SHEAR FLOW EFFECT ON PHASE BEHAVIOR AND MORPHOLOGY IN POLYMER BLENDS

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SUMMARY: The effect of simple shear flow on the phase behavior and morphology was investigated for both polystyrene/poly(vinyl methyl ether) (PS/PVME) and poly(methyl methacrylate)/poly(styrene-*co*-acrylonitrile) (PMMA /SAN-29.5) blends, which have LCST (lower critical solution temperature)-type phase diagram. The measurements were carried out using a special shear apparatus of two parallel glass plates type. The PS/PVME blends showed shear-induced demixing and shear-induced mixing at low and high shear rate values, respectively. In addition, the rotation speed and the sample thickness were found to have a pronounced effect on the phase behavior under shear flow. On the other hand, PMMA/SAN blend showed only shear-induced mixing and the magnitudes of the elevation of the cloud points were found to be composition and molecular weight dependent. The morphology of the PMMA/SAN=75/25 blend indicated that shear-induced mixing occurred at a critical shear rate value, below which the two phases were highly oriented and elongated in the flow direction.

INTRODUCTION

There are not so many studies on the phase behavior of polymer blends under shear flow both experimentally and theoretically and still remains a challenging area of research. Therefore the experimental data are still scarce. The data showed that flow greatly affected the miscibility of polymer blends and even shear rates of less than 1 s^{-1} are sufficient to induce changes in phase behavior[1-5]. So far, there are still several important issues that have not yet been addressed adequately which are necessary for developing a complete phenomenology, and thus for gaining a better understanding of the mechanisms of flow-induced phenomena in polymer blends. For example, these are the following: (i) what is the effect of high shear rate values, higher than the literatures ones[3,5,6] (>20 s^{-1}) on the phase behavior of the blend; (ii) how does the molecular weight and the viscosity of the two polymer components interplay with the shear influences on the phase characteristic; (iii) how does the shear-induced mixing starts from two-phase structure of the blend (the mechanism and its dependence of viscosity ratio). In this paper, the above issues have been studied for PS/PVME and PMMA/SAN blends, which have LCST-type phase diagram.

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EXPERIMENTAL

Samples: The blend specimens of PS(M_w=180,000)/PVME(M_w=99,000) were prepared by solvent cast using toluene as a common solvent. On the other hand, the THF was used for the PMMA/SAN blends. The SAN(M_w=40,000) sample contains 29.5 wt% acrylonitrile. Different PMMAs ranged from M_w= 7,000 (7k) to 396,000 (396k) were used in order to study the effect of viscosity (the polydespersity index of all PMMAs is almost 2).

Apparatus: In order to investigate the phase behavior under shear flow, a special shear apparatus of two parallel glass plates type[7,8] was used. The measurements were carried out from one-phase region to two-phase region under constant rotation speed and heating rate (1 °C/min). In addition, the measurements were repeated several times at different rotation speeds Ω = 0.2-5 rad/s, which give shear rate value up to 180 s^{-1} (very wide range compared to the literature values.[3,5,6]). The morphologies of the blends under different shear rate values were detected by TEM for the quenched sample.

RESULTS AND DISCUSSION

(a) PS/PVME

Phase behavior under shear flow: The shear rate dependence of the cloud points for different compositions is shown in Figure 1. Obviously, the cloud points-shear rate curves can be divided into three regions, I-III. In region I, which is at the low shear rate values, the cloud points start to decrease with shear rate until reaching a minimum value, indicating shear-induced demixing. The depression in the cloud points under a constant value of shear rate was found to be composition dependent, as it can be clearly seen in this figure. In region II, the cloud points increase with shear rate to be higher than the cloud points of quiescent state, indicating shear-induced mixing. In region III, the cloud points become almost constant

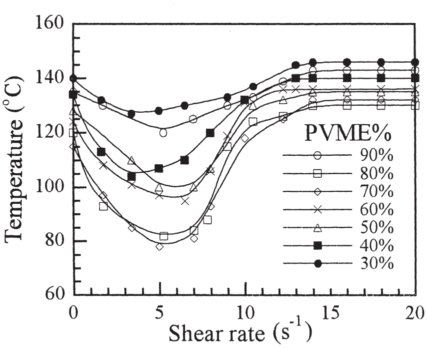

Fig.1 Shear rate dependence of cloud points for different composition ratios of PS/PVME (0.5 rad/s rotation speed).

