (\tau_1 - \tau_2)}{1 + \omega^2 \tau_1^2} \quad (1)$$

$$G''_{\text{blend}} = \phi_A G''_A + \phi_B G''_B + \frac{\omega \eta_0 (1 + \omega^2 \tau_1 \tau_2)}{1 + \omega^2 \tau_1^2} \quad (2)$$

where ϕ_A and ϕ_B are the volume fractions of component A and B. η_0 is the zero-shear viscosity of the blend mixture, and τ_1 is the longest relaxation time while τ_2 is a retardation time and they are expressed as

$$\eta_0 = \eta_m \frac{10(\lambda + 1) + 3\phi(5\lambda + 2)}{10(\lambda + 1) - 2\phi(5\lambda + 2)} \quad (3)$$

$$\tau_1 = \frac{R\eta_m}{4\sigma} \frac{(19\lambda + 16)(2\lambda + 3 - 2\phi(\lambda - 1))}{10(\lambda + 1) - 2\phi(5\lambda + 2)} \quad (4)$$

$$\tau_2 = \frac{R\eta_m}{4\sigma} \frac{(19\lambda + 16)(2\lambda + 3 + 3\phi(\lambda - 1))}{10(\lambda + 1) + 3\phi(5\lambda + 2)} \quad (5)$$

where $\lambda = \eta_d/\eta_m$ is the ratio of viscosity between dispersed phase and matrix phase, ϕ is the volume fraction of dispersed droplet phase, σ is the interfacial tension, and R is the average droplet radius. There is one crucial restriction on the morphology of our system when applying these expressions, that is, the radius distribution of the droplets cannot be too wide, *i.e.*, more than 2.2^[13]. If we fix all of the parameter except the droplet dimension R and let

$$C_1 = \frac{\eta_m}{4\sigma} \frac{(19\lambda + 16)(2\lambda + 3 - 2\phi(\lambda - 1))}{10(\lambda + 1) - 2\phi(5\lambda + 2)} \quad (6)$$

$$C_2 = \frac{\eta_m}{4\sigma} \frac{(19\lambda + 16)(2\lambda + 3 + 3\phi(\lambda - 1))}{10(\lambda + 1) + 3\phi(5\lambda + 2)} \quad (7)$$

then Eq. (1) can be written as

$$G'_{\text{blend}} = \phi_A G'_A + \phi_B G'_B + \frac{\omega^2 R \eta_0 (C_1 - C_2)}{1 + \omega^2 C_1^2 R^2} \quad (8)$$

The derivative of G' with R is expressed as

$$\frac{\partial G'_{\text{blend}}}{\partial R} = (C_1 - C_2) \omega^2 \eta_0 \frac{1}{\left(\frac{1}{C_1 R} + C_1 \omega^2 R\right)^2} \left(\frac{1}{C_1^2 R^2} - \omega^2\right) \quad (9)$$

It is obvious that there exists a critical radius $R_c = (C_1 \omega)^{-1}$ in Eq. (9) for the storage modulus G' . Below this critical dimension G' will increase with the increasing of the droplet dimension R while above this value it will decrease with the increasing R . Zhang *et al.*^[7] has used this concept to explain the competition between the nucleation and growth for off-critical PB/LPI blend very well. Since the critical radius is inversely proportional to the angular frequency, thus it is expected that the coarsening of droplet-matrix structure will result in different kinds of time evolution of storage modulus in different angular frequency regions. In fact, according to Eq. (1)

there are really two angular frequency regions where the droplet dimension dependent storage modulus is quite different.

1) when $\omega^2 C^2 R^2 \gg 1$, Eq. (8) can be approximated as

$$G'_{\text{blend}} \approx \phi_A G'_A + \phi_B G'_B + \frac{\eta_0 (C_1 - C_2)}{C_1^2 R} \quad (10)$$

Taking the detailed value of C_1 and C_2 into Eq. (10), then we have the following expression

$$G_p = G'_{\text{blend}} - (\phi_A G'_A + \phi_B G'_B) \approx 20 \frac{\sigma}{R} \phi \frac{1}{(2\lambda + 3 - 2\phi(\lambda - 1))^2} \quad (11)$$

where G_p is the so-called platform modulus. From Eq. (11) it is clear that the platform modulus is independent of the frequency but inversely proportional to droplet dimension R .

2) when $\omega^2 C^2 R^2 \ll 1$, Eq. (8) can be approximated into

$$G'_{\text{blend}} \approx \phi_A G'_A + \phi_B G'_B + \omega^2 R \eta_0 (C_1 - C_2) \quad (12)$$

Taking the detailed value of C_1 and C_2 into Eq. (12), then we have the following expression

$$G'(\omega, R)_T = G'_{\text{blend}} - (\phi_A G'_A + \phi_B G'_B) \approx \eta_m \omega^2 \frac{R}{4\sigma} \frac{5\phi(19K + 16)^2}{[10(K + 1) - 2\phi(5K + 2)]} \quad (13)$$

where $G'(\omega, R)_T$ is the terminal modulus.

