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The Phase Behavior of Polymer Blends under High Shear Flow / High Pressure Fields

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The phase behavior of a miscible poly(vinyl methyl ether) (PVME) / polystyrene (PS) blend and a immiscible poly(p-phenylene sulfide) (PPS) / polyamide46(PA46) blend was measured under high shear flow / high pressure fields using the rheo-optical method. The flow induced mixing was observed in the PVME/PS blends under high shear field, resulting in the extension of the single-phase state. The pressure induced mixing was also observed in the same blend system under high pressure field. The flow induced mixing was observed in the PPS/PA46 blends under high shear flow field above 1000/s. The miscible region was observed not only in the PA46 rich side but also in the PPS rich side of the blends.

Key words: phase behavior, polymer blends, high shear flow field, high pressure field, flow induced mixing

1. INTRODUCTION

The behavior of polymer blends under the external fields such as shear flow, elongation flow, and pressure is of a fundamental interest and also technologically important, since deformation and related stresses are unavoidable in many steps of processing, as in melt mixing extrusion and injection molding. The processing under high shear flow is considered to be a nanoscale materials processing, because the technique makes the immiscible polymer blends miscible under high shear. In this study, the *in-situ* phase behavior measurement of miscible polymer blends under high shear flow and high pressure fields was done using the rheo-optical method. The phase behavior of the immiscible blends was also measured using the same method. Though the PPS/PA46 blends are completely immiscible in the quiescent state, An et al. [1] have reported that the miscible region appeared for the PPS/PA46=20/80 composition at a high shear rate, above 150/s at 310℃ and 189/s at 320℃. Therefore, we performed the *in-situ* phase behavior measurement of the blends under higher shear flow above 200/s.

2. EXPERIMENTAL

The poly (vinyl methyl ether) (PVME) was obtained from Scientific Polymer Products, Inc., with a number-average molecular weight (Mn) of 46500. The PVME (50 % aqueous solution) was evaporated by keeping the polymer under high vacuum at 70 ℃ for 4 days to remove water. The monodisperse polystyrene (PS) was obtained from Polymer Laboratories Ltd. The Mn was 50120. The transparent PVME/PS blend films were prepared at room temperature by casting from 10 % toluene solution on quartz glass surfaces. The films were further dried under vacuum at 90 ℃ for at least a week. The linear type poly (p-phenylene sulfide) (PPS) was a commercial polymer, from DIC Co. with Mn = 25000. The polyamide 46 (PA46) in this study was used as a commercial polymer from JSR Co., with Mn=45000. Both PPS and PA46 were dried in a vacuum oven at 80 ℃ for 2 days. They were melt-blended using a twin-screw extruder. The blends were then hot-pressed at 300 ℃ to a thin film with a thickness of 100 μ m, followed by rapid quenching in ice water.

The *in-situ* phase behavior measurement was done using the Linkam CSS-450 and a custom-made apparatus (Fig. 1).

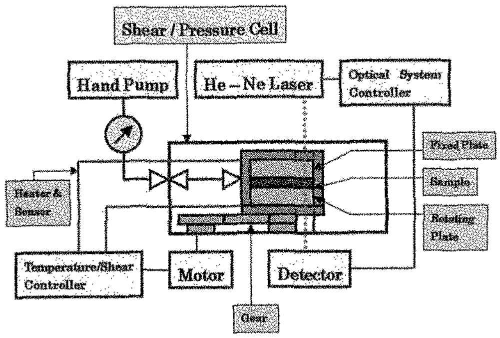

Fig. 1 Block diagram of the rheo-optical device.

The cloud point of PVME/PS blend film was determined by the light transmission method using the apparatus. The sample is subjected to a pressure field of 10 Mpa. The cloud point temperature was determined by the cut-off of the light transmitted intensity. The in-situ observation of phase structures of PPS/PA46 blends were performed under the shear rate of 1 to 3000/s, using the shear cell which was mounted upon an Olympus BX-61 optical microscope equipped with a CCD video camera system.

