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Effect of the shear flow on the phase behaviour of polystyrene/poly(vinyl methyl ether) blend

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Abstract

The effects of simple shear flow on the phase behaviour of polystyrene/poly(vinyl methyl ether) (PS/PVME) blend, which shows a lower critical temperature (LCST)-type phase diagram, have been studied by cloud point measurements, by using a special shear apparatus. The shear-induced demixing and mixing have been observed for all of the compositions at low and high shear rate, respectively. However, at higher shear rate, the cloud points were independent of the shear rate and almost constant. In addition, the shear effect was found to be composition dependent and the largest change took place near the critical composition. The effects of rotation speed and sample thickness were also studied for the sample of PS/PVME = 30/70. The values of the cloud point were strongly affected by the rotation speed and the minimum of the cloud point systematically shifted to higher shear rate values with increasing rotation speed under the constant sample thickness. The sample thickness was also found to have a pronounced effect on the cloud point under constant rotation speed, where the immiscibility region in the cloud point–shear rate diagram seemed broader with increasing sample thickness. However, the samples of PS/PVME = 30/70 completely phase separated at 17°C above the quiescent cloud point at high shear rate, regardless of the applied rotation speed and sample thickness. © 1998 Elsevier Science Ltd. All rights reserved.

Keywords: PS/PVME; Shear rate; Cloud point

1. Introduction

The polymer blends have received much attention recently because it is an easy way to perform attractive new applications for which the individual polymer components are not suited. The ability to produce blends which have a better combination of properties than that of the individual components depends on the miscibility of the system. The effect of flow is of industrial relevance in the processing of blends where temperature gradients and high deformation rates are encountered, as in melt extrusion or injection molding. Thus, the behaviour of blends in the flow field is of a fundamental interest and also technologically important, since deformation and related stresses are unavoidable in many processing steps. So, the influence of flow field on the phase transitions in mixtures of small molecules or macromelecular fluids has been the subject of a number of investigations recently [1–10]. Flow field was found to exert a marked influence on the phase behaviour of liquid–liquid mixtures, and it is apparent that this effect must be taken into account, in particular, in understanding the state of polymer blends during processing. Shear-induced mixing and demixing have been observed in polymer solutions, as opposed to the case of small molecular mixtures where only shear-induced mixing has been reported.

The first report of the phenomenon of flow-induced miscibility of polymer blend was made by Mazich and Carr [11], who studied a blend of polystyrene (PS) and poly(vinyl methyl ether) [PVME] in steady shear flow using cone and plate geometry. The viscosity was measured using a Rheometrics Mechanical Spectrometer operated at a constant shear stress. They reported no measurements of turbidity, but an abrupt change in the slope of the viscosity versus temperature curve was interpreted as an indication of a phase transition. They found that the shearing of the blend could increase its lower critical solution temperature (LCST) by 2–7K.

Katsaros et al. [12] reported an increase in the cloud point of the PS/PVME blend in a planar stagnation flow by as much as 12K, the magnitude depends on the extension rate, strain and blend composition. They also found flow-induced miscibility in the shear flow between two parallel plates. On the other hand, at lower temperatures as much as 30K below the quiescent cloud point, the flow-induced

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phase separation was observed in both shear flow and extensional flow.

Two-dimensional light scattering and excimer fluorescence have been studied for the PS/PVME blend by Werner et al. [13]. They applied a shear rate of 8 s^{-1} in a parallel plate cell for 1 min at a temperature lower than the quiescent cloud point. The scattering pattern first shrinks, and then elongates and develops into a butterfly pattern. They identified these findings as shear-induced phase separation. On the other hand, when they sheared the sample by a shear rate 16 s^{-1} for 1 min at a temperature of the two-phase region, the scattering pattern elongated and then deformed into a butterfly pattern, and finally the pattern disappeared. At this point, the sample is believed to be homogenized, i.e. shear-induced mixing.

The influence of flow on the cloud point curves for three different binary polymer blends of poly(ethylene-co-vinylacetate)/solution chlorinated polyethylene (EVA/SCPE), poly(butyl acrylate)/SCPE and PS/PVME was studied using a rheo-optical light scattering device by Hindawi et al. [14]. At low shear rates, the cloud point curves shifted to lower temperatures indicating shear-induced demixing. This behaviour reversed at a critical shear rate above which the cloud point curves increased in temperatures due to shear-induced mixing.