EXPERIMENTAL SECTION

Materials

The two polymers used in this study, polybutadiene (PB) and low vinyl content polyisoprene (LPI), were both anionically polymerized by Yanshan Branch, SINOPEC Beijing Research Institute of Chemical Industry. The characterization data of these two polymers are shown in Table 1. For convenience, PB/LPI blend was labeled as LPIx, where x represents the volume fraction of LPI in the blend.

Table 1. Characterization data of polymers

Sample code	M_n (g/mol)	M_w/M_n	T_g (°C)	ρ (g/cm ³)
PB	44000	1.03	-93	0.895
LPI	66000	1.04	-66	0.897

Sample Preparation

Appropriate amounts of PB and LPI were dissolved in methylene chloride (net mass fraction of 2%) containing a mass fraction of 0.02% antioxidant, butylated hydroxytoluene (BHT). The resulting mixture was filtered through a 0.45 μm Millipore filter, and the solvent was evaporated at 35 °C with stirring. The remaining solvent was finally removed in a vacuum oven at 35 °C until no more weight changes could be detected (that takes about 5 days).

Optical Microscopy (OM) Observations

The morphology evolutions of the phase-separating blend LPI50 and LPI70 at 110 °C was performed at an Olympus (BX51) phase contrast optical microscope (PCOM) and the results were recorded with an Olympus (C-5050ZOOM) camera. The experimental temperature was controlled by a Linkam (LTS 350) hot stage and fresh nitrogen gas was circulated in the hot stage to avoid possible thermal degradation. Samples were sandwiched between clean microscope slide and cover glass with a spacer about 30 μm in thickness.

Small-angle Light Scattering (SALS)

Phase separation kinetics of LPI50 and LPI70 at 110 °C was detected by a homemade time-resolved light

scattering (TRLS) instrument. The incident beam with a wavelength of 633 nm, and a vertically polarized light was applied to the sample film. Light scattering profile was recorded every 30 s during the curing process. The sample films for TRLS were sandwiched between two glass slides, with a poly(tetrafluoroethylene) spacer to fix the thickness during the whole curing process.

Rheological Measurements

All the rheological measurements were performed by an Advanced Rheometric Expansion System (ARES, Rheometric Scientific, Piscataway, NJ), which is 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. The phase separation process has been probed by small amplitude oscillatory measurements. Temperature control in the rheometer is carried out by hot nitrogen gas with accuracy of ± 0.1 °C. Before measurements all blends were kept at 4 °C in a refrigerator and then put into a vacuum oven at 35 °C for 2 days to remove air bubbles and to ensure the same thermal history.

RESULTS AND DISCUSSION

Phase separation kinetics of LPI50 and LPI70 at 110 °C

In our previous studies^[28], we have obtained the static phase diagram of PB/LPI blends. As shown in Fig. 1, the PB/LPI system exhibits a lower critical solution temperature (LCST) type phase diagram with the critical temperature at about 65.0 ± 1.0 °C and the critical composition of LPI is about 0.50 ± 0.02 by volume fraction. In this current study we are mainly focusing on the phase separation of LPI50 and LPI70. According to Fig. 1, after a temperature jump from room temperature to 110 °C, both LPI50 and LPI70 will be unstable and phase separate. Since both samples are within the unstable region at 110 °C, the spinodal decomposition is expected. It is well known that the spinodal decomposition is usually associated with the formation of co-continuous structure, thus we performed the PCOM observations to investigate the morphology evolution of these two samples.

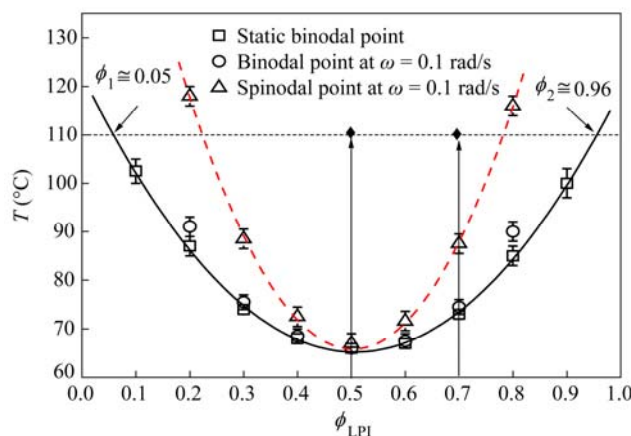


Fig. 1 Phase diagram of PB/LPI blends determined by PCOM and rheological measurements^[28]
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Figure 2 shows the phase contrast optical micrographs of LPI50 and LPI70 at 110 °C for different isothermally phase separation time. In Fig. 2(a) we can observe the co-continuous structure after isothermally phase separated 5 min. With the time elapsed, the co-continuous structure grew rather fast, and after 20 min the interfaces and the outlines of these phase-separated structure started to become blurred since the domains were too large to be focused on a single focal plane by PCOM. Compared to LPI50 sample, the domain growth of LPI70 was much slower. Although the phase separation of LPI70 after temperature jumped to 110 °C should be the spinodal decomposition according to the phase diagram of PB/LPI blends in Fig. 1, we did not observe the