3. RESULTS AND DISCUSSION

Figure 2 shows the phase diagram of PVME/PS blends based on the cloud point curve. In this figure, the lower curve designates the typical LCST curve in the quiescent state, while the upper one shows the curve under high shear flow (shear rate = 500/s). The lower

LCST curve is in fairly good agreement with the result of Halary et al. [2] using fluorescence emission analysis. As shown in this figure, the flow induced mixing was observed in the blend system under high shear flow, resulting in the extension of the single-phase state. Many researchers have reported the complicated phase behavior of the blend system under the shear flow, however, Madbouly et al. [3] have reported that both shear-induced demixing and mixing were observed depending on the applied shear rate and composition. At least, it is likely that the shear-induced mixing will be found in the blend system under the shear rate above 30/s. The extension of the single-phase state was considered to be originated from the suppression of the growth in the concentration fluctuation under high shear flow.

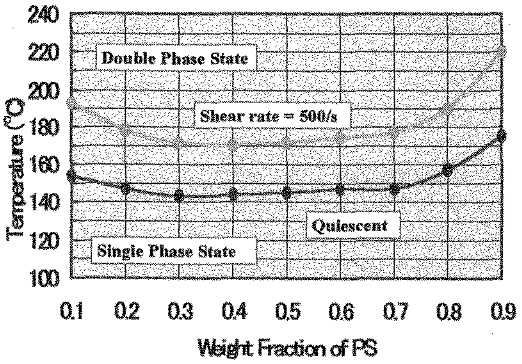

Fig. 2 Phase diagram of PVME/PS blends under the quiescent and the high shear flow fields.

As shown in Figure 3, the pressure induced mixing was also observed in PVME/PS blends under high-pressure field (10MPa). The shift of phase diagram of the blends was considered to be originated from the increase in the attractive interaction under the high pressure field. In this case, the pressure effect of mixing was dependent upon the concentration of PS, resulting in the extension of the single-phase state at the PS rich side.

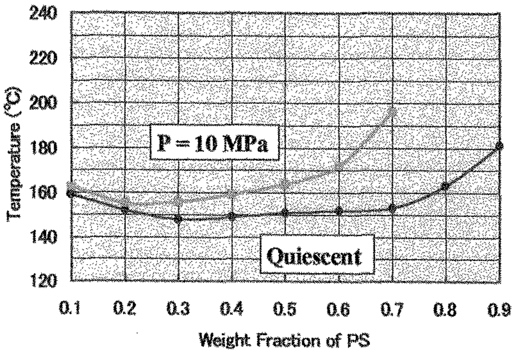

Fig. 3 Phase diagram of PVME/PS blends under the quiescent and the high pressure fields.

Figure 4 shows optical micrographs of PPS/PA46=20/80 blend under high shear at 300℃. As shown in this figure, the phase separated morphology disappeared at the shear rate of 1000/s, resulting in the transparent and homogeneous state. The same morphology was observed in the PPS/PA46=80/20 composition under the shear rate of 1000/s at 290℃. On the other hand, only the phase separated (dispersed) morphology was observed in the PPS/PA46=50/50 composition under high shear flow at above 290℃.

Figure 5 shows optical micrographs at quiescent state 5 minutes after cessation of the shear (3000/s) at 300℃. In this case, the transparent and homogeneous structures of PPS/PA46=20/80 and 80/20 compositions under the high shear rate of 3000/s were found to change the co-continuous structures after cessation of the shear flow. The appearance of the co-continuous structure is considered to be an evidence of the miscibility under the shear flow. From the results of a series of measurements of the blend morphology under the high shear flow, the phase diagram of the blend were summarized in Figure 6.

Figure 6 shows the phase diagram of PPS/PA46 blends under the high shear flow fields. As shown in this figure, the flow induced mixing was also observed in the blend under the high shear flow field above 1000/s. It is worth noting that the miscible region is found not only in the PA46 rich side but also in the PPS rich side of the blend. Moreover, the extension of the miscible region was observed in the blend under the higher shear rate of 3000/s.

4. CONCLUSIONS

The flow induced mixing of PVME/PS blends was observed under the high shear field (shear rate = 500/s). The pressure induced mixing of the blends was also observed under the high pressure field (pressure = 10 MPa). The miscible region of PPS/PA46 blends was found under the high shear flow field above 1000/s. The extension of the miscible region of the blend was observed under the higher shear rate of 3000/s. It can be mentioned that the *in-situ* phase behavior measurement of polymer blends under the external fields such as high shear flow and high pressure fields is quite useful for elucidating the mechanism of polymer processing.