It must be stated here that the measurements of the effect of applied shear rate on the phase behaviour of the PS/PVME blend in the literature have been carried out over a narrow range of shear rate (up to 16 s^{-1}) [12–14]. In addition, the measurements concentrated on using a constant rotation speed with constant sample thickness. Accordingly, we have studied the phase behaviour for the PS/PVME blend with different compositions under shear with different rotation speeds ranging from 0.2 to 4 rad/s. For a 0.5 mm sample thickness, this value corresponding to shear rate ranged from 0 to 160 s^{-1}. Therefore, we extended our measurements to a wide shear rate range by using different rotation speeds under constant sample thickness. As another measurement, on the other hand, we kept the rotation speed constant and changed the sample thickness in order to explore the effect of changing the sample thickness on the phase behaviour of the blend under shear.

The PS/PVME blend was selected for this study because it has the following advantages:

1. When the phase separation takes place, the blends turn white very quickly and intensely, so the cloud points under different shear rates can be precisely measured.
2. A big mismatch in the viscosity of the two components, so pronounced effects of the shear rate on the phase behaviour of the blend as a function of composition can be seen very clearly.
3. The glass transition temperatures (T_g) of the two components are separated from each other by about 130°C, so the sample can be quickly removed from the shear apparatus and quenched after the shear measurement in order to detect the T_g of the blend under different shear rates by using a differential scanning calorimeter (d.s.c.) as a complementary measurement.

2. Experimental

2.1. Materials and sample preparation

The PS sample was obtained from Denki Kagaku Industry, Japan, with $M_w = 180\,000$ g/mole and $M_w/M_n = 2$. PVME was supplied from Scientific Polymer Products with M_w and M_w/M_n equal to 99 000 g/mole and 2.13, respectively.

PS/PVME blends were prepared by dissolving the corresponding weights of the two polymer components in toluene. The blend solution was then poured on a Petri dish and left to dry in the air for about three days, after that, final solvent removal was accomplished under vacuum at 60°C for another three days. About 0.5 g of the blend was taken and pressed at a temperature lower than the cloud points of the corresponding sample composition in order to prepare a blend of 0.5 mm thickness and 40 mm diameter, in the same time we used 0.75 g in order to prepare 0.75 mm thickness sample.

2.2. Apparatus

A schematic illustration of the shear apparatus is shown in Fig. 1. The sample is located between two parallel silica glass plates, the top one is fixed and the bottom one can be rotated by different rotation speeds. The lower rotating glass plate is restricted inside a copper ring attached to driving gear, and the upper glass plate is fixed inside a copper cylinder. The copper cylinder and copper ring can be moved and taken out from the hot chamber. The simple shear flow is generated to the sample by applying constant rotation speeds. The sample is preheated to a temperature lower than the quiescent cloud point by about 40°C (75°C), and then heated by constant heating rate (1°C/min) under the value of the constant rotation speed. Under this condition, the phase separation of the sample takes place at different radii and different temperatures according to the values of the applied shear rate. The shear apparatus was designed to observe the sample under shear by two methods, the first by directly seeing the sample through the upper window of the shear apparatus, the second by a video recording camera connected to a monitor through a mirror fixed below the lower window of the shear apparatus. Once the measurement is finished, the two plates can be released very rapidly to allow a rapid quenching for a thermal analysis to measure the T_g of the samples under different shear rates.

For the parallel plate measurements, the shear rate is a linear function of the radius given by:

