Stabilization of Dispersed Domains in Polymer Blends by Addition of Low Molecular Weight Diblock Copolymer

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Abstract: About 5 wt% of low molecular weight poly(isoprene-block-dimethylsiloxane) was added into a poly-isoprene/polydimethylsiloxane 3:7 blend and a polydimethylsiloxane/polyisobutylene 3:7 blend and tested as a surfactant. Samples were sheared at a constant shear rate (16 sec\(^{-1}\)) by a rheometer using cone-plate geometry. Viscoelastic properties of blends with and without diblock copolymers (bcp) after the pre-shear measured by dynamic measurements were almost the same. After the pre-shear, small amounts of samples were carefully removed from the cone-plate and the variation of domain size was observed by a microscope. After several hours, the domain size of blends without bcp became 4 to 6 times as large as that observed after the cessation of pre-shear, while that of blends with bcp was stable for a long time. Under the successive shear flow with lower shear rate than the pre-shear, it was observed that the dispersed domains of polyisoprene/polydimethylsiloxane/bcp system first coalesced till the size became twice as large as the original size. Then the domains became stable for a long time.

Key words: Polymer blend, Diblock copolymer, Surfactant, Domain structure, Shear flow

1. INTRODUCTION

It is well known that two homopolymers A and B are normally immiscible and possess various domain structures depending on the preparation condition. Since physical properties of immiscible polymer blends are affected by the domain structure, numerous studies on morphology control, especially for making finely dispersed structure (usually called compatibilization) have been carried out for a long time.

As briefly reviewed in recent papers [1, 2], various types of compatibilization methods have been examined. Among them, addition of a small amount of A-block-B to A/B blends is the most simple one. Even in this case, however, there exist some difficulties for effective compatibilization and stabilization of the domain structure due to thermodynamic and mechanical reasons.

By a simple and qualitative thermodynamic consideration, it is assumed that block copolymers (bcp) macroscopically phase separate from homopolymers and form micelles if their molecular weights are too large. On the other hand, bcp dissolve into A and/or B, if their molecular weights are too low. Even if the molecular weight of bcp is adequate to form "interface" between A and B, bcp chains cannot be always stable at the interface.

It was reported for A/B/A-block-B system that the bcp chains were pulled out from the interface forming micelles under steady shear flow with lower shear rate than the initial shear rate used for the mechanical mixing procedure [3]. As a consequence, dispersed domains coalesce under the flow and the average size of dispersed domains increases with time.

In recent studies [2, 4, 5], the third or even fourth component was employed as bcp components (e.g. A/B/A-block-C or C-block-D systems) to achieve more effective compatibilization. In those systems, at least one of the block component and a homopolymer have exothermic interaction so that the interfacial adhesion of bcp was strengthened than that in the A/B/A-block-B system. In the most cases, size of dispersed domains became smaller and the size distribution became narrower compared with the blends without bcp. However, coalescence of domains and macroscopic phase separation of bcp and homopolymer are still observed in some cases. Further, there are two many parameters to consider in these systems for the generalization of the phenomena. Also, it is not easy to find exothermic combination of components for the most polymer species.

Considering merits and demerits for above mentioned exothermic systems, it is still worth to study further the most simple (athermal combination) system, A/B/A-block-B. In this work, we test a low molecular weight bcp as a surfactant based on simple assumptions mentioned below.

Since there is no appropriate theoretical consideration, we simply assume that the mechanical pull out of bcp from the interface and resulting coalescence of dispersed domains under the flow can be suppressed by lowering the number of entanglement point per block chains. Then, the next question is to what extent we can lower the molecular weight of bcp. If we use low enough ones, they may dissolve into homopolymers. Despite of many studies, molecular weight criteria for the localization of bcp at the interface is not established yet [6].