Acknowledgements

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References

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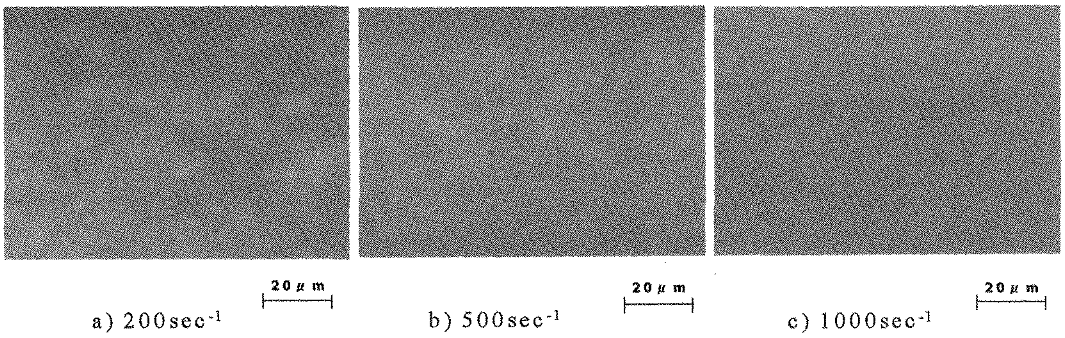
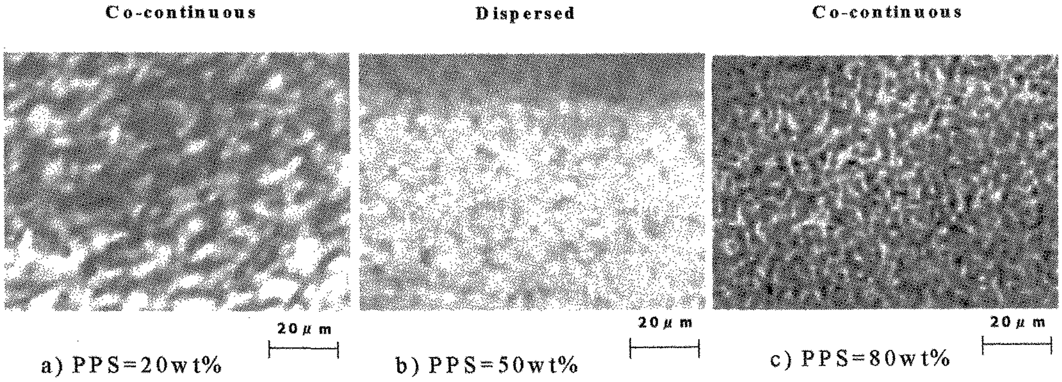


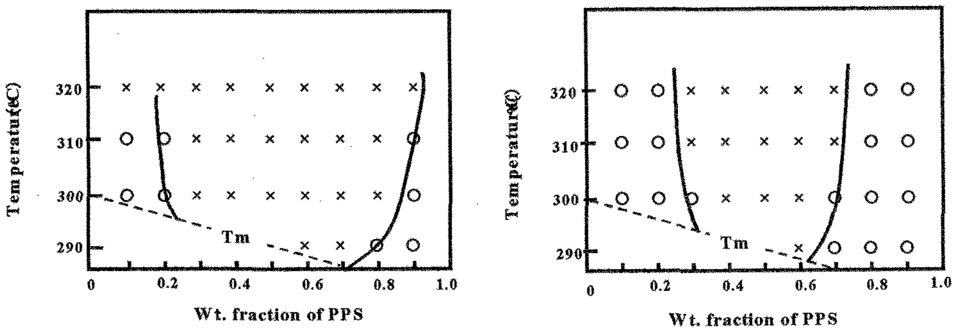
a) 200sec^{-1} b) 500sec^{-1} c) 1000sec^{-1}

Fig. 4 Optical micrographs of PPS/PA46=20/80 under high shear at 300℃.


Co-continuous Dispersed Co-continuous

a) PPS=20wt% b) PPS=50wt% c) PPS=80wt%

Fig. 5 Optical micrographs at quiescent state 5 minutes after cessation of the shear (3000/s) at 300℃.



a) 1000sec^{-1} b) 3000sec^{-1}

Fig. 6 Phase diagram of PPS/PA46 blends under high shear.
(○ means miscible, × means immiscible)

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