$$\dot{\gamma} = \Omega r/h$$

where h is the sample thickness, r the radius and Ω the

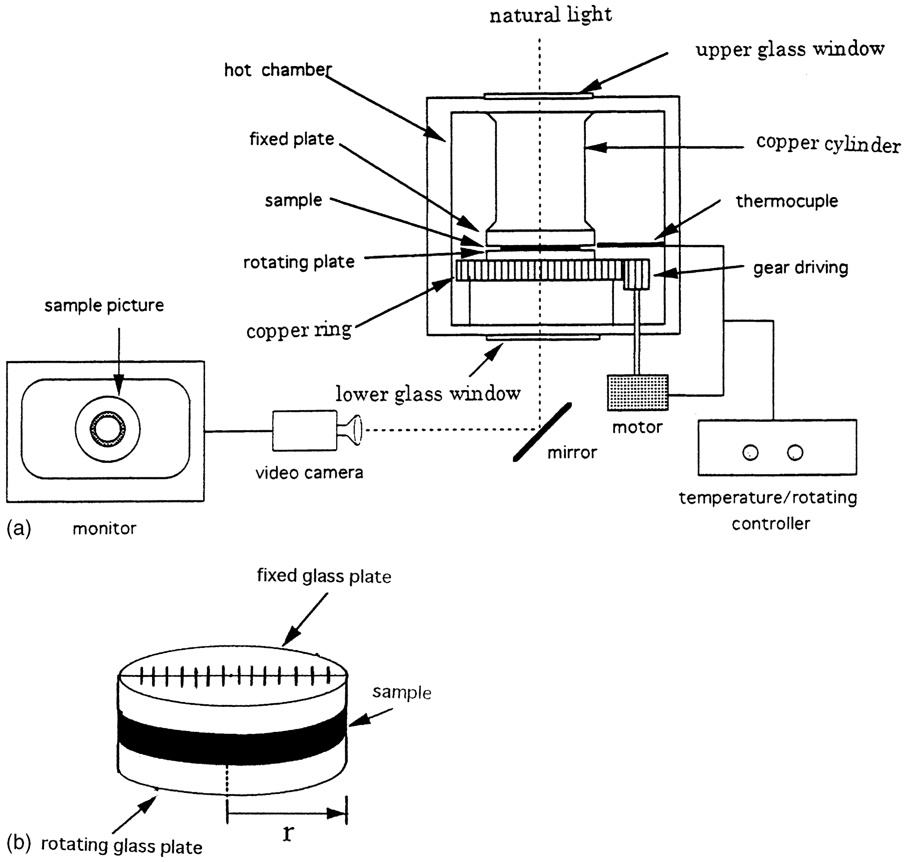

Fig. 1. (a) Schematic representation of the shear flow apparatus used in this work. (b) Schematic representation of the sample inside the two parallel glass plates.

rotational speed (rad/s). $\dot{\gamma}$ is at a maximum at the outer edge of the disk ($r = 20$ mm) and decreases to zero at the centre of the disk ($r = 0$).

Seven samples with different compositions, i.e. 90, 80, 70, 60, 50, 40 and 30 wt% PVME have been used to study the effect of flow as a function of temperature, composition and shear rate, as well as rotation speed and sample thickness.

2.3. Thermal analysis

T_g was measured calorimetrically by a d.s.c. (Seiko Instruments EXSTAR6000). The heating rate was 10°C/min for all of the measurements. The T_g was defined as the temperature of half of the step height in specific heat curve.

3. Results and discussion

3.1. Phase behaviour under shear

Fig. 2 shows the quiescent cloud point curve of the PS/PVME blend as a function of PS wt%. The phase diagram was obtained by heating the samples from one phase region to two phase region by using 1°C/min heating rate. This is a typical LCST-type phase diagram.

Fig. 3 shows schematic representations of the cloud region in the PS/PVME 30/70 blend specimen under shear in three temperatures. Fig. 3a represents the cloud region of the blend that sheared by 0.5 rad/s rotation speed at 80°C (35°C below the quiescent cloud point), and it can be seen in this figure that near the centre and at the outer edge of the disk the blend is transparent, but at the intermediate region the blend is opaque (shear-induced demixing). Fig. 3b shows the same sample when the temperature increased (1°C/min) to be 125°C (10°C above its quiescent cloud point), the cloud area increases gradually with increasing

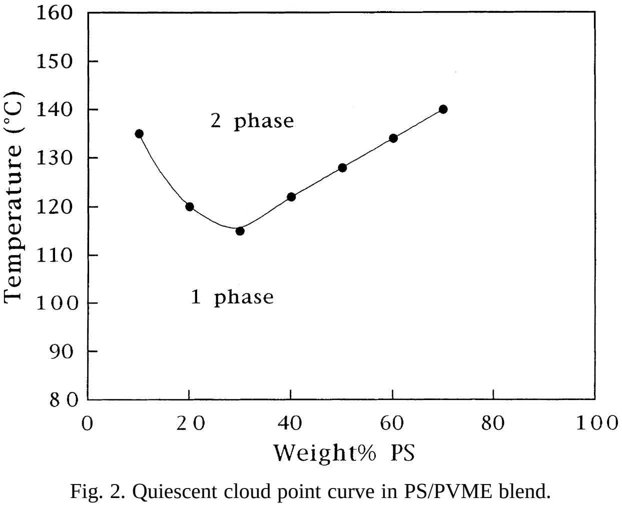

Fig. 2. Quiescent cloud point curve in PS/PVME blend.