co-continuous structure by the PCOM. Instead, there were always the droplets in matrix which should be ascribed to the fact that the initial co-continuous structure of the early and mediate stage of spinodal decomposition is too small to be clearly detected by the PCOM. As shown in Fig. 2(b), the domain size after phase separation 60 min is already very small and a little hard to be clearly distinguished. In the late stage of spinodal decomposition, the co-continuous structure grew further and began to break up into droplets. For the droplet-matrix structure, the coarsening of the domains by diffusion is rather slow because of the high viscosity of polymer melts. Thus, it is clear that after phase separated for 4 h, the sizes of these droplets were no more than 5 μm .

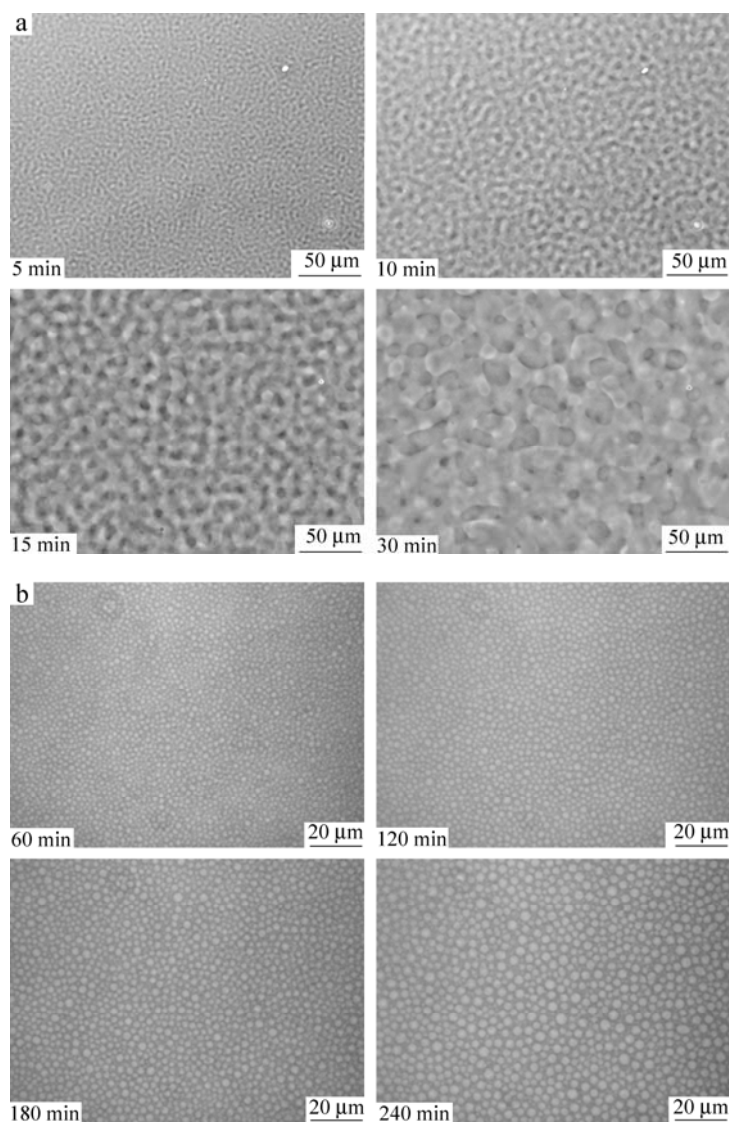


Fig. 2 Phase contrast optical micrographs of (a) LPI50 and (b) LPI70 isothermally phase-separated at 110 °C for various times

Small-angle Light Scattering (SALS) Results

SALS has been widely used to study phase separation in the quiescent state, since it allows not only phase boundaries to be determined but also the dynamics of the phase separation process to be followed. In the analysis of the phase separation process, time evolution of the magnitude of the scattering vector q_m at which scattering intensity has a maximum value is often described by power laws,

$$q_m \propto t^{-\alpha} \quad (14)$$

The scaling exponent α characterizes the time evolution of phase-separated structure.

Figure 3 shows the time evolution of the maximum wave-vector, q_m , for LPI50 and LPI70 at 110 °C. It was shown in Fig. 3 that the time change of q_m for LPI50 and LPI70 both obeys the power law. For LPI50 which is a near-critical mixture, α becomes nearly 1.0 in the time limit of present experiments. On the other hand, the value of α for LPI70 in the long time limit is nearly 0.33. These kinds of scaling exponent have been reported and discussed extensively by Hashimoto *et al.*^[29]. Since the phase-separated domain size is inversely proportional to q_m , it means that the coarsening of LPI50 is much faster than that of LPI70 due to the large difference in the scaling exponent in Eq. (14). Such a result is well consistent with the corresponding PCOM observation for LPI50 and LPI70. As will be discussed later, it is the power laws coarsening of the phase-separated domain that makes the corresponding rheological properties be scalable with the phase separation time.