Therefore, we refer to the studies of diblock copolymer/homopolymer blends in which bcp are the major...
component (90 wt% or more) [7]. It was reported that homopolymers dissolved into homologous micro-domain of bcp are concentrated in the middle of lamellae even if the molecular weight of homopolymer is about one order magnitude lower than that of block component. Since the systems studied here have opposite composition of homopolymer and bcp, we simply invert the molecular weight ratio of bcp and homopolymer. That is, we use bcp having one order lower molecular weight than the homopolymers, expecting that such bcp still localize at the interface by analogy of the above result.

In this study, we report the preliminary results on the domain structure of such A/B/A-block-B system at rest and under a weak flow after mechanical mixing with high shear rate in comparison with the sample without diblock copolymer. A/C/A-block-B system having similar condition, but not exothermal was also examined.

2. EXPERIMENTS

Polyisoprene (PI) and PI-block-polydimethylsiloxane (PI-block-PDMS) were prepared by living anionic polymerization in vacuo. The solvent and the initiator used for polymerization of PI were hexane and sec-butyl lithium, respectively. PI-block-PDMS was prepared by sequential addition of dimethylsiloxane monomer dissolved in THF into the living PI. Polyisobutylene (PIB) was prepared by living cationic polymerization following a literature [8]. PDMS was supplied from Shinetsu Chemical Co.

Number averaged molecular weight $M_n$ and composition of PI-block-PDMS were determined by H$^+$ NMR. Weight averaged molecular weight $M_w$ of homopolymers and $M_w/M_n$ of all the samples were determined by GPC (columns: Tosoh GMHXL × 2 or G3000HXL + G4000HXL). The viscosities of component homopolymers and viscoelastic properties of blend samples were measured by a RSR200 rheometer of Rheometrics using cone-plate geometry. The characteristics of the samples are listed in Table 1.

PI/PDMS and PDMS/PIB blends (3:7 by weight) were prepared by gentle mixing of components by the same manner as in the previous work [9]. Two sets of each blend, i.e. one with PI-block-PDMS (5 wt% of total weight) and another without bcp were prepared.

Each sample was sheared at a constant shear rate (16 sec$^{-1}$) till the steady state was achieved (monitored by stress measurement) by a RSR200 using cone-plate geometry. A small amount of samples was carefully removed from the cone-plate, then sandwiched in glass plates and the change in domain size (diameter) was observed by a VH-5910 Keyence monitor microscope. The time was set 0 when the observation was started.

For PI/PDMS/PI-block-PDMS system, the effects of successive flow were also examined by decreasing the shear rate to 0.8 sec$^{-1}$ at $t=0$. The system was kept flowing for a long time. The flow was interrupted several times to take out the samples to observe the structure. All the measurements were performed at room temperature.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$M_n$</th>
<th>$M_w/M_n$</th>
<th>Viscosity (Pa·s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PI</td>
<td>1.1×10$^4$</td>
<td>1.03</td>
<td>12.4 (25°C)</td>
</tr>
<tr>
<td>PI</td>
<td>5.0×10$^5$</td>
<td>1.47</td>
<td>41.8 (50°C)</td>
</tr>
<tr>
<td>PDMS</td>
<td>5.0×10$^6$</td>
<td>1.82</td>
<td>28.8 (25°C)</td>
</tr>
<tr>
<td>PDMS</td>
<td>2.3×10$^8$</td>
<td>0.49</td>
<td>19.0 (50°C)</td>
</tr>
</tbody>
</table>

Fig. 1. Double logarithmic plots of $G'$ and $G''$ vs. $\omega$ for PI/PDMS blends with and without bcp. The symbols are denoted in the figure.

Fig. 2. Double logarithmic plots of $G'$ and $G''$ vs. $\omega$ for PDMS/PIB blends with and without bcp. The symbols are denoted in the figure.
3. RESULTS AND DISCUSSION

Figures 1 and 2 show double logarithmic plots of storage ($G'$) and loss ($G''$) moduli vs. frequency ($\omega$) for PI/PDMS and PDMS/PIB blends, respectively, measured just after the pre-shear ($t=0$). It is clear that $G'$ and $G''$ curves for the samples with and without bcp in respective systems are almost the same. These results may imply that the domain sizes and their distributions and interfacial tension of the blends are not so much influenced by addition of bcp.

