



Morphology evolution and dynamic relaxation behavior of solution-polymerized styrene-butadiene rubber/polyisoprene/silica ternary composites influenced by shear



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ABSTRACT

The influence of SiO₂ nanoparticles on the morphology evolution and rheological properties of solution-polymerized styrene-butadiene rubber/low vinyl content polyisoprene/nano-silica (SSBR/LPI/SiO₂) ternary composites after cessation of various shear flows was studied by the combination of rheological and rheo-optical techniques. It was found that the nano-sized SiO₂ acted as compatibilizer or filler and restricted the coalescence of polymer droplets under weaker shear flow, which led to less deformed droplets. Under stronger shear flow, the addition of SiO₂ had no influence on the formation of string-like domain phase. After cessation of pre-shear flow, the presence of SiO₂ nanoparticles did not change the relaxation mechanism of deformed domains, but retarded the breakup process of deformed domains and hindered the simultaneous coalescence of dispersed droplets by serving as compatibilizer or filler. It was proved that the SiO₂ nanoparticles effectively reduced the droplet size and stabilized the morphology of SSBR/LPI blends.

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1. Introduction

Blending is an attractive route to produce new polymeric materials with excellent properties. In the process of solution mixing or melt blending of two or three polymer components, the polymer blends are subjected to strong shear and elongational flows, and the dispersed phase breaks up into smaller domains due to the deformation of the dispersed phase and evolves to form a final morphology [1,2]. After cessation of shear flows, deformed droplets are retracted and/or ruptured, and finally yield a coarse morphology with poor interfacial adhesion between the blending components, thus affecting their final properties [3,4]. The control of blend morphology during and after process is therefore of great importance for ultimate performance of polymer materials.

The relationship between shear flow and microstructure of immiscible liquid-liquid blends has been the subject of many studies [2,5,6], which was systematically reviewed by Tucker [3]. The morphology evolution of droplets in immiscible blends under

steady shear flow can be described by the capillary number $Ca = \eta_m R \dot{\gamma} / \sigma$ (η_m , R , $\dot{\gamma}$, and σ , respectively, the matrix viscosity, the droplet radius, the shear rate and the interfacial tension). When the mixture was a binary phase-separating fluid, shear flow not only changed the phase structure but also reduced the interfacial tension if it is with shear mixing effect [7–9]. Han [10–13] and Hashimoto [14–16] systematically studied the domain structure evolution and rheological characteristic of such diluted polymer blends. A general conclusion has been drawn that under very weak shear, the balance between shear stress that deformed droplets from their sphere to an elongated shapes and interfacial force that recovered deformed droplets to its original spherical shape led to the formation of nearly spherical droplet structure. With increased $\dot{\gamma}$, the dispersive spherical domains would be elongated along flow direction and ruptured into smaller ones. At higher $\dot{\gamma}$, the droplets became much smaller and gradually interconnected with each other along flow direction, as a consequence a stable string-like structure was formed. Upon increasing shear rate even higher, the shear-induced mixing effect was more obvious and the interfacial tension was reduced significantly. Then, the blends might be brought into a single phase [10,11,17]. After stopping flow, the deformed domains would be retracted back to spherical structure and/or broke up into small droplets governed by capillary instabilities, depending on

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their primary phase morphologies formed under pre-shear flow [17–19].

Inorganic fillers played an important role on controlling the phase structure and material properties of polymer blends, the effect of which on the morphology evolution under and after shear flow was then extensively studied [20–23]. Nanofillers locating at the interface between two polymer phases could restrict coalescence of droplets and reduce droplet size [22]. Kong [24] studied the effect of SiO₂ on the relaxation behavior of a single polyamide 6 (PA6) droplet in polystyrene (PS) matrix and found that SiO₂ could increase the viscoelastic properties of PA6 droplet, inducing slow relaxation dynamics. Dharaia [4] reported that clay particles could reduce interfacial tension of polyamide 6/polypropylene blend and result in thin fibrils, which in turn rapidly broke up into small droplets. However, the relaxation behavior of a single deformed droplet could not generally reflect the bulk properties of filled polymer blends. So, more attention should be paid on the effect of nanofiller on the relaxation kinetics and corresponding morphology evolution mechanism. Because the microstructure of polymer melts contributes directly to the modulus and viscosity through the variation of interfacial tension, rheological measurements were commonly used to probe the microstructure evolution under and after shear flow of polymer blends [8,18,23,25]. Molde-naers [1,2,22,26–28] systematically investigated the morphology evolution of the unfilled and filled immiscible polyisobutylene/polydimethylsiloxane blends by rheological and rheo-optical techniques. The corresponding rheological characteristic properties after cessation of shear flow were interpreted by the morphology evolution in relaxation process.