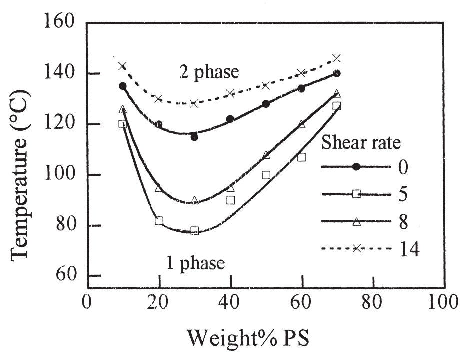

Fig.2 Comparison of the phase diagrams of PS/PVME blends for different shear rates under 0.5 rad/s rotation speed.

regardless of increasing the applied shear rate. This phase behavior under shear rate in regions I and II showed good agreement with the results of Hindawi et al.[5], who detected the same behavior for only PS/ PVME = 30/70 under shear rate up to 7.38 s^{-1}. The magnitude of maximum decrease of cloud point was almost same in both results though the shear rate value at that point was different[5,7]. Figure 2 shows the phase diagrams of the blends under the effect of different shear rate. At low shear rate, the cloud point curves shift to low temperature with increasing shear rate, i.e. the two-phase region becomes larger and maximum decrease occurred when the applied shear rate was around 5 s^{-1}. Then, the cloud point curves shift to high temperature with increasing share rate up to $\dot{\gamma}$ =14 s^{-1} (shear-induced mixing).

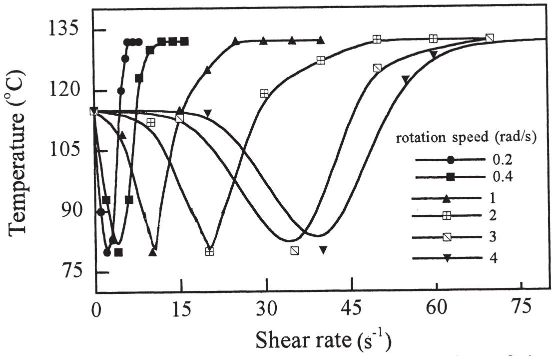

Fig. 3 Changes in the cloud points as a function of shear rate of PS/PVME = 30/70 blend under different rotation speeds.

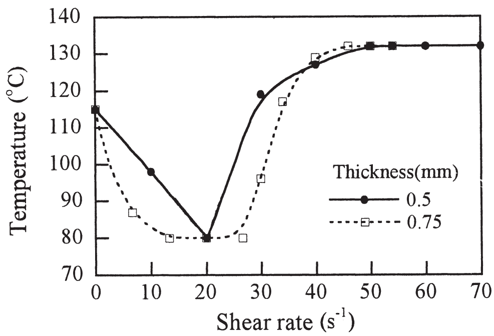

Fig.4 Shear rate dependence of the cloud points for PS/PVME=30/70 blend with different sample thickness.

Effects of rotation speed and sample thickness: The measurements were also extended to a higher shear rate values by using constant sample thickness and different rotation speeds (Ω=0.2-4 rad/s). A typical experimental data of the shear rate dependence of the cloud point for PS/PVME=30/70 under different rotation speed is represented in Figure 3. One can see that, the shear-induced demixing could be detected under all values of rotation speeds and the shear rate value of maximum decrease in the cloud point was systematically shifted to higher values with increasing rotation speed. This experimental fact of the effect of rotation speed was considered as a good answer to the question as why the values of the shear rate, which were needed for shear-induced demixing and shear-induced mixing were completely different from group to group in the literature[4,5]. Moreover, the sample thickness was also found to have a pronounced effect on the cloud point under constant rotation speed, where the miscibility region in the cloud point-shear rate diagram seemed broader with increasing the sample thickness as shown in Figure 4. It appears that the cloud area (immiscible region) becomes broader for thick sample (0.75 mm), though the shear rate which shows maximum decrease of the cloud point does not shift and the minimum cloud point is also same. Therefore, the effect of changing sample thickness may be not equivalent to that of changing rotation speed.

(b) PMMA/SAN-29.5

Phase behavior under shear flow: In this system we detected only shear-induced mixing for all the measured samples of different PMMA molecular weight and the magnitudes of the elevation of the cloud points under shear flow were found to be composition dependent. Figure 5 shows the phase diagrams of PMMA-26k/SAN blend under different shear rates, obviously the cloud points are elevated few degrees to higher temperature under shear flow.