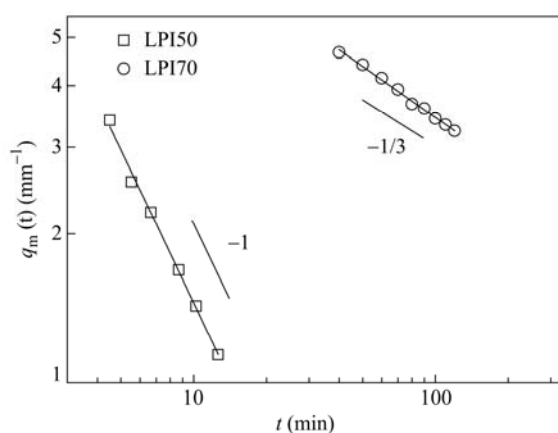


Fig. 3 Time evolution of the maximum wave-vector (q_m) for LPI50 and LPI70 isothermally phase-separated at 110 °C

Rheological Responses of the Phase-separating LPI50 and LPI70

Before discussing the rheological properties of the phase-separated blends, we have investigated the rheological behavior of the pure component melts, PB and LPI. Figure 4 shows the dynamic complex viscosity and modulus of PB and LPI at 110 °C as a function of angular frequency. For PB and LPI, both of them have relatively low molecular weight and rather low glass transition temperature as reported previously^[28], therefore, their rheological properties at 110 °C are expected to display the typical terminal relaxation behaviors. In Fig. 4(a) we can easily obtain the zero-shear viscosity, η_0 , for both pure components, and the values are 3.15×10^2 Pa·s and 1.55×10^2 Pa·s, respectively. Figure 4(b) shows the dynamic storage modulus and loss storage modulus of PB and LPI pure melts and both of them displayed the $G' \propto \omega^2$, $G'' \propto \omega$ behaviors, which demonstrated that in the present experiments both components exhibited the terminal relaxation behaviors.

There are lots of reports involving the investigation of the rheological behavior of phase-separating polymer blends. Among these reports, some focus on how to distinguish the different kinds of phase-separated structure, like droplet-matrix structure and co-continuous structure^[5, 18–20]. And it is found that the above two kinds of structure can be well reflected by the rheological responses which are typically analyzed with the frequency dependence of storage modulus. Others paid more attention to the time evolution of storage modulus during phase separation^[2, 7–9, 24–26]. In fact, quite different kinds of storage modulus changes have been reported during the phase separation *via* nucleation and growth or spinodal decomposition. When phase separation takes place in the metastable region, it is reported that both the formation of nuclei and the growth of the droplets can help to increase the storage modulus^[7]. Once the matrix phase reaches the equilibrium composition and the volume fraction of the dispersed phase keeps constant, the further growth of droplets may result in a decrease of storage

modulus as suggested by Zhang *et al.*^[7]. However, other researchers stand out that it is the interface that dominates the value of storage modulus^[3, 5, 8, 24]. In the late stage of the phase separation, the matrix phase reaches the equilibrium and the total interface area starts to decrease, which makes a decreasing interfacial contribution to the storage modulus. Here we choose the PB/LPI blend as a model polymer blend and carry out the systematic investigation to try to clarify some of the controversies.

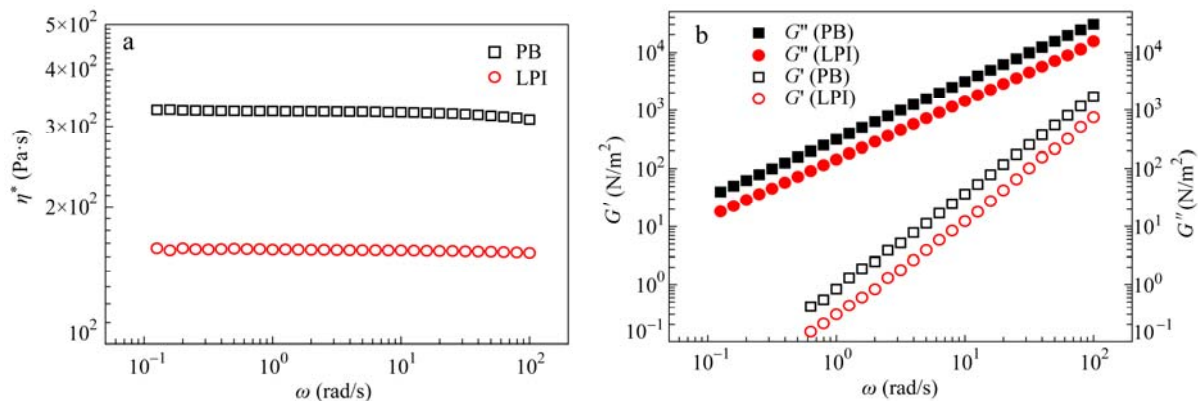


Fig. 4 (a) Dynamic complex viscosity and (b) storage and loss modulus of PB and LPI pure melts at 110 °C as a function of angular frequency