Previous literature predominantly focused on the influence of fillers on droplet breakup and coarsening process in immiscible polymer blends [4,21–23,25]. However, no unambiguous relationship between the morphology evolution and rheological behavior has been established up to date for the filled partially miscible polymer blends, in which both shear flow [9,16] and filler [29,30] can change the interfacial tension and viscoelasticity properties of blends. The corresponding changes of this ternary composite in morphology and rheological properties under and after shear flow may be different from those of the filled immiscible polymer blends. In practical applications of the enhanced synthetic rubbers, for example, carbon black, silica, clay particles and so on are the main selected fillers. Therefore, it is important to make it clear how nanofillers affect the phase separation dynamics and what is the characteristic of the rheological behavior and corresponding phase morphology evolution under shear and after cessation of shear for the filled partially miscible elastomer blends. In present work, the effects of pre-shear history and SiO₂ content on relaxation behavior of the filled partially miscible SSBR/LPI/SiO₂ blends, including morphology evolution process, evolution kinetics, and rheological properties after cessation of steady shear were systematically studied.

2. Experimental section

2.1. Materials

The solution-polymerized styrene-butadiene rubber (SSBR) and low isopropenyl content polyisoprene (LPI) used in this work were kindly supplied by Yanshan Branch, SINOPEC Beijing Research Institute of Chemical Industry. Both of them were synthesized by anionic polymerization. Yanshan Branch, SINOPEC Beijing Research Institute of Chemical Industry (Table 1). Various tests were carried out to characterize the basic physical properties of SSBR and LPI, and the results were listed in Table I. The mass fraction of bound styrene in SSBR was 24.1% (mass ratio). In our previous work [31], it

Table 1
Basic parameters of SSBR and LPI.

Sample	Mn (g/mol)	Mw/Mn	$\eta^{(a)}$ (Pa·s)	Tg (°C)	Chemical structure, mol%		
					1,4-	1,2-	3,4-
SSBR	44,000	1.1	1924.9	-40.0	54.9 ^(b)	45.1 ^(b)	—
LPI	45,000	1.1	127.5	-58.6	93.1	—	6.9

^a $\dot{\gamma} = 0.1 \text{ s}^{-1}$, $T = 60 \text{ }^\circ\text{C}$.

^b Based on^athe total vinyl content^b in butadiene unit.

was found that the SSBR/LPI blend system exhibits the upper critical solution temperature (UCST) type phase behavior. The binodal temperature of SSBR/LPI (70/30) blend, determined by dynamic temperature sweep test, was $136.2 \pm 2 \text{ }^\circ\text{C}$. Hydrophobic nanosilica particles, DM-30 (TOKUYAMA, Japan) with a specific surface area of $230 \pm 20 \text{ m}^2/\text{g}$, a primary particle diameter of 7 nm and dichlorodimethylsilane (DCDMS) coating were used as received.

2.2. Sample preparation

The SSBR/LPI (70/30) and SSBR/LPI/SiO₂ were prepared by mixing of the components in dichloromethane and stirred for 2 h at room temperature. Different particle concentrations (0.2, 0.5, 1.0 wt % based on total blend) were chosen for the polymer blends. The SiO₂ was first dispersed in dichloromethane by ultrasonication for 30 min and then mixed with the SSBR/LPI (70/30) solution and stirred for 4 h at room temperature. The solvent was evaporated at 30 °C under stirring for 12 h. The residue solvent was finally removed at 30 °C under vacuum until no more weight changes. In order to study the interaction between the fumed silica particles and pure components, the SSBR/SiO₂ and LPI/SiO₂ blends with different SiO₂ contents were also prepared with the same procedure. Samples are designated x/y/z, where x and y is the weight percentage of SSBR and LPI in the blends respectively, and z is the weight percentage of SiO₂ nanoparticles with respect to the blend.

2.3. Rheological measurements

Rheological experiments were performed on a stress controlled rheometer DHR-2 (TA Instrument Ltd., US) with the parallel plates geometry (diameter 25 mm). All measurements were carried out at 60 °C. Before measurement, all the samples were kept at 30 °C in a vacuum oven for 3 days to remove air bubbles and form primary stable morphologies. In order to erase the thermal/mechanical history and to start the measurements with identical initial state, all the samples were preconditioned by shearing until a constant shear stress (shear rate) was obtained [5]. Here, the samples were pre-sheared at 10, 1 and 0.1 s⁻¹ for 600, 6000 and 10000 s, respectively, to generate an apparent stable and reproducible morphology. The small amplitude oscillatory time sweep tests were immediately carried out after cessation of steady shear. The dynamic frequency sweep tests were performed during the time sweep test at 1 h interval to characterize the domains growing kinetics.

2.4. Rheo-optical microscopy

The Linkam optical shearing system (CSS450) was used to study the morphology evolution of SSBR/LPI/SiO₂ under and after shearing. Olympus (BX53) phase contrast optical microscope (PCOM) with a Q-imaging camera was used. The samples were sandwiched between two cover glasses with a spacer about 50 μm in thickness. The samples were firstly sheared under the same

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