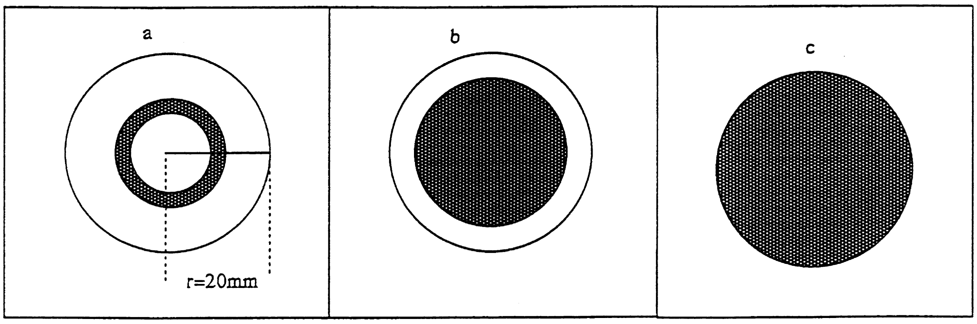

Fig. 3. Schematic representations of the cloud region in the PS/PVME (30/70) blend between two parallel plates under shear (rotation speed 0.5 rad/s). The shadow region is opaque. (a) 80°C (35°C below the quiescent cloud temperature). (b) 125°C (10°C above the quiescent cloud temperature). (c) 132°C (17°C above the quiescent cloud temperature).

the temperature under constant rotation speed (0.5 rad/s), but the outer edge of the disk is still transparent (shear-induced mixing). With increasing the temperature to 132°C (17°C higher than the quiescent cloud point), the whole sample turns cloudy regardless of the values of the applied shear rate, as can be seen in Fig. 3c.

Typical experimental data of the effect of shear rate on the cloud points are shown in Fig. 4. One can see that the cloud points values are greatly affected by the applied shear rate. 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 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 regardless of increasing the applied shear rate. The phase behaviour of PS/PVME under shear rate in regions I and II is in good agreement with that of Hindawi et al. [14], who detected the same behaviour at high and low shear rate up to 7.38 s^{-1} for PS/PVME = 30/70. To the best of our knowledge, it is the first time that the phase behaviour of the PS/PVME blend under simple shear flow has been investigated at shear rate higher than 16 s^{-1}. This large effect of the shear rate on the miscibility behaviour of this system is attributed to the big mismatch in the viscosity of PS and PVME components, where the bigger mismatch in the viscosity the larger effect of shear [14]. For example, in the EVA/SCPE system, the viscosity of the two components is more closely matched, so the maximum drop in the cloud points was approximately 5°C [14].

A comparison between the phase diagrams of the PS/PVME blends under the different shear rates is represented in Fig. 5. It can be seen in this figure that the phase diagrams are strongly affected by the values of the applied shear rate. At low shear rate, the cloud point curves shift to low temperature with increasing shear rate, i.e. the two-phase region

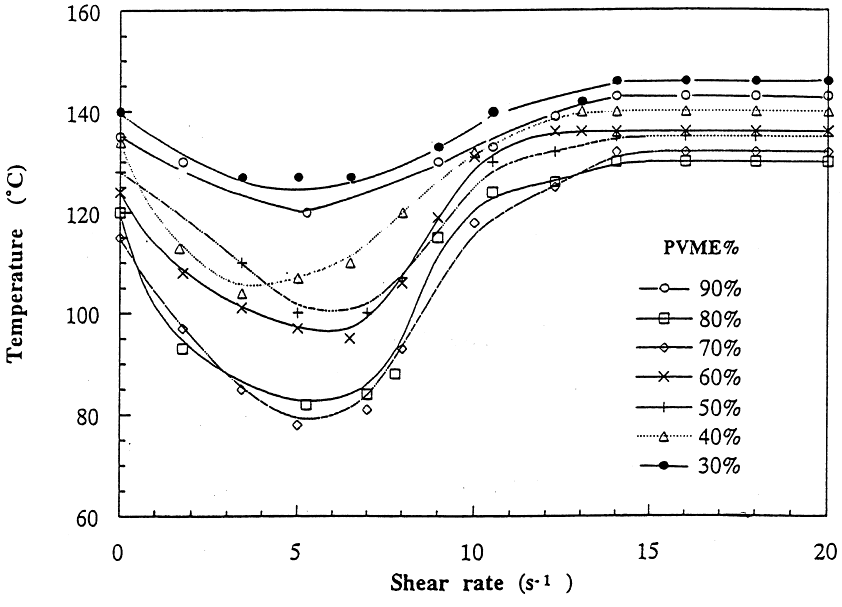

Fig. 4. Shear rate dependence of cloud points for different composition ratios of PS/PVME.