Figure 5 shows the dynamic storage modulus as a function of angular frequency for LPI50 and LPI70, which have been isothermally phase separated at 110 °C for 30 min and 60 min respectively. As a reference, the pure component melt data are also given. It is clear that at high frequencies, the phase-separated domains contribute little to the storage modulus, and for both samples these high frequency modulus data can be well described by the log-additive mixing rule based on the pure component data. At low frequencies, the increased storage moduli are observed. However, the changes of storage modulus with angular frequency are quite different between LPI50 and LPI70. For the former, its co-continuous structure results in nearly a power law behavior for storage modulus versus angular frequency, that is $G' \propto \omega^{0.5}$. Actually, several research groups have reported this kind of rheological behavior for co-continuous structure^[5, 6, 8, 19, 30–32]. Despite of the similar experimental results, the interpretations of the power law are still not well understood. Niu *et al.*^[8] and Polio *et al.*^[6] suggested that the co-continuous structure are similar with the gel and the power law can be well

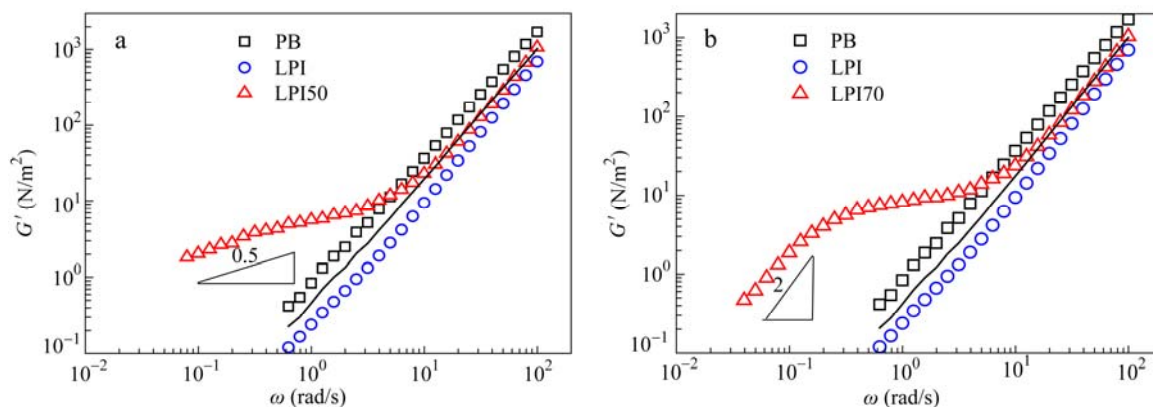


Fig. 5 Dynamic storage modules as a function of angular frequency for (a) LPI50 and (b) LPI70 isothermally phase-separated at 110 °C for 30 min and 60 min respectively. As a reference, the pure component melt data are also given. The solid line is calculated by the lg-additively mixing rule based on the pure component values.

described by the Gel theory. While Vinckier *et al.*^[5, 25] and Zhang *et al.*^[3] considered the co-continuous structure as the network and stood out that the number of crosslinks per unit volume was the key parameter for the elastic behavior. Besides, it is still not sure whether the power law behavior for co-continuous structure can sustain for infinitesimal angular frequency, or instead of going back into the terminal relaxation behavior. For LPI70 sample, Fig. 5(b) shows a platform modulus at the mediate angular frequencies and the typical terminal relaxation behavior at the low angular frequencies. To our knowledge, there are few reports on such a complete rheological behavior for the phase-separating droplet-matrix structure. And the dynamic storage modulus curve is quite similar to the Palierne^[12] model's prediction for the droplet-matrix structure. The main reason for the coincidence between experiments and theoretical models may exist in the fact that both PB and LPI exhibit the terminal relaxation behavior at the present study. As a result, it is convenient for us to discuss the interfacial contribution to the dynamic modulus.

Another research of great interest exists in the study of the relationship between the time dependent domain structure and their corresponding dynamic storage moduli. As discussed above, we have acquired two kinds of domain structure and their time evolutions by changing with the composition of the polymer blend. Here we are trying to investigate their temporal evolution of the dynamic storage modulus. Figure 6 shows the developments of the storage modulus during cyclic frequency sweeps for LPI50 and LPI70 at 110 °C. These experiments enable us to investigate the storage modulus change with phase separation time under different applied angular frequencies. Figure 6(a) describes how the coarsening of co-continuous structure influences the storage modulus. At low frequencies, the storage modulus decreases with increasing domains size. There are several reasons to explain the common observation of the decrease of storage modulus during the spinodal decomposition. First, since the co-continuous structure can be considered as the network and the crosslinks of the network are the key parameter to influence the storage modulus, as the co-continuous structure becomes larger and larger, the crosslinks generally decrease and further make the interface interfacial contribution to the storage modulus decrease. Secondly, the growths of the concentration fluctuation and the subsequent coarsening of co-continuous structure in spinodal decomposition are usually very fast, especially at large quench depth. Compared to the fast phase separation kinetics, the time needed in the low frequency rheological measurements is relatively long. However, the fluctuation and domain structure contribute to storage modulus generally in the low frequencies. Thus, it is understandable that most literatures only report the monotonous decrease of storage modulus in spinodal decomposition. For the LPI70 blend, the development of storage modulus with phase separation time is much more complex. As shown in Fig. 6(b), at the mediate angular frequencies, the monotonous decrease of storage modulus can be observed. While at the low angular frequencies, the storage modulus exhibits the monotonous increase. To our knowledge, it is the first time to observe such a complex rheological behavior.

