General paper

Domain Structures and Rheological Properties of Immiscible Polymer Blends under Shear Flow in Parallel Plates

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Abstract: Domain structures and rheological properties of immiscible polymer blends composed of components having almost the same viscosities in a parallel-plate (PP) geometry are studied in comparison with those in a cone-plate (CP) geometry. Both steady states and transient states after step increase of shear rate are examined. At steady states, it was confirmed that the domain size becomes smaller inversely proportional to the distance from the center (i.e., shear rate) along the radial direction of PP, consistent with the data in CP compared at the same shear rate. The related rheological data are also consistent. At transient states after the step increase of shear rate, there was no apparent long-range interference in the transient behaviors undergoing in different time scales at different positions along the radial direction of PP. The structure change and the related excess stresses of immiscible polymer blends with the nearly same viscosities under shear flow in PP are consistent with those in the CP geometry.

Key words: *Domain structure, Rheological properties, Immiscible polymer blend, Parallel plate, Transient state*

1. INTRODUCTION

In previous papers [1-4], we studied rheological properties of immiscible Newtonian fluid mixtures and immiscible polymer blends composed of components having nearly the same viscosities in shear flows in relation to the domain structures under the shear flow observed by use of a video-microscope. The main results are briefly summarized below.

At steady states, both (excess) shear stress σ_{12} and (excess) first normal stress difference N_1 are proportional to shear rate $\dot{\gamma}$ over a wide range of $\dot{\gamma}$. The shorter diameter (a) of observed ellipsoidal domains had narrow size distributions and their average values were inversely proportional to $\dot{\gamma}$. These results are consistent with theories of Onuki [5], and Doi and Ohta [6], assuming that the excess stresses are due to the interfacial tension.

In transient states after step increase of shear rate, the rescaled transient stresses (i.e., the transient stresses divided by the initial steady values) compose respective master curves as a function of strain as long as the shear rate ratio was kept constant. This scaling relation is also consistent with the Doi-Ohta theory [6]. An undershoot of σ_{12} and an overshoot of N_1 corresponding to the extreme elongation of dispersed droplets at the initial stage, followed by rupture and gradual approach to the final steady state were observed. Qualitatively the same results were also reported from different groups [7-10] and more quantitative discussions of transient stress curves were reported by Vinckier et al. [10].

Above studies are performed with a cone-plate (CP) geometry in which shear rate is constant over the whole sample. Since the domain structure is determined by the

shear rate and the transient behavior is strain dependent, the structure change is uniform in CP geometry except at around the center where the gap between cone and plate become too narrow.

In later studies, different type of flow geometry such as parallel-plate (PP) is used. Except the center part where shear rate is too low to control the structure, it is expected that the domain size in PP at steady states become smaller inversely proportional to the distance from the center, consistent with the data obtained in CP at corresponding shear rate.

In the transient state, the structure is different at different positions in PP since it is strain dependent. That is, the structure reaches steady state in shorter time at the outer part of PP. If the structure change at a certain position in PP is not affected by the change in other part where structure changes in different time scale, it is also expected to be the same as that observed by CP at corresponding shear rate.

Recently, some interesting observations of the domain structure change, i.e. stabilization of string-like structure [11], hysteresis in the shear rate dependence of domain size [12], etc., have been reported. The reasons for those behaviors are not well elucidated yet but it is speculated that hydrodynamic interactions are playing an important role. From these results, we cannot neglect the possibility that transient behaviors in CP and PP are different even though the final steady states are the same.

In this study, we examine the rheological properties and the variation of domain size along the radial direction in the PP geometry in comparison with those obtained in the CP geometry both at steady and transient states after step increase of shear rate.

2. EXPERIMENTAL

Polymers used as blend components were polyisoprenes and polydimethylsiloxanes supplied from Japan Synthetic Rubber Co., Ltd. and Shinetsu Chemical Co., respectively. Characteristics of the components are tabulated in Table 1. Two blend samples (blend 1: LIR-20000/KF96H60000 and blend 2: PIP-2/KF96H200000) composed of components having nearly the same viscosities containing 30 wt% polyisoprenes were prepared by the same procedure as in the previous papers [1-4]. Interfacial tension measured by the pendant drop method is 3.2×10^{-3} N/m at 25 °C for the both blends.

