



Rheological properties of polybutadiene/polyisoprene blend in the unstable and metastable regions under oscillatory shear



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ABSTRACT

The rheological properties of polybutadiene (PB)/polyisoprene (PI) in the unstable and metastable regions under oscillatory shear flow has been studied. Based on the shear quench experiment, it showed that the time dependent storage modulus G' initially increased and then decreased with time in the unstable region. The concentration fluctuation led to the increasing part and the coarsening of the bicontinuous structure led to the decreasing of the storage modulus. The rheological response of the nucleation/growth in the metastable region was similar to that of spinodal decomposition. The fluctuation-assisted nucleation theory proposed by Balsara et al. was similar to the spinodal decomposition mechanism, which led to the similar rheological response. However, the continuous nucleation led to the slow growth and the almost linear decayed rheological curve, which was different from that in the unstable region. According to this theory, the relative nucleation rate on the early stage of nucleation could be calculated, which increased exponentially with the reciprocal of quench temperature in the metastable region. The spinodal point under oscillatory shear was also determined by the difference of maximum value of the storage modulus and the bulk modulus.

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1. Introduction

The rheology of polymer blends has attracted great attention due to the scientific and industrial importance. These studies could be divided into the following categories: studies focused on the rheology of polymer blends in homogeneous, phase-separated and phase transitional regions. In the homogeneous region the focus was mainly on the concentration dependence of viscosity and linear dynamic properties [1–3]. Irving relation could be used to describe these rheological properties well [4–7]. Also the time–temperature superposition (TTS) applied well in the homogeneous region for most polymer blends [8–12]. Then, the rheological behavior of the phase-separated polymer blends was also researched [13,14]. In this phase-separated regime, it normally shows a very long relaxation time and pronounced elastic properties due to the phase structures. The TTS was not applicable in this region. Several excellent models which were proposed by Palierno, Gramesbacher and Meissner were used to depict the viscoelastic behavior of polymer blends with droplet–matrix structures and were agreeing well with some experiment results [15–17].

Complex changes in the viscoelastic properties were exhibited when the partially miscible polymer blends were quenched from the homogeneous region to the phase-separated region, which resulted to the difficulty on the determination of phase diagram under shear [7–9]. Recent researches have determined the binodal points and spinodal points by rheology [18–32]. The time dependent storage modulus exhibited interesting behavior when the partially miscible polymer blends were in the phase-separated region, which were related to the kinetics of phase separation [33–35]. The rheological properties of polymer blends during the nucleation/growth and the spinodal decomposition phase separation were studied. The storage modulus firstly increased and then decreased in the nucleation/growth process, but it decreased monotonically with time in the spinodal decomposition case. The different phase separation mechanisms in these processes led to the different rheological responses. However, the nonclassical behaviors of the nucleation/growth were observed by Balsara et al. in the initial stage of phase separation in the metastable high-molecular-weight polymer blends with small-angle neutron scattering (SANS), which showed that the nuclei were created by concentration fluctuations and their structures were diffusive and self-similar [36–39]. It was very similar to the spinodal decomposition case. Based on this theory, what is the relationship of

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rheological properties between spinodal decomposition and the nucleation and growth phase separation? Whether this new nucleation theory is fit for the rheological behavior at the early stage of nucleation/growth phase separation? Could the rheological experiments be used to study the early stage of nucleation except for small-angle neutron scattering? These physical questions are definitely needed to be answered.

In the present paper, the phase diagrams of the partially miscible blend PB/LPI at static state and under shear are measured by microscopy and rheology method separately. We take the advantage of shear-induced mixing effect under strong shear to investigate the rheological properties in the metastable and unstable region. We also interpret the rheological behavior and calculate the nucleation rates at the early stage of nucleation in the metastable region. Meanwhile, the spinodal point can be determined in a simple method. The relationship between the rheological property and phase structure can be established.

2. Experimental section

2.1. Materials

The two polymers, polybutadiene (PB) and low vinyl content polyisoprene (LPI) which are random copolymers were synthesized in our laboratory by anionic copolymerization. The chemical composition of these polymers was determined by ^1H and ^{13}C nuclear magnetic resonance (NMR). The number and mass-average molecular weight (M_n and M_w) were obtained by gel permeation chromatography (GPC) using polystyrene as standard. The glass transition temperature was measured by differential scanning calorimetry (Perkin–Elmer DSC-7) in which the scanning rate was $10^\circ\text{C}/\text{min}$. The detailed structure information was summarized in Table 1. PB/LPI blend was labeled as PBx, where x represents the weight fraction of PB in the blend.