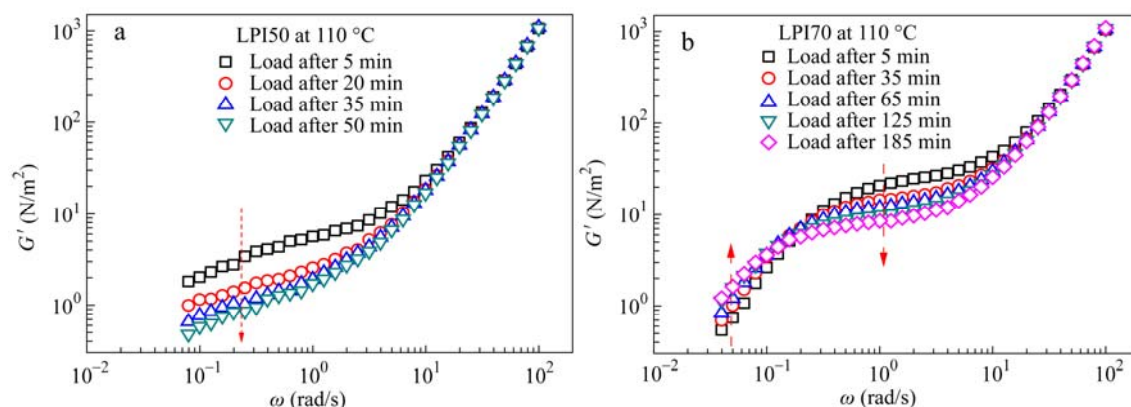


Fig. 6 Dynamic storage modules of (a) LPI50 and (b) LPI70 during phase separation at 110 °C (The frequency sweeps have been performed from high to low.)

Up to now, it seems that the monotonous decrease and increase of storage modulus can be found in the same phase separation process. If it is common in the coarsening of the droplet-matrix structure, then the different kinds of dynamic modulus evolution which are reported should be understandable, since they may carry out in experiments at different frequency regions. In the next, we will try to give the theoretical interpretation of the above complex rheological behaviors for droplet-matrix structure.

From Eq. (13) it is clear that the terminal modulus is dependent on both the angular frequency ω and droplet dimension R . For a given R , $G'(\omega, R)_T$ is proportional to ω^2 and for a given ω , $G'(\omega, R)_T$ is proportional to R . In fact, the above two kinds of treatments of the simplified Palierne model do not conflict. In Eq. (9), the critical droplet radius R_c for a given frequency is $1/(C_1\omega)$, thus when $R > R_c$, that is $\omega C_1 R > 1$, Eq. (10) can be reached and it is obvious that G' decreases with increasing R . When $R < R_c$, that is $\omega C_1 R < 1$, Eq. (12) can be reached and it means that G' increases with increasing R .

Although the rheological behavior of the droplet-matrix structure as shown in Fig. 6(b) can be well described by the above theory, such as, the decreasing platform modulus and the increasing terminal modulus with the growth of the droplet dimension, and the appearance of the terminal behavior at low frequencies, it is still necessary to verify some other predictions, such as the angular frequency independent platform modulus, the angular frequency and droplet dimension dependent terminal modulus. In particular, according to the scaling relations in $R \sim t^{1/3}$ and $G'_p \sim 1/R$ (at the mediate angular frequencies) or $G'_p \sim R$ (at the low frequencies), it should exist the scaling relation between G'_p (G'_T) and phase separation time t . Figure 7 shows the time evolution of the platform modulus and terminal modulus at various angular frequencies. In Fig. 7(a), time evolutions of the platform modulus at four different frequencies are shown. It is clear that the platform modulus decreases with phase separation time but for a given phase separation time it is independent of the angular frequency. Besides, we really observe a power law decrease of the platform modulus, that is, $G'_p \sim t^{-1/3}$. In Fig. 7(b), time evolutions of the terminal modulus at three different frequencies are shown. Compared to Fig. 7(a), the increase of storage modulus is observed and it is found that these three curves are almost parallel to each other by lg-lg display, giving the exponents varied from 0.30 to 0.37, which is well consistent with the predicted value, 0.33.