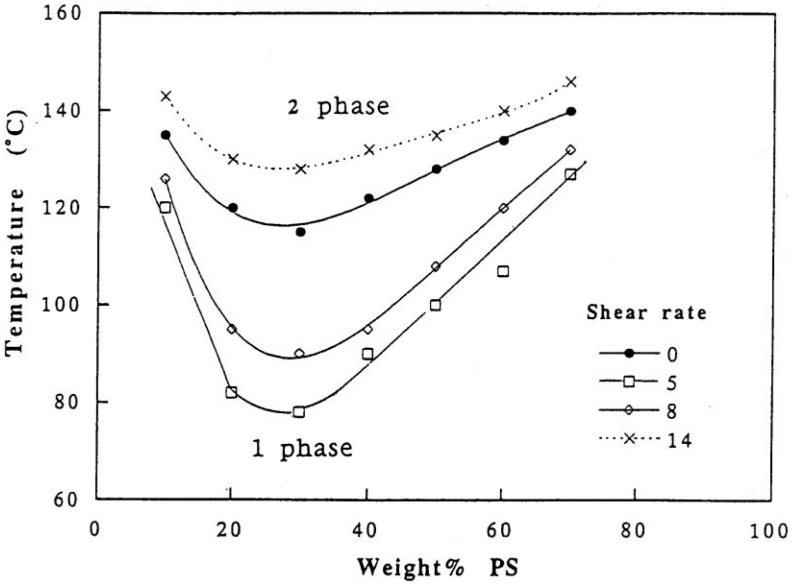

Fig. 5. Comparison between the phase diagrams of PS/PVME blends under the effect of different shear rate.

becomes larger and a maximum decrease occurs when the applied shear rate value was around 5 s^{-1}. Then, the cloud point curves shift to high temperature with increasing shear rate up to $\dot{\gamma} = 14\,\mathrm{s}^{-1}$, at which the cloud point curve is higher than that of the quiescent state. When the shear rate is greater than $\dot{\gamma} = 14\,\mathrm{s}^{-1}$, the cloud point curve does not change and becomes constant.

Based on the above results, it appears that shear flow can induce both phase demixing and mixing, as in the case of polymer solutions [10]. The fact that both were observed in the same blend suggests that two competition effects occur during flow. One of these effects tends to suppress growing spatial composition fluctuation and this effect would tend to promote phase mixing. The other effect causes the growth of the composition fluctuation and consequently phase demixing. This effect can be attributed to the elastic deformation which may act to enhance some concentration fluctuation, promoting the uphill diffusion that occurs in phase separation, as has been reported by Helfand and Fredrickson [15], and Onuki [16]. Thus, the first effect could be dominated at high shear rate and high temperature, while the second effect dominated at low shear rate and low temperature.

The measurement of the T_g was carried out as a second means in order to confirm the change of the miscibility in the blend. The d.s.c. thermograms of PS/PVME 40/60 samples are represented in Fig. 6*a*. These measurements were carried out for a blend specimen with 0.5 mm thickness which was sheared at 110°C (lower than the quiescent cloud point by 14°C) by a rotation speed equal to 0.5 rad/s for 3 min, and after shearing the two glass plates were quickly taken out of the shear apparatus and quenched in an ice-water bath. Six samples were then taken from different radial positions of the sample disk and their d.s.c. thermograms were measured. At $r = 0$, a single T_g was observed as expected, on the other hand, at $r = 0.25$ mm ($\dot{\gamma} = 2.5\,\mathrm{s}^{-1}$),

