
General paper

COMPARISON BETWEEN CRITICAL SHEAR RATES FOR FLOW-INDUCED HOMOGENIZATION OF POLYMER BLEND STUDIED BY RHEOMETRY AND FLOW-LIGHT SCATTERING

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Abstract: The critical shear rate for flow-induced homogenization of a polystyrene/poly(vinyl methyl ether) blend with nearly critical composition in the phase-separated region near the phase separation temperature was studied by rheological and light scattering measurements under steady shear flows. The critical shear rate by rheometry was determined from the change in shear rate dependence of first normal stress difference as in a previous study. This critical shear rate was almost consistent with the critical shear rate by flow-light scattering at which the intensity deviates from the value in the phase-separated region.

Key words: Flow-induced homogenization, Polymer blend, Polystyrene, Poly(vinyl methyl ether), Steady shear flow, First normal stress difference, Flow-light scattering

1. INTRODUCTION

It has been well known that many polymer blends as well as polymer solutions show flow-induced phase transition, i.e., flow-induced homogenization (flow-mixing) and flow-induced phase separation (flow-demixing)[1-3]. Two major experimental methods frequently used to study the above phenomena are rheometry and scattering under flow. In general, the former is suitable for relatively high viscosity samples, while the latter is suitable for relatively low viscosity samples.

In a previous paper[4], we studied viscoelastic properties of polymer blends with the nearly critical compositions near the phase separation temperatures under steady shear flows. The blend sample used was polystyrene/poly(vinyl methyl ether) (PS/PVME) blend, which is one of the most well studied polymer blends, having a phase diagram of the LCST type[5]. Hereafter, we call the temperature regions where the samples are homogeneous and phase-separated at quiescence, as one-phase and two-phase regions, respectively.

We reported that the viscoelastic behaviors of PS/PVME in the one-phase region are practically the same as those of homopolymers[6]. In the two-phase region, viscoelastic behaviors at low shear rates are similar to those of binary mixtures of equiviscous immiscible Newtonian fluids[7] and immiscible polymers[8]. That is, first normal stress difference $N_1$ is enhanced more than the value in the one-phase region and its shear rate dependence is close to first power of shear rate, entirely different from those of components, whereas the shear stress $\tau_{12}$ and its shear rate dependence are not significantly different from those of components, though small enhancement is also observed. These rheological features are qualitatively explained by the theories of Onuki[9], and Doi and Ohta[10], considering deformation of interface by flow.

In the two-phase region, the enhancements of $\tau_{12}$ and $N_1$ disappear at higher shear rates and they become consistent with the data in the homogeneous region when the shear rates become higher than their respective critical shear rates. Since the critical shear rates for $N_1$ are always larger than those for $\tau_{12}$ in all the samples, we consider that the critical shear rate for $N_1$ is almost equal to the critical shear rate for flow-mixing.

It is worth discussing the results from rheometry and scattering experiments under flow together for further understanding of flow-induced phase transition, but such discussions are difficult since studies of the two kind are usually carried out independently. For instance, the molecular weights and composition of components in one of PS/PVME samples in our previous study[4] are almost the same as those of a deuterated-PS/PVME (PSD/PVME) sample used in small angle neutron scattering (SANS) experiments under shear flow[11]. However, we could not discuss the data in both studies quantitatively, since the phase-separation temperatures of PS/PVME and PSD/PVME were about 40K different, which was considered as the effect of deuteration.

Recently, systematic experimental studies using both methods are in progress for polymer solutions[12, 13], though there exists difficulties in rheological measurements. For polymer blends, however, even the relationship between the critical shear rates determined by the both methods are not clear. In this work, therefore, we compare the critical shear rates for flow-mixing of a PS/PVME blend determined by both rheological and light scattering measurements under steady shear flow.

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2. EXPERIMENTAL SECTION

PVME sample used in this work was prepared by cationic polymerization in our laboratory as in a previous work[14]. The number-average molecular weight, \( M_n \), and the molecular weight distribution index, \( M_w/M_n \), were determined to be 2.2\( \times 10^4 \) and 1.18 by \(^1\)H-NMR (with unity-INNOVA, Varian) and GPC (with Tosoh GMHXL mixed column \( \times 2 \)), respectively. PS sample used was a Tosoh standard polystyrene F-40. The nominal \( M_w \) and \( M_w/M_n \) of F-40 are 3.6\( \times 10^5 \) and 1.02, respectively. Seven blend samples with different compositions were prepared to determine phase diagram, but only one sample near the critical composition was used for further studies. Homogeneous and transparent blend samples were prepared by freeze-drying the uniform benzene solutions of blend samples, followed by drying \textit{in vacuo} at about 353 K for one to a few days. Then the samples were moulded to disks (1 mm thick) with a hot press at temperatures well below the cloud points.