Effect of rotation speed: The cloud point of this blend under high shear rate values up to 180 s^{-1} was also investigated by using constant sample thickness and different rotation speeds (Ω=0.5-5). Figure 6 illustrates the shear rate dependence of the cloud points of PMMA-26k/ SAN=50/50 under different rotation speeds. One can see that the cloud point is monotonically increased with small value of shear rate and then became almost constant regardless the values of the applied shear rate. For this behavior one could draw only one master curve without rotation speed effect on the position of the cloud point in contrast to the PS/PVME blend (see Figure 3). This finding may be attributed to the fact that PMMA and SAN have almost same *Tg's* and comparable viscosity, in addition, only shear-induced mixing was detected. On the other hand, PS and PVME have a very big mismatch in the *Tg's* and viscosity, furthermore, both shear-induced demixing and shear-induced mixing were detected within single blend composition depending on temperature, composition, rotation speed

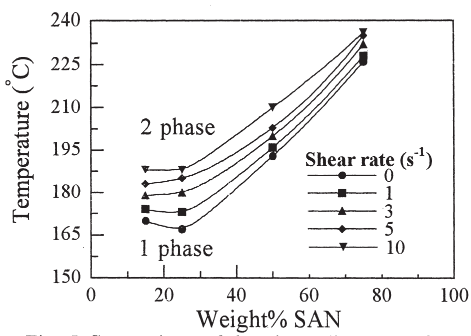

Fig. 5 Comparison of the phase diagrams of PMMA -26k/SAN blends for different shear rates.

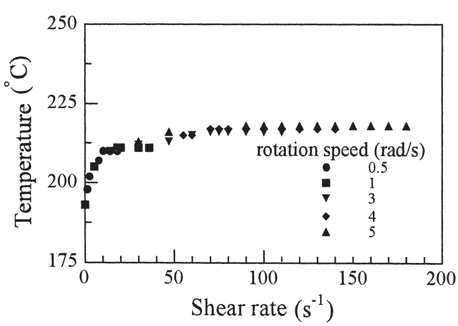

Fig.6 Changes in the cloud points as a function of shear rate of PMMA-26k/SAN=50/50 blend under different rotataion speeds.

and the experimental procedure. Therefore, there is big difference between the two systems, for this reason it is concluded that, only in the case of blend which shows shear-induced demixing, the rotation speed might be affected on the position of the cloud point.

Effects of molecular weight and viscosity ratio: The molecular weight of PMMA was also found to have a pronounced effect on the phase behavior of the blend under constant shear rate. In order to compare the shear effect between different M_w blends, the normalized shift of the cloud point, $\Delta T(\dot{\gamma})/T(0) = \{T(\dot{\gamma}) - T(0)\}/T(0)$, is shown in Figure 7 as a function of M_w of PMMA for PMMA/SAN=25/75 blends at $\dot{\gamma}$ =10 s^{-1}. It appears that the normalized shift, at first increases with M_w and then decreases, exhibiting a maximum. This behavior was attributed to the fact that the change in M_w of PMMA leads to a large change in the viscosity ratio of the blends at constant shear rate. Figure 8 exhibits the effect of the viscosity ratio of the blend on the normalized shift of the cloud point at $\dot{\gamma}$ =10 s^{-1}. It is worth noting that a maximum elevation of the cloud point is detected at viscosity ratio (η_{PMMA}/η_{SAN}) near to unity. Therefore, the values of the viscosity in the two polymer components of the blend should be taken into account to explain the phase behavior of polymer blends under shear.

Morphology: The two-phase morphology of PMMA-26k/SAN=75/25 blend at 185 °C (20 °C above the quiescent cloud point) under different shear is shown in Figure 9. Three regimes that depend greatly on the applied shear rate values were revealed. In regime I, at nearly zero shear rate, a well-defined phase separation with co-continuos structure took place. Regime II corresponds to modest shear rate values (up to $\dot{\gamma}$ =7 s^{-1}); the morphology indicated a highly elongated two-phase occurrence with a high degree of orientation parallel to the flow direction. Finally, in regime III at $\dot{\gamma}$ =10 s^{-1}, no morphology was observed as a result of shear-induced mixing at the critical shear rate value ($\dot{\gamma}$ =10 s^{-1}). According to this finding it is concluded that, the macroscopic phase separation could not occur under steady shear flow.