2.2. Sample preparation

The PB/LPI blends were prepared by a solution blending method. Appropriate amounts of PB and LPI were dissolved in dichloromethane (mass fraction of 2% of the total polymer), which contains a mass fraction of 0.02% antioxidant butylated hydroxytoluene (BHT). Then the solution was stirred at room temperature for 24 h and filtered through a $0.45\ \mu\text{m}$ Millipore filter. The solvent was evaporated at 40°C with stirring. The remaining solvent was finally removed in a vacuum oven at 25°C for a week.

2.3. Optical microscopy (OM)

An Olympus (BX51) phase contrast optical microscope (PCOM) with an Olympus (C-5050ZOOM) camera was chosen. The experimental temperature was controlled by a Linkam (LTS350) hot stage. The prepared samples with about $30\ \mu\text{m}$ in thickness firstly phase separated into two phases which could be observed by optical microscope in 24 h as temperature increased, and then the temperature was lowered to find out at which temperature the blend

Table 1
Characterization data of polymers.

Sample code	M_w (g/mol)	M_w/M_n	T_g ($^\circ\text{C}$)	Microstructure, mol %		
				1,4-	1,2-	3,4-
PB	44,000	1.05	−98	89	11	0
LPI				88	0	12
	101,000					

was in the homogeneous states. This process was repeated until the binodal point was determined.

2.4. Rheological measurements

All the rheological measurements were performed by an ARES rheometer. The 25 mm diameter parallel plate–plate fixture was chosen. All of the measurements were carried out under the nitrogen atmosphere. The samples were put into a vacuum oven at 25°C for 3 days to remove air bubbles before experiments. The following oscillatory shear experiments were carried out at the shear strain of 10% which was in the “apparent” linear viscoelastic region. (i) Dynamic time ramp tests were carried out at the shear strain of 10% under $0.5\ \text{rad/s}$ at the homogenous and two-phase regions. (ii) Shear quench experiments were carried out at a certain temperature in the phase separated region. The procedure was as follows: the dynamic temperature ramp test at the frequency of $25\ \text{rad/s}$ from the homogenous state was conducted to a certain measured temperature, at which no phase separation occurred of this frequency and strain amplitude of 10%. After reaching the research temperature, the dynamic time sweep test was started with the frequency to a fixed $0.5\ \text{rad/s}$ at the strain amplitude of 10%.

3. Results and discussion

3.1. Phase diagram under static state and oscillatory shear

Before the rheological experiments, the phase transition temperatures of PB/LPI blends under static condition were determined by phase contrast optical microscopy. The PB/LPI system displayed an LCST type phase diagram with the critical temperature at about $27 \pm 1^\circ\text{C}$ at static condition. The critical composition of PB was about 0.6 by weight fraction.

Before our rheological study, the appropriate rheological conditions were determined. Fig. 1 showed the polymer blends exhibited an “apparent” linear viscoelastic region even the strain amplitude reached to 40% whether they were in homogenous state or two-phase region. In this region, the modulus was nearly constant for constant temperature when the two-phase structure existed. So the strain amplitude was set at 10% to simplify our data analysis and discussion.

Then the dynamic frequency sweep tests were carried out, which was shown as Fig. 2. It showed a plateau modulus at the

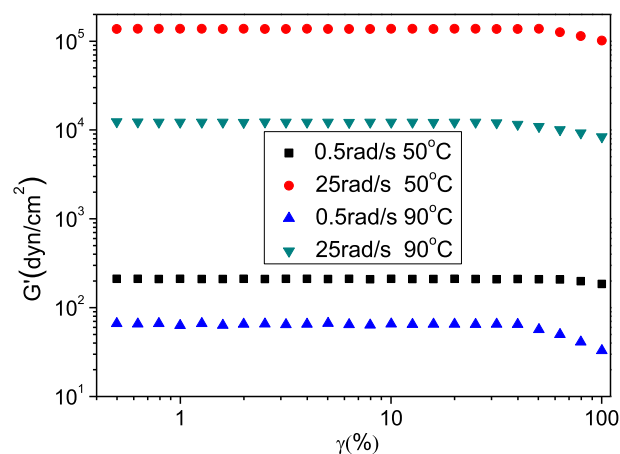


Fig. 1. The strain dependence of the storage modulus of PB20 is shown, with frequencies of 0.5 and 25 rad/s at 50 and 90°C , respectively.

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