Flow-induced mixing and demixing in polymer blends*

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The effect of shear flow on the phase behaviour of partially miscible polymer blends exhibiting a lower critical solution temperature behaviour was investigated. Miscibility was detected, with and without the application of flow, as a change from optical clarity to turbidity using light scattering and as a shift in the glass transition temperature. Light scattering data were collected on a rheo-optical device that was designed to monitor phase changes in polymer blends undergoing shear flow between parallel glass plates in a temperature-controlled environment. Glass transition temperatures of quenched sheared blends were measured using a differential scanning calorimeter. It was found that shear-induced demixing and shear-induced mixing may be observed within the same blend depending on the magnitude of the applied flow. The magnitude of the increase or decrease in the lower critical solution temperature varied with the blend composition and also among the three blends used in this study.

(Keywords: shear flow; miscibility; polymer blends; cloud point; light scattering; glass transition; demixing; lower critical solution temperature)

INTRODUCTION

Polymer–polymer miscibility was once considered to occur very rarely, but miscible polymer blends have been reported more and more frequently in the recent literature[1–3]. This is due to the extensive efforts being devoted to this promising field, which offers the possibility of developing materials with a full range of properties by adjusting the composition and controlling the phase behaviour. Recent studies in this area have primarily concentrated on theoretical and experimental studies of blend miscibility[1,2] and the kinetics of phase separation in partially miscible blends[4–9] under equilibrium conditions. 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 moulding. This demands a better understanding of the flow dependence of the phase behaviour in polymer blends, since the morphology and hence properties of the finished product are influenced to a great extent by the morphology of the flowing melt. In a similar vein, the kinetics of phase separation of the resulting morphologies may very likely be affected by the stress state of the melt.

The influence of flow fields on the phase transitions of mixtures of small-molecule or of macromolecular fluids has recently been the subject of a number of investigations. Flow 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. There have been a number of important differences noted in the direction and in the magnitude of the shift in the coexistence curves in different mixtures under flow. Onuki *et al.*[10,11] and Beysens *et al.*[12,13] found that the upper critical solution temperature (*UCST*) is lowered for mixtures of small molecules under shear flow. The drop in the critical temperature was usually less than 1°C and a minimum shear rate of the order of $10^3\ \mathrm{s}^{-1}$ was needed to observe any changes. For polymer solutions, however, shear flows have been reported to change the *UCST* by as much as 28°C[14] and the minimum shear rate needed to induce changes were of the order of $10\ \mathrm{s}^{-1}$. Shear-induced mixing and shear-induced demixing have been observed in polymer solutions, as opposed to the case of small-molecule mixtures where only shear-induced mixing has been reported. Owing to the relative ease in observing shear effects in polymer solutions, a significant body of data now exists for polymer solutions, and this has been comprehensively reviewed by Rangel-Nafaile[14] and more recently by Hindawi[15]. The phase behaviour of polymer blends under flow is as yet largely unexplored both experimentally and theoretically, and still remains a challenging area of research. Studies of these systems began only recently and experimental data are still scarce. The data show that flow greatly affects miscibility in polymer blends and shear rates of less than $1\ \mathrm{s}^{-1}$ are sufficient to induce changes in the phase behaviour. In the few reported studies[16–24], shear-induced mixing was always observed and there has been only one reported case of shear-induced demixing[19] for a binary polymer blend.

In an earlier paper[23], we described studies of the blend of poly(ethylene-*co*-vinyl acetate) with solution-

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chlorinated polyethylene under simple shear flow using a custom-built sliding-plate apparatus. Improvements in miscibility were observed up to nearly 30°C above the quiescent cloud point. However, limitations of the apparatus precluded evaluation of a wide range of shear rates as well as changes in the shape of the coexistence curve. In the present paper, we report more extensive results using a new instrument design that allowed us to measure the cloud point under shear over a wide range of shear rates, temperatures and compositions.

In our earlier publication[23], a review of the literature on the effect of flow fields on miscibility was presented. Most results on polymer–polymer systems reported flow-induced miscibility. A few more recent publications are reviewed below.

Rector *et al.*[17] developed an expression that predicts the effect of an external flow on the spinodal curve in the framework of the Cahn–Hilliard model for spinodal decomposition. In their treatment, they considered that the free energy of the blend is additive with the stored elastic energy as estimated using the elastic dumbbell model. They concluded that a determination of the sign of the second derivative of the first normal stress difference with respect to composition will predict the effect of flow on the miscibility of polymer blends. Using a cone-and-plane rheometer, they measured the steady shear properties of the blend of polystyrene (PS) and poly(vinyl methyl ether) (PVME) and also marked phase separation by a discontinuity in the viscosity–temperature relationship. Calculations using the developed model predicted a cloud-point rise smaller by two orders of magnitude than the experimental results.