Table 1. Characteristics of component polymers

Samples	$10^{-4}M_w^*$	ρ (kg/m ³)	η (Pa·s)
Polyisoprene			
LIR-20000	2.4	912	80
PIP-2	3.1	912	150
Polydimethylsiloxane			
KF96H60000	9.1	976	74
KF96H200000	20	976	160

* nominal values

Domain structures were observed with a Keyence Monitor Microscope VH-5901 attached to a Weissenberg rheogoniometer R17 and recorded with a video recorder as detailed previously [3,4]. To observe the domain structures at arbitrary points, the system was further modified so that the lens can be moved in both radial and tangential directions. Both parallel plates and cone-plates (10 cm diameter and 0.017 rad cone angle), consisting of an upper quartz plate and a lower stainless steel cone or plate were used. The shear rate at the observed points in PP was calculated by using $\dot{\gamma}_r = r\Omega/h$, where r , Ω and h are the radius at the midpoint of view, the angular velocity of rotor and the gap between parallel plates, respectively. The relative difference of the highest and lowest shear rates in the view from the midpoint value was always less than 10 %.

Rheological measurements were carried out with a Rheometrics mechanical spectrometer RMS800 at room temperature. Both PP (5 cm diameter) and CP (0.04 rad cone angle and 5 cm diameter) geometries were used in all the measurements.

3. RESULTS AND DISCUSSIONS

Domain structures in PP at a constant rotating speed are observed at a few selected positions. The observed domains are nearly spherical and their sizes are not controlled by the flow around the center, while those at the outer positions are ellipsoidal and the sizes become rather uniform. The diameters of ellipsoids become smaller with an increase of the distance from the center, suggesting that the sizes are controlled by the shear rate.

The number averaged shorter diameter " a " of ellipsoidal domains can be used as a characteristic length of domain structure if their distribution is narrow as discussed in previous work [3, 4]. Figure 1 compares histogram of a in PP with that in CP at the same shear rate. The distribution in PP is slightly broader than that in CP, which is common for all the shear rates examined. However, they are always narrower than the critical condition [4] so that we also use number averaged values of a as a characteristic domain length in this work.

Figure 2 shows double logarithmic plots of a against $\dot{\gamma}$. The data for blend 2 are shifted by a factor of 0.1. Apparently, the data for both blends in the PP and CP geometries coincide with each other and are inversely proportional to the shear rate, though the data for blend 2 are somewhat scattered. Thus, we conclude that the domain sizes are inversely proportional to r at steady state in the PP geometry.

In the PP geometry, the measured torque τ and normal force F are related to shear viscosity η and N_1 by

Fig. 1. Histograms of domain size a at 10 sec^{-1} for blend 1 in CP (left) and PP (right).

Fig. 2. Double logarithmic plots of average a against $\dot{\gamma}$ for blend samples. Symbols are denoted in the figure.

$$\tau = \frac{2\pi R^3}{\dot{\gamma}_R^3} \int_0^{\dot{\gamma}_R} \dot{\gamma}_r^3 \eta(\dot{\gamma}_r) d\dot{\gamma}_r, \quad (1)$$

and

$$F = \frac{\pi R^2}{\dot{\gamma}_R^2} \int_0^{\dot{\gamma}_R} \dot{\gamma}_r [N_1(\dot{\gamma}_r) - N_2(\dot{\gamma}_r)] d\dot{\gamma}_r, \quad (2)$$

respectively, where $\dot{\gamma}_r$ is the shear rate at the distance r from the center, R is the radius of the plates, and N_2 is the second normal stress difference [13]. If the shape and orientation of domains in the PP are the same as those in the CP at the corresponding $\dot{\gamma}$, the excess stresses due to interfacial tension are proportional to $\dot{\gamma}_r$, and become dominant in the measured stresses for the present sample. If excess N_2 is also proportional to $\dot{\gamma}$, as theoretically predicted [5,6], eqs. (1) and (2) can be rewritten as

$$\sigma_{12} = \eta \dot{\gamma}_R = 2\tau/\pi R^3 \quad (3)$$

and

$$N_1 - N_2 = 3F/\pi R^2. \quad (4)$$

Figure 3 shows double logarithmic plots of σ_{12} , N_1 and $N_1 - N_2$ against $\dot{\gamma}$ for the blend samples obtained in the PP together with the data obtained in the CP. Here, $\dot{\gamma}_R$ for PP is used as $\dot{\gamma}$. At the lower shear rate region $\dot{\gamma} < 1 \text{ s}^{-1}$, σ_{12} values obtained in the PP and CP geometries are somewhat different and show slightly gentle shear rate dependence than those at higher shear rates. In the same region, shear rate dependences of N_1 and $N_1 - N_2$ are slightly steep than those at higher $\dot{\gamma}$.