Figure 3 compares the observed domain structures at $t=0$ and at $t=12$ hrs for PI/PDMS systems. At time equal to 0, domain sizes of both systems with (Fig. 3a) and without (not shown) bcp are similar, consistent with the results on viscoelastic properties shown above. After a certain rest time ($t=12$ hrs), domain size of the blend sample without bcp (Fig. 3b) becomes larger due to coalescence, while that of the sample with bcp (Fig. 3c) is stable as expected. To characterize such time dependence of domain size, diameter of dispersed domains is measured and their histograms are obtained.

Figures 4 and 5 show histograms of diameter for PI/PDMS blends with and without bcp at different rest times. As mentioned above, the blend samples without bcp coalesce so that the peak position in the histogram increased and size distribution became very broad with increase of rest time. On the other hand, only small portion of droplets coalesced for the sample with bcp so that the peak position in the histogram was not much changed and the size distribution became only slightly broader. Similar histograms are obtained for PDMS/PIB systems.

To observe the time dependency of coalescence behavior, the average diameter of droplets plotted against time for PI/PDMS and PDMS/PIB systems are shown in Figs. 6 and 7, respectively. In both figures, the average domain size of blends with and without bcp at $t=0$ were the same. The domain sizes of blends without bcp increase up to say, 4 to 6 times as large as than the original size. The level off of average size at long time for the blends without bcp may be due to the confinement of glass plates in which the samples are sandwiched.

In contrast, the domain sizes of blends with bcp only very gradually increase due to the growth of small portion of domains as shown in histograms. We speculate that these growing domains were not well covered by bcp during the mixing procedure. It is clear that the added bcp prevent coalescence of most of dispersed droplets for a long time and the numbers of growing domains do not increase. This result implies that the most of low molecular weight bcp distributed at the interface of domains are stable, having no tendency to phase separation. It is interesting that qualitatively the same result was obtained for non exothermal A/B/A-block-C, i.e., PDMS/PIB/PI-block-PDMS blend.
Finally, we discuss the effects of successive flow with shear rate lower than that of mixing pre-shear for PI/PDMS systems. The histograms of domain size and plots of the average diameter against time for the samples with and without bcp are shown in Figs. 8 and 9, respectively. For the blends without bcp, the domain size grows in a similar manner as that observed at rest states but the distribution of domain size was slightly narrower than that at rest states. These observations are qualitatively the same to those reported in a recent publication [10].

In contrast to the above results for the sample without bcp, the corresponding results for the sample with bcp were rather complicated. As shown in Fig. 9, about the half of the domains rapidly coalesce, while others remain almost unchanged at short time. Consequently, there exist two peaks in histogram (Fig. 9, middle) and the average size shown in Fig. 10 became larger by almost the same rate as that of the blend without bcp till the average size became twice as large as the initial value. During that process, remaining domains also coalesce by somewhat lower rate, while coalescence rate of larger ones slow down, resulting into a rather broad single peak (Fig. 9, bottom). Then, the domains became stable and the average size remains constant for a long time under the flow. From these results, we speculate that there may exist a kind of re-distribution process of bcp in the initial stage of flow. At this moment, however, we have no explanation of such process. At longer time, it is clear that pulling out of bcp by the flow does not occur.

4. CONCLUSION

Low molecular weight poly (isoprene-block-dimethylsiloxane) (A-b-B) was tested as a surfactant for A/B and A/C blends 5% A-b-B was added and pre-sheared, then the structure was observed. At quiescent, A-b-B was an effective surfactant. It was also an effective surfactant for A/B system under the successive flow, suppressing the pull out of bcp from the interface under the successive flow. However, the stabilized domain size was larger than the original size controlled by the pre-shear (mixing procedure).
REFERENCES