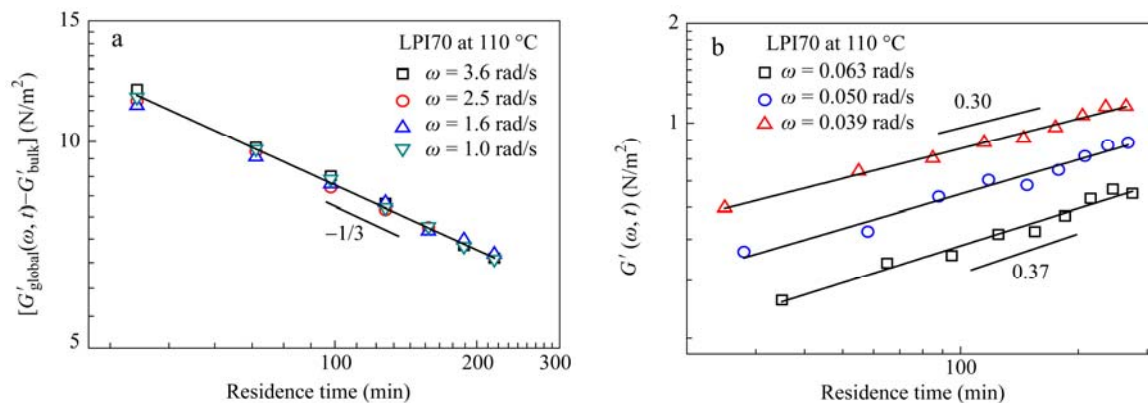


Fig. 7 Time evolution of storage modulus at (a) mediate angular frequency region and (b) low angular frequency region for LPI70

Characteristic Relaxation Time and Domain Size of the Droplet-Matrix structure

For the droplet-matrix structure, there exist several well defined theoretic models to describe their linear viscoelastic properties. In literatures, fitting the experimental dynamic modulus data by the models, such as the Palierne model, is the most widely used method to acquire the droplet size. Another method to acquire the droplet size is to first obtain the whole relaxation spectrum of the two-phase polymer blends. In this method, generally a peak of relaxation time appears at the long time regime and this value is usually attributed to the characteristic relaxation time for the droplets. Using Eq. (4) then the droplet size is obtained. In fact, there should exist a very simple way to acquire the relaxation time of the droplet from the typical dynamic frequency sweep curves, as shown in Fig. 8.

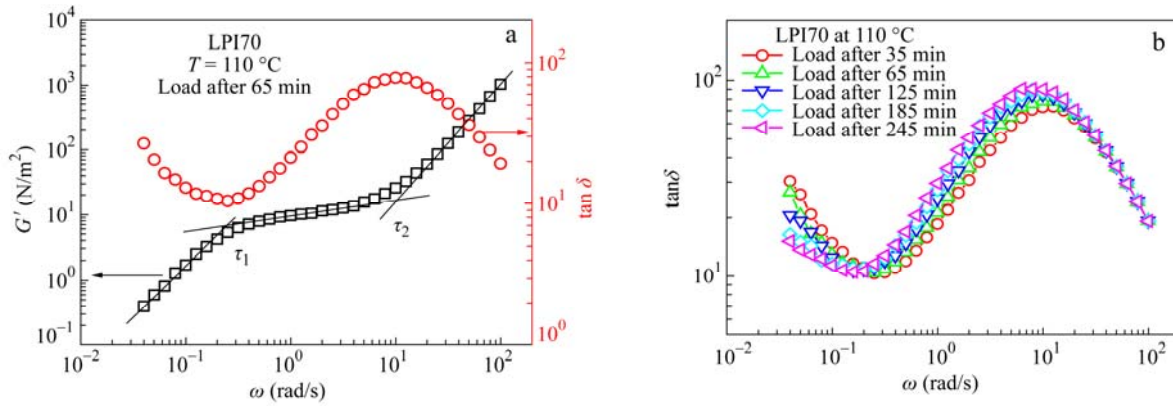


Fig. 8 (a) The dynamic storage modulus and loss tangent $\tan \delta$ as a function of angular frequency at 110°C for LPI70; (b) the developments of $\tan \delta$ during cyclic frequency sweeps at 110°C for LPI70

From Fig. 8 we can observe two important characteristic times, the longest relaxation time τ_1 and the retardation time τ_2 . The detailed expressions about τ_1 and τ_2 have been given by Eq. (4) and Eq. (5) respectively. It is clear that τ_1 and τ_2 correspond to the lowest and the highest angular frequencies where the platform of the storage modulus due to the deformation of the droplet appears, thus τ_1 is defined as the longest relaxation time of the droplets. Besides, from Fig. 8(a) we can also use the times where the loss tangent $\tan \delta$ reaches its minimum and maximum to define these two characteristic times. Figure 8(b) shows the loss tangent curves where LPI70 was kept isothermally at 110°C for different times. It is found that with increasing phase separation time, the frequencies with respect to the minimum and maximum of $\tan \delta$ both shift to low values, which means a longer relaxation time of the droplets. If we can precisely define the frequency where the minimum of $\tan \delta$ appears, then this method can be used to obtain the characteristic droplet size. However, since the data point at which the minimum of $\tan \delta$ appears is rather limited, it is believed that a quantitative extracting of the “real” characteristic relaxation time is a doable but challenging task in the loss tangent curve. Here we convert the dynamic frequency sweep curves shown in Fig. 6(b) into the corresponding relaxation spectrum, and the result is showed in Fig. 9. The above transformation was performed by TA Orchestrator software which is supported by ARES. During the transformation, the dynamic frequency sweep data are chosen. In the Transformation Default option, the nonlinear spectrum method is chosen and the number of points in relaxation spectrum is set to 40. Once the relaxation spectrum has been obtained, the relaxation time data between 0.2 s and 30 s had been chosen and analyzed by polynomial fit supported by Origin 8. The relative error of relaxation is ± 0.01 s. Then the peak of the spectrum was chosen as the longest relaxation time, τ_1 .