Fig. 3. Double logarithmic plots of σ_{12} , N_1 and $N_1 - N_2$ against $\dot{\gamma}$. Symbols are denoted in the figure.

As partly discussed in previous papers [1-4], there exist certain limitations for the applicability of the scaling relationship mentioned in the Introduction. At low shear rates in this type of experiments, domain structures cannot be well controlled by the flow so that the reproducibility of rheological data becomes worse. Details of such behavior in relation with hysteresis [11] will be discussed elsewhere [14]. In this work, we limit our discussions at the high shear rate region ($\dot{\gamma} \geq 1 \text{ s}^{-1}$).

As shown in Fig. 3, not only the σ_{12} values but also the $N_1 - N_2$ and N_1 values obtained in the PP and CP geometries agree with each other within experimental errors at high shear rate. Thus, it is concluded that excess N_2 is negligibly small in comparison with the excess N_1 and both the structural observation and rheological data obtained in PP at steady states are the same as those obtained in CP for immiscible polymer blends having nearly same viscosities.

After the step increase of shear rate in the CP geometry, the ellipsoidal domains at the initial steady state elongate, rupture and finally become smaller ellipsoids at the final steady state. Since the transient behaviors are function of strain $\gamma = \dot{\gamma} t$, where t is the time after the change of shear rate, the time scale of the stress behavior became shorter with an increase of shear rate in the CP geometry. Therefore, position dependent transient behavior in the radial direction is expected in the PP.

Actually, qualitatively the same structure change was also observed in PP when it was monitored at a constant position but the time scale was different at the different positions. If there is no long range interference in the transient behaviors undergoing at different time scales at different positions, the structure change observed at a constant position in PP should be the same as that observed in CP at corresponding shear rate. Consequently, excess transient stresses obtained in both geometries should be consistent.

It is difficult to quantitatively discuss the transient structure. Therefore, we discuss the transient stresses in the PP geometry, on the basis of the transient data obtained in the CP geometry. Here, we only discuss σ_{12} in terms of torque since σ_{12} are more accurately measured than N_1 .

Figure 4 shows plots of rescaled transient torque $\tau(t)/\tau_i$ against t obtained after the step increase of $\dot{\gamma}_R$ from 4 to 8 sec^{-1} , where τ_i denotes the initial steady value. Three data obtained in the CP with different initial shear rates maintaining the same shear rate ratio 2, are shown for comparison.

An undershoot of τ is observed for each data but their time dependencies are different. As already mentioned, rescaled transient stress is a function of strain, so that the PP data at a certain time t must be the summation of rescaled transient stresses at different strains $\dot{\gamma}_r t$ along the radial direction.

The CP data shown in Fig. 4 correspond to those in the circular area having radius r with narrow width (Δr)

in the PP, in which $\dot{\gamma}_r$ equals to $\dot{\gamma}$ in the CP. We evaluated τ_{calc} by summing these three CP data, which correspond to the positions in PP, $r = 25.0, 12.5$ and 6.25 mm with $\Delta r = 0.15$ mm and compared with the PP data in Fig. 5.

The calculated data agree with the PP data, though there exist a small deviation after the undershoot (around $t = 15$ sec). Since only 3 different CP data are used in the calculation of τ_{calc} in this figure, we can easily speculate that the agreement between measured and calculated values become much better if we use more CP data. That is, the PP data can be obtained by the summation of CP data at different shear rates corresponding to those along radial direction of PP in the transient states.

From above results, we conclude that the structure change after step increase of the shear rate and the related excess stresses of immiscible polymer blends under shear flow in PP are consistent with those in the CP geometry. There is no long-range interference in the transient behaviors undergoing at different time scales at different positions.

Fig. 4. Plots of $\tau(t)/\tau_i$ vs. t . Symbols and shear rates for the CP data are denoted in the figure.

Fig. 5. Comparison between measured and calculated τ .

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