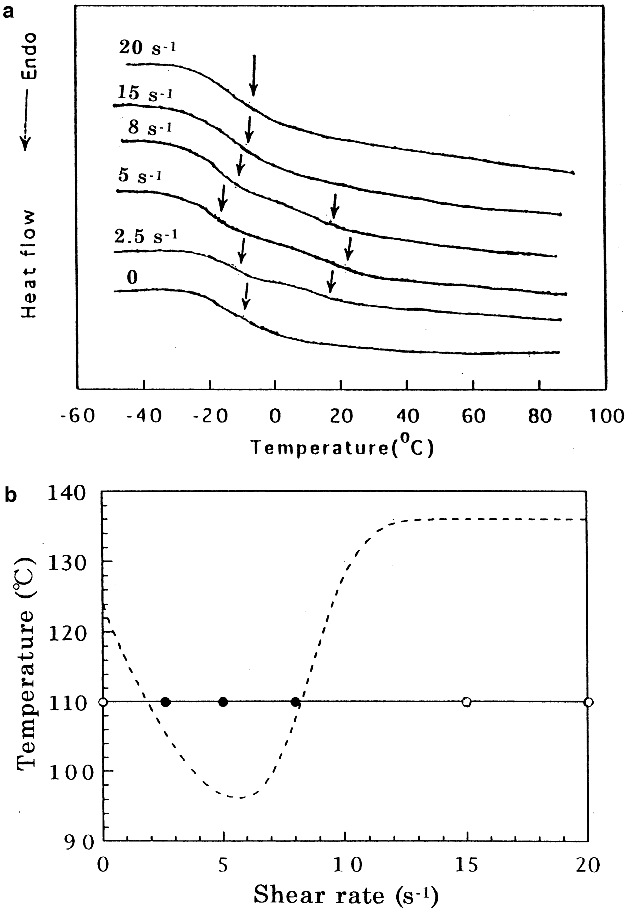

Fig. 6. (a) d.s.c. thermograms of specimens taken from six different radial locations (different shear rates) of a PS/PVME (40/60) blend, which is quenched into ice-water after shearing at 110°C. The shear values are shown in the figure. (b) Comparison between results of shear rate dependence of cloud point and d.s.c. thermograms; ○: one-phase, ●: two-phase.

the blend was phase-separated as evidenced by the two T_gs in the d.s.c. thermogram. At $r = 0.5$ mm ($\dot{\gamma} = 5\ \mathrm{s}^{-1}$), the two T_gs still existed, but became far from each other, indicating more demixing, these two T_gs moved closer together again with increasing shear rate up to 8 s^{-1} (0.8 mm), and finally only one T_g was detected at shear rates greater than 10 s^{-1}. These results were plotted in Fig. 6b which shows the shear rate dependence of the cloud point. There is good agreement between the calorimetric and cloud points measurements under shear. The T_g results can also be taken as convincing evidence that the cloud point shifts reflect a real thermodynamic mixing phenomenon not to break up domains into a very small domain size.

3.2. Effects of rotation speed and sample thickness

Throughout these measurements, we try to extend our results to a condition of higher shear rate. We repeated the measurements six times by using six samples with the same composition (PS/PVME = 30/70) and thickness (0.5 mm), thus only the rotation speed was changed and the effect of increasing shear rate on the cloud points was investigated.

Fig. 7 shows the effects of shear rates on the cloud points of the blends with different rotation speed values. Six samples with different rotation speeds, i.e. 0.2, 0.4, 1, 2, 3 and 4 rad/s, were measured, and the measurements started from 75°C (40°C below the quiescent cloud point). In this figure, one can see that the shear rate which shows the maximum decrease in the cloud points systematically shifted to higher values with increasing rotation speed. However, the minimum value of the cloud point was constant at 80°C (35°C below the quiescent cloud point) regardless of the applied rotation speed values. According to these experimental facts, one can say that the shear effects on the phase behaviour of polymer blends of PS/PVME are strongly dependent on both rotation speed and measuring temperature, where shear-induced demixing takes place at a temperature lower than the quiescent cloud point, and the effect is still preserved even under high shear rate values (40 s^{-1} when the rotation speed value is equal to 4 rad/s). On the other hand, the shear-induced mixing occurs at a higher temperature than the cloud point of the quiescent state even under a small value of the applied shear rate (6 s^{-1} when the rotation speed value is equal to 0.2 rad/s). So, one can conclude that under high shear rate, not only the shear-induced mixing, but also shear-induced demixing can be observed depending on the values of both measuring temperature and rotation speed used.

These things seem to be very peculiar. For a blend of poly(methyl methacrylate)/styrene-acrylonitrile random copolymer and other blends which show only the shear-induced mixing, the shear rate dependence of the cloud point was not affected by rotation speed (which will be reported separately), though it can be considered that only for the blends which show the shear-induced demixing is the shear rate dependence of the cloud point affected by rotation speed, the reason is not clear at present.

Our result is one of the new experimental facts which was detected for this polymer system. In the literature, various authors have investigated the effect of flow on polymer miscibility by different techniques, and the types of flow to which samples were subjected also vary from group to group. The above experimental finding is unexpected and we consider that this is partly a consequence of the difference between the experimental procedures used by us and those adapted by most other authors. In the literature, it is