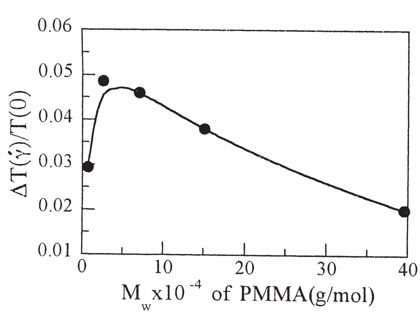

Fig. 7 Molecular weight dependence of normalized shifts in the cloud points of PMMA/SAN=25/75 blends at $\dot{\gamma}$ =10s^{-1}.

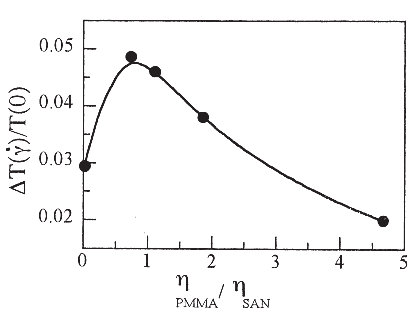

Fig. 8 Viscosity ratio dependence of normalized shifts in the cloud points of PMMA/SAN=25/75 blends at $\dot{\gamma}$ =10s^{-1}.

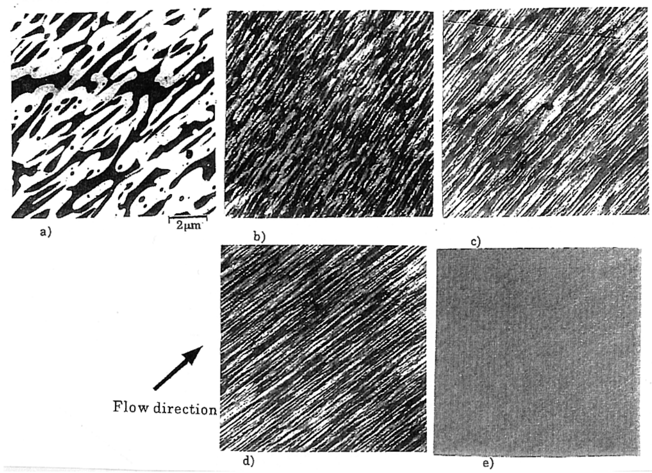

Fig. 9 TEM pictures of PMMA-26k/SAN (75/25) samples that were sheared at 185 °C (20 °C above their quiescent cloud point) at 0.5 rad/s for 3 min and then quenched in water bath. Samples were then taken from different radial positions and consequently different shear rate (a) $\dot{\gamma} \approx 0 s^{-1}$; (b) 1.17 s^{-1}; (c) 2.33 s^{-1}; (d) 4.7 s^{-1}; and (e) 7 s^{-1}.

CONCLUSIONS

Shear-induced demixing and shear-induced mixing have been observed within single composition for PS/PVME blend at small and high shear rate value, respectively. The depression or the elevation of the cloud points were found to be composition and shear rate dependent. In addition, the rotation speed and sample thickness were found to have a pronounced effect on the phase behavior during the shear flow. On the other hand, only shear-induced mixing was detected for PMMA/SAN blend and the phase behavior under shear was found to be composition, molecular weight and viscosity ratio dependent. In addition this blend seems to have the shear rate as a reduced parameter without rotation speed or sample thickness effect in contrast with PS/PVME blend. The morphology of two-phase blend of PMMA/SAN=75/25 indicated that shear-induced mixing occurred at a critical shear rate value, below which the two phases were highly oriented and elongated in the flow direction.

RFERENCES

(1) K. Mazich and S. H. Carr, *J. Apll. Phys., 54*, 5511 (1983).
(2) J. Lyngaae-Jorgensenn and K. Sondegaard, *Polym. Eng. Sci., 27*, 351 (1987).
(3) J. Fernandez, J. S. Higgins, R. Horst and B. Wolf, *Polymer*, *36*, 149 (1995).
(4) J. D. Katsaros, M. F. Malone and H. H. Winter, *Polym. Eng. Sci., 29*, 1434 (1989).
(5) I. A. Hindawi, J. S. Higgins and R. A. Weiss, *Polymer*, *33*, 2522 (1992).
(6) H. W. Kammer, C. Kummerloewe, J. Kressler and J. P. Melior, *Polymer*, *32*, 1488 (1991).
(7) S. A. Madbouly, M. Ohmomo, T. Ougizawa and T. Inoue,*Polymer, 40,* 1465 (1999)
(8) S. A. Madbouly, T. Chiba, T. Ougizawa and T. Inoue, *J. Macromol. Sci.-Phys. B38(1&2),* 79 (1999).