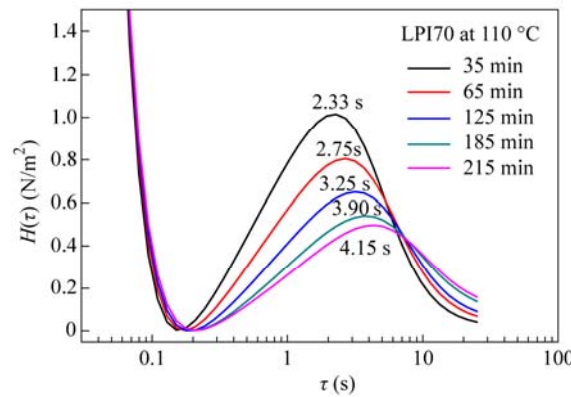


Fig. 9 Developments of relaxation time $H(\tau)$ at 110°C for LPI70

In Fig. 9 we then choose the time with respect to the peak as the characteristic relaxation time of the droplets. It is clear that the characteristic relaxation time increases with the phase separation time. In the next, we will use Eq. (4) to calculate the droplet size based on the data shown in Fig. 9. Before this, we need to know other parameters in Eq. (4). In Fig. 3 we have obtained the zero-shear viscosities for the two pure component melts and the value are 315 Pa·s and 155 Pa·s for PB and LPI respectively. According to Fig. 1, at the temperature of 110 °C, LPI70 will separate into coexisting two phases with the LPI volume fraction of these two phases being $\phi_1 = 0.06$ and $\phi_2 = 0.95$. If we assume that the shear viscosities of the coexisting two phases can be calculated by the simple log-additive mixing rule, then we can obtain $\eta_d = 304$ Pa·s and $\eta_m = 159$ Pa·s with $\lambda = 1.9$. The volume fraction of the dispersed phase can be calculated by the level rule and the value is 0.28. Another important parameter in Eq. (4) is the interfacial tension. According to Broseta and Helfand^[33], for asymmetric polymers, the simple expression relating the interfacial tension σ to the interaction parameter is:

$$\sigma = \frac{kT}{a^2} (\chi/6)^{1/2} \quad (15)$$

where k is the Boltzmann constant, T is the absolute temperature, and a is the statistical segment length. For the specific PB/LPI blend, χ is 0.00183 at 110 °C according to the equation $\chi = 0.0042 - 0.906/T^{[34]}$. The statistical segment length can be expressed as $a = (a_{PB}a_{LPI})^{1/2}$ in which a_{PB} and a_{LPI} are 0.65 nm and 0.55 nm^[34] respectively. Therefore, the estimated value of σ from Eq. (15) is about 0.26 mN/m. Based on the above parameters, the droplet sizes at different phase separation times can be calculated and are shown in Table 2. Compared to the SALS and PCOM results, it is concluded that the droplet sizes determined by the rheological method is reliable.

Table 2. The characteristic relaxation times and dimension size of droplets

t (min)	75	105	135	165	195	225	255
τ (s)	2.75	3.00	3.25	3.69	3.90	4.15	4.34
R_2 (μ m)	1.28	1.35	1.46	1.66	1.75	1.87	1.94

CONCLUSIONS

Two kinds of phase-separating structure evolutions of the PB/LPI blends have been investigated by the optical microscopy, small-angle light scattering and rheometry. For the near-critical and symmetric blend LPI50, the co-continuous phase-separating structure is observed and leads to a power law behavior of the dynamic storage modulus at low angular frequencies. With the growth of the co-continuous structure, the storage modulus at low angular frequencies decreases dramatically. For the off-critical and asymmetric blend LPI70, the droplet-matrix two-phase structure appears and results in a rather complex elastic behavior at the mediate and low angular frequency regions. Based on the simplified Palierne model, the decreasing platform modulus and increasing terminal modulus with the growth of droplets exhibited in LPI70 have been well interpreted by the varied droplet dimension dependence. The platform and terminal moduli at a given frequency are found to be scalable with the phase separation time. Finally, we have obtained the characteristic relaxation time and domain size of the droplets by rheology. And it seems that the rheologically determined droplet dimensions are consistent with the ones determined by PCOM and SALS.

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