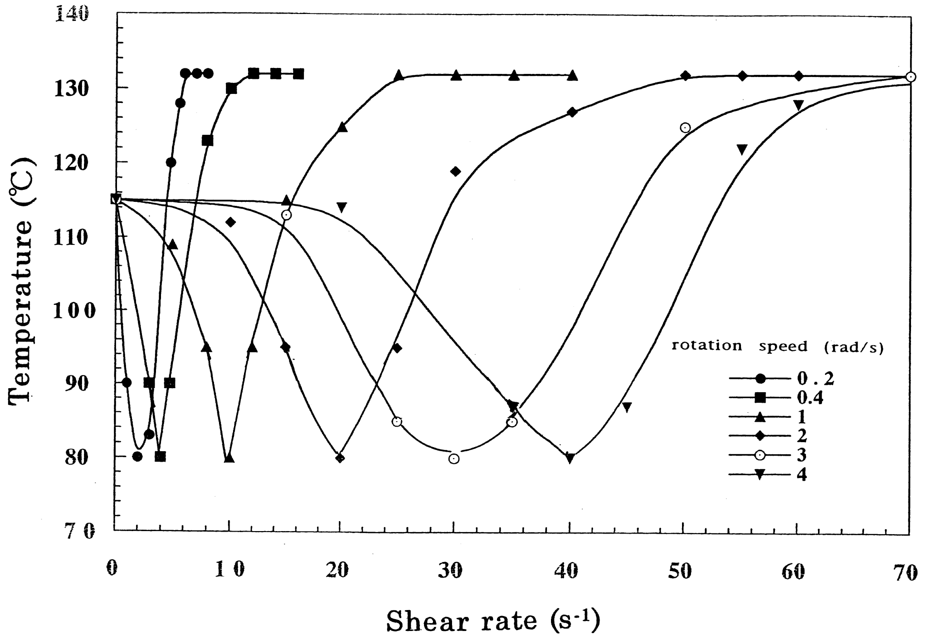

Fig. 7. Changes in the cloud points as a function of shear rate of the PS/PVME 30/70 blend under different rotation speeds.

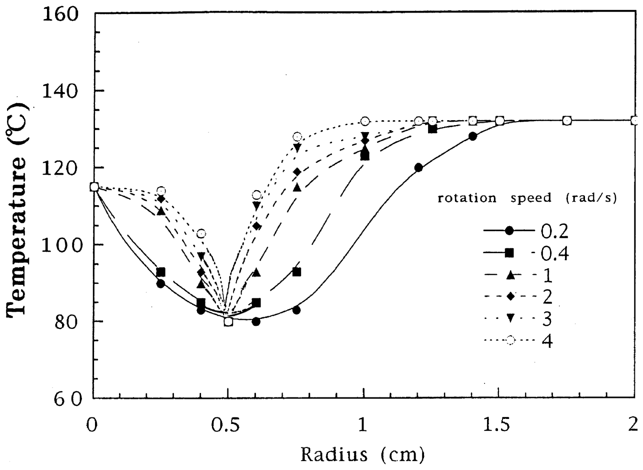

Fig. 8. Changes in the cloud points as a function of the radius of the disk for the PS/PVME 30/70 blend under different rotation speeds.

common to first heat the sample of constant thickness in one- or two-phase regions, and then apply a constant rotation speed, thus missing the rotation speed effect completely. Hindawi et al. [14] observed shear-induced demixing for the PS/PVME blend around 5 s^{-1}, in contrast to Katsaros et al. [12], who detected shear-induced mixing at a shear rate of 2.9 s^{-1} by using 0.16 rad/s rotation speed. Of course, the above two experimental findings greatly depend on the experimental procedures adopted by the two authors. Hindawi et al. started the measurement from the one-phase region and applied a constant rotation speed higher than that used by Katsaros et al., thus, they observed shear-induced demixing at 5 s^{-1}. On the other hand, Katsaros et al. carried out the measurement by applying 0.16 rad/s rotation speed to the sample which was preheated at the two-phase region, therefore they observed a mixing effect at 2.9 s^{-1}. The two lots of experimental data of Katsaros et al. and Hindawi et al. are in good agreement with our results under rotation speed values of 0.2 and 0.4 rad/s, respectively. Similar experimental data for shear-induced mixing at small shear rate (2.68 s^{-1}) and shear-induced demixing at high shear rate (8 s^{-1}) have been observed by Chen et al. [17] and Werner et al. [13], respectively. These literature data can be taken as strong evidence of the effect of rotation speed and measuring temperature on the phase behaviour of the PS/PVME blend. According to the above discussion, shear-induced demixing can be observed at a shear rate higher than the value which was needed to produce shear-induced mixing depending on the measuring temperature and the applied rotation speed values. These experimental facts can be considered as a good answer to the question as to 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.