Katsaros *et al.*[19] used planar extensional flow and also shear flow between parallel plates to investigate isothermally flow-induced changes in the miscibility of PS/PVME blends. Optical clarity was used to determine the homogeneity of the blend, where a decrease in turbidity indicated an increase in miscibility. At temperatures inside the spinodal, they reported flow-induced mixing using both types of flow, with increasing miscibility at increased extension or shear rate. Changes were observed from 3 to 12°C above the equilibrium lower critical solution temperature. They also observed flow-induced phase separation in both shear and extensional flows at temperatures as low as 30°C below the coexistence curve. They argued that the overall contribution of specific interactions to the free energy of mixing depends on the strength of the interactions and on the ability of these interactions to come in contact. Therefore, it is possible that any small changes in the probability that groups may come together and form specific interactions can significantly alter the phase behaviour of the polymer blend. Also, if any of the blend components is stretched and oriented, the entropy of mixing will be reduced, which is unfavourable to mixing. The authors concluded that flow-induced changes are best explained in terms of the competing effects of the enthalpic and entropic contributions to the Gibbs free energy of mixing. Deformations tend to enhance specific interaction contacts and can increase miscibility by increasing the favourable enthalpic contribution. It may also decrease miscibility by reducing the entropy of mixing. The authors believe that the entropic term dominates at lower temperatures while the enthalpic term dominates at higher temperatures. They also think that the blend may exhibit an upper critical solution temperature (*UCST*) behaviour below its glass transition temperature, which would be difficult to interpret. Therefore, it is possible that enhancing the specific interaction contacts by flow elevates the lower critical solution temperature (*LCST*) while entropy reduction raises the *UCST*.

Nakatani *et al.*[24] used small-angle neutron scattering to study the concentration fluctuations of binary polymer blends under tangential shear flow between a pair of coaxial cylinders. Measurements were made as a function of shear rate at temperatures below and above the zero-shear-rate optical cloud point, and the data were extrapolated to give values for the spinodal temperature. Two systems were studied: (1) blends of deuterated polystyrene and poly(vinyl methyl ether) (dPS/PVME) and (2) blends of deuterated polystyrene and polybutadiene (dPS/PB). The first blend exhibited an *LCST* while the second exhibited a *UCST*. For the dPS/PVME blend, the apparent spinodal temperature increased with increasing shear rate in the direction parallel to flow. No systemic changes in the spinodal temperature were observed perpendicular to flow. They concluded that there is a shear-induced mixing effect in the direction of the flow and no consistent effect in the perpendicular direction. For the blend of dPS/PB, they found that the scattered intensity decreased with increasing shear rate at temperatures below the cloud point in both parallel and perpendicular directions to flow, indicating shear-induced miscibility in both directions.

In summary, flow-induced changes in the miscibility of polymer blends have been observed, though no general conclusion can yet be drawn about the observed behaviour. Thermodynamic treatments of the problem[17,20] have only considered the added elastic energy due to deformation of the chains, and no attempt has been made to modify the enthalpy-of-mixing term. Since shearing may perturb the specific intermolecular interactions responsible for miscibility in high-molecular-weight polymer blends, the omission of an enthalpic contribution may be serious. Alternative non-thermodynamic theories based on the growth of concentration fluctuations[25,26] fail to account for the flow-induced mixing observations for polymer blends.

In the work reported here, light scattering was employed to measure quantitatively the shift in the cloud-point curves of three polymer blends undergoing simple shear flow. The cloud-point observations were complemented by measurements of the glass transition temperatures of sheared and unsheared blends.

EXPERIMENTAL

Materials

The three blends that were used in this study were: (1) poly(ethylene-*co*-vinyl acetate) and solution-chlorinated polyethylene (EVA/SCPE11); (2) poly (butyl acrylate) and solution-chlorinated polyethylene (PBA/SCPE12); (3) polystyrene and poly(vinyl methyl ether) (PS/PVME). EVA was obtained from ICI (Evatone 45) and SCPE11 was prepared by photochlorination of a commercial linear polyethylene[27] obtained from BDH. PBA was obtaind from Polysciences Inc. and was supplied in a toluene solution. It was dried in a Petri dish at room temperature for 1 week and then in a vacuum oven at 50°C for 3 weeks. SCPE12

Table 1 Properties of the polymers used in the various blends

Blend	Polymer	VA (%)	Cl (%)	M_w	M_n	T_g (°C)	Index of refraction
1	EVA	45	–	1.06×10^5	3.87×10^4	−26	1.42
	SCPE11	–	54.8	3.32×10^5	6.27×10^4	47	1.51
2	PBA	–	–	7.55×10^4	2.74×10^4	−44	1.46
	SCPE12	–	57.1	2.36×10^5	4.43×10^4	46	1.51
3	PS	–	–	3.02×10^5	9.21×10^4	107	1.59
	PVME	–	–	6.97×10^4	1.58×10^4	−28	1.47

Table 2 Solvents used in preparing cast films

Blend	Solvent
EVA/SCPE11	Tetrahydrofuran
PBA/SCPE12	Methyl ethyl ketone
PS/PVME	Toluene