Cloud points \( T_{C0} \) of blend samples at the zero heating rate were determined by measuring transmitted intensity of He-Ne laser through the sample disks as reported previously[15]. Light scattering measurements were performed to determine spinodal temperature \( T_s \) of blend samples. From the scattering data at each temperature, the correlation length \( \xi \) was obtained by Ornstein-Zernike's (O-Z) plots, and then, \( T_s \) was determined as the temperature \( T \) at which \( \xi^{-1} \) becomes zero by the extrapolation in plots of \( \xi^{-1} \) vs \( T \). In the light scattering measurements, the experimental set-up for the cloud point measurements were used with minor modifications including replacement of the detector to a 38 elements photo diode array (Hamamatsu Photonics S411135Q).

A homemade flow-birefringence apparatus[16] equipped with parallel plates made of quartz was used for light scattering measurements under steady shear flow (flow-LS). To perform flow-LS measurements with this apparatus, the optical system was replaced by the same one as used in the static light scattering measurements mentioned above. The incident laser beam was vertically applied from the top of quartz plate. Moreover, photo diode array was set on a rotatable plate so that we can measure the scattered intensity in both directions parallel and perpendicular to the flow.

The shear rates in flow-LS measurements were calculated by using \( \dot{\gamma} = r\Omega/h \), where \( r \), \( \Omega \) and \( h (= 1 \) mm) are the radius of quartz plate at the point where laser beam go through, the angular velocity of rotor and the gap between parallel plates, respectively.

Viscoelastic properties of blend samples were measured under steady shear flows with a Mechanical Spectrometer RMS 800 of Rheometrics Co., equipped with the cone and plate geometry of 25 mm diameter and 0.1 radian cone-angle. The temperature control chambers of flow-LS apparatus and RMS 800 were purged with dry nitrogen gas to avoid sample degradation and adsorption of moisture.

3. RESULTS AND DISCUSSIONS

Figure 1 shows the phase diagram of PS/PVME. The figure indicates that the volume fraction of PS, \( \phi_{PS} \), for the critical composition is about 0.15, therefore, rheological and flow-LS measurements were carried out at this composition (0.15). Since the purpose of this paper is to study flow-mixing behavior, we discuss the data measured in the two phase region, at 363.0 \( \pm 0.5 \) K (ca. 5\(^\circ\) quench) only, in which the measurements were started at 60 minutes after the measuring temperature was reached. It should be noted that viscoelastic properties of component PVME and those of tested blend sample in the one-phase region are consistent with those in our previous studies[17, 18].

Figures 2 and 3 show double logarithmic plots of \( \sigma_{12} \) and \( N_1 \) against shear rate \( \dot{\gamma} \), respectively. The shear rate

\[ \begin{align*}
\sigma_{12} &\text{(Pa)} \\
N_1 &\text{(against shear rate \( \dot{\gamma} \))}
\end{align*} \]

Fig. 2. Double logarithmic plots of \( \sigma_{12} \) vs. \( \dot{\gamma} \).
dependence of $\sigma_{12}$ is quite similar to those of homopolymers [6]; $\sigma_{12}$ is proportional to shear rate at low shear rates, but the shear rate dependence becomes lower with increasing shear rate, showing nonlinear behavior. Thus influence of flow-mixing is not apparent on $\sigma_{12}$.

On the other hand, apparent change in the shear rate dependence of $N_1$ is observed in Figure 3. That is, $N_1$ is proportional to $\dot{\gamma}$ at low shear rates, but it becomes proportional to $\dot{\gamma}^2$ at the higher shear rates, though the range where $N_1 \propto \dot{\gamma}^2$ is narrow. At the still higher shear rates where the nonlinear behavior was observed in $\sigma_{12}$, the shear rate dependence of $N_1$ becomes lower with increasing shear rate, also showing nonlinear behavior. All these features of rheological properties are practically the same as those observed in the previous work [4]. From this figure, therefore, we evaluated the critical shear rate for flow-mixing by rheometry, $\dot{\gamma}^*_R$, as 0.1 s$^{-1}$ for the experimental condition in this study.

Figures 4 and 5 show plots of scattered intensity $I(q)$ vs. scattering vector $q$ measured at various shear rates in the directions parallel and perpendicular to the flow, respectively, where $q=(4\pi/\lambda)\sin(\theta/2)$, $\lambda$ and $\theta$ are the wave length of incident beam and the scattering angle, respectively. At the first sight, it can be pointed out that $I(q)$ are not equal in the two directions. However, the same tendency is observed on the both directions. At low shear rates, both $I(q)$ values are very small, but they increase with increase of shear rate reflecting the decrease of turbidity due to the flow-mixing. At the higher shear rates, however, they decrease with increase of shear rate. It should be noted that the latter observation does not mean the increase of turbidity, which was confirmed by the direct observation by eyes. This feature may be due to the suppression of fluctuations by flow.