Fig. 8 shows the relation between the cloud points and the radius of the disk for the above six samples. It is clear that all of the samples are phase separated at the same temperature (80°C which is 35°C lower than the quiescent cloud point) and at the same radius (0.5 cm from the centre of the disk), regardless of the applied rotation speed values, but with increasing rotation speed the miscibility region increases gradually until it becomes so sharp with rotation speed equal to 4 rad/s. So, one can say that with increasing rotation speed (high shear rate), the shear-induced demixing still occurred with a narrower cloud area compared with that at small rotation speed values (small shear rate). Schematic representations of the cloud region were shown in Fig. 9, two samples with the same thickness (0.5 mm) and different rotation speed, the first at a rotation speed equal to 0.2 rad/s and the second at a rotation speed equal to 2 rad/s at 80°C (below the quiescent cloud point by 35°C). Although the values of rotation speed are different (also different shear rates), the two samples are phase separated (shear-induced demixing) at almost the same radius (0.5 cm from the centre of the disk), but by increasing temperature by 1°C/min, the sample at the lower rotation speed value has a larger cloud area than that at higher rotation speed, which shows the sharpness of the miscibility region at high shear rate.

Fig. 10 represents the cloud point changes as a function of shear rate for two samples with different thickness (0.5 and 0.75 mm) under the same rotation (2 rad/s). It can be seen in this figure that the cloud area (immiscible region) becomes broader for the thick sample, though the shear rate which shows a maximum decrease of cloud point does not shift and the minimum cloud point is also the same. That is, the change in sample thickness produces the shift in position of the cloud area in the sample disk, and this behaviour is different to that in the case of changing rotation speed.

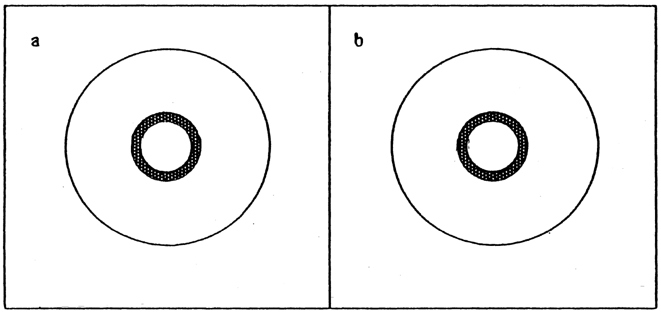

Fig. 9. Schematic representations of the cloud region in the PS/PVME (30/70) blend at 80°C (lower than the quiescent cloud point by 35°C) under different rotation speeds. The shadow region is opaque. (a) 0.2 rad/s. (b) 2 rad/s.

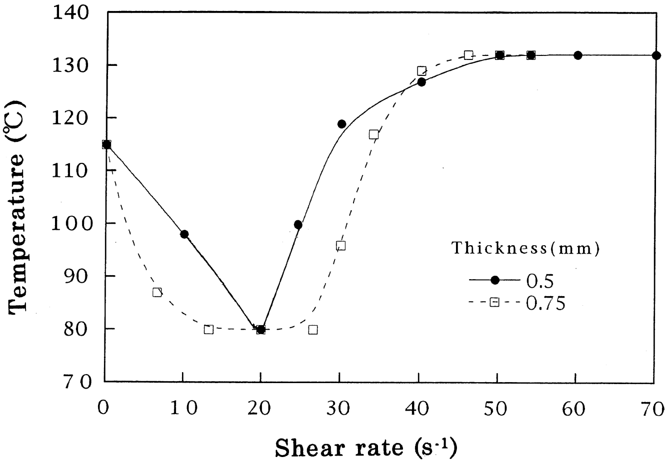

Fig. 10. Shear rate dependence of cloud points for the PS/PVME 30/70 blend with different sample thickness.

Therefore, the effect of changing sample thickness may be not equivalent to that of changing rotation speed.

The effects of sample thickness were also unexpected and may be peculiar. However, at the moment we do not understand this behaviour well. Therefore, more discussion should be necessary by using the results from other measurements, e.g. rheological properties.

4. Conclusions

Both shear-induced demixing and mixing were observed in each composition of the PS/PVME blend, and the changes in cloud point depended on the applied shear rate and composition. The curves of cloud point versus shear rate indicated three regions I–III; region I was at a small rate for shear-induced demixing, region II was at a modest shear rate for shear-induced mixing, and region III was at a high shear rate for a constant cloud point regardless of the applied shear rate values. The effect of shear rate on the cloud points was confirmed by d.s.c. measurements as convincing evidence that the cloud point shifts reflect a real thermodynamic mixing and demixing phenomena. Changes in rotation speeds and sample thickness have a pronounced and peculiar effect on the shear rate dependence of the cloud point in the PS/PVME blend. It is important to repeat the above measurements using different blends having LCST or UCST in order to extend the experimental basis, and to obtain deeper insights into the phase behaviour of polymer blends under shear, and this work is ongoing.

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