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In the scattering experiments under flow, two types of analysis have been employed. A rather simple analysis is to use the integrated intensity $S$ ($=\Sigma I(q)$) used to determine the turbidity [19]. The other one is the application of mean field approach, which is used to examine composition fluctuations [20] and to determine spinodal condition under flow as reported for SANS experiments [11]. In this work, we first use $S$ for the analysis and later mention the application of mean field approach.
Figures 6 and 7 show plots of normalized integrated intensity $S(\dot{\gamma})/S_0$ vs. $\dot{\gamma}$ in the parallel and perpendicular directions, where $S_0$ is the integrated intensity at quiescence. At low shear rates, $S(\dot{\gamma})/S_0$ is constant but it starts to increase with increase of shear rate in both directions. The slope is steeper in the parallel direction than in the perpendicular direction, reflecting the anisotropy of scattered intensities shown in Figs. 4 and 5. At the higher shear rates, $S(\dot{\gamma})/S_0$ in both directions decrease, also reflecting the features in Figs. 4 and 5.

To determine the critical shear rate for flow-mixing from these data in the consistent manner with the phase diagram at quiescence (Fig. 1), we first examine the integrated intensity data at quiescence $S_0(T)$ measured with the flow-LS apparatus at various temperature. Figure 8 shows plots of $S_0(T)/S_0(T_{\text{cloud}})$ against temperature $T$, where $S_0(T_{\text{cloud}})$ is the integrated intensity at the cloud point, which was evaluated as the average value of three almost constant values of $S_0(T)$ at high temperature as described below. At low temperature (in the one-phase region), $S_0(T)$ slightly increases with increase of temperature. This result is due to the increase of fluctuations with approaching the phase boundary. At the temperature higher than 338 K, $S_0(T)$ starts to decrease with increase of temperature and finally becomes almost constant. It is to be noted that only scattering data at $T<343$ K can be well represented by O-Z scattering and used to determine spinodal temperature in Fig. 1.

There are a few possible reasons why $S_0(T)$ decreases. The peak of scattering intensity might move far away from our experimental $q$ range to the smaller $q$ values by approaching the spinodal point. The component polymers are not really monodisperse, so that the high molecular weight fractions might be already partly phase-separated and hence slightly turbid in this temperature range. Therefore, there may exist some discussions on the determination of the cloud point. Experimentally, however, the temperature at which $S_0(T)$ becomes almost constant is very close to the cloud point shown in Fig. 1, so that we simply assume that this temperature in the plots of $S_0(T)$ vs. $T$ correspond to the cloud point. In other words, the temperature at which $S_0(T)$ deviates from the constant value at the high temperature region (two-phase region) obtained by flow-LS is consistent with the
cloud point. Since Figs. 6 and 7, the plots of $S(\dot{\gamma})$ vs $\dot{\gamma}^{-1}$ are quite similar to Fig. 8, we assume that the critical shear rate at which $S(\dot{\gamma})$ starts to increase in the plots of $S(\dot{\gamma})$ vs. $\dot{\gamma}$ correspond to the critical shear rate for flow-mixing by flow-LS measurement $\dot{\gamma}_{*LS}$, as assumed in the other studies[19, 21].

The $\dot{\gamma}_{*LS}$ values thus determined are almost the same in both directions as shown in Figs. 6 and 7, though there exists the difference in the scattering intensities at the higher shear rates. The value 0.2 s$^{-1}$ determined by the flow-LS is almost the same but slightly higher than that determined by rheometry (0.1 s$^{-1}$) in Fig. 3. According to above definition, $\dot{\gamma}_{*LS}$ corresponds to the cloud point determined by the turbidity, while $\dot{\gamma}_{*R}$ is determined by the contribution of deformed interface to the stress. Though both of them are due to phase separation, these two critical shear rates need not be exactly the same since the size and proportions of phase separation detected by different experimental methods are different. The residual difference in $\dot{\gamma}_{*R}$ and $\dot{\gamma}_{*LS}$ may be caused by above reason. From the above results, we conclude that the critical shear rate for flow-mixing determined by rheometry and by flow-LS measurements are consistent, if we can assume the above definitions.

Finally, we mention the application of O-Z scattering to the flow-LS data. Only the data at high shear rates ($\dot{\gamma}>0.5$ s$^{-1}$) can be fitted to O-Z scattering. As already mentioned, the static light scattering data in the one-phase region can not be well represented by O-Z scattering at the temperature range close to the cloud point. Comparing Figs. 6, 7 and 8, we can point out that only the region at $\dot{\gamma}>0.5$ s$^{-1}$ correspond to the temperature range where our static light scattering data can be represented by O-Z scattering. Therefore, it is understandable that the flow-LS data cannot be fitted to O-Z scattering at low shear rates in this study. Moreover, the $q$ range of flow-LS data fitted to O-Z scattering ($\dot{\gamma}>0.5$ s$^{-1}$) was narrower than that for the static light scattering data. Hashimoto et al.[19, 20] further analyzed their flow-LS data by the linear combination of O-Z scattering and Porod scattering, which can not be applied to our data. More systematic measurements covering wider $q$ range are needed to perform such analysis.

4. CONCLUSION

Critical shear rate for flow-induced homogenization of polymer blends was obtained by rheometry and flow-light scattering measurements. The critical shear rate by rheometry was determined from the change in shear rate dependence of first normal stress difference. This value was almost consistent with critical shear rate by flow-LS measurements defined as the shear rate at which the integrated intensity deviates from that in the phase-separated region.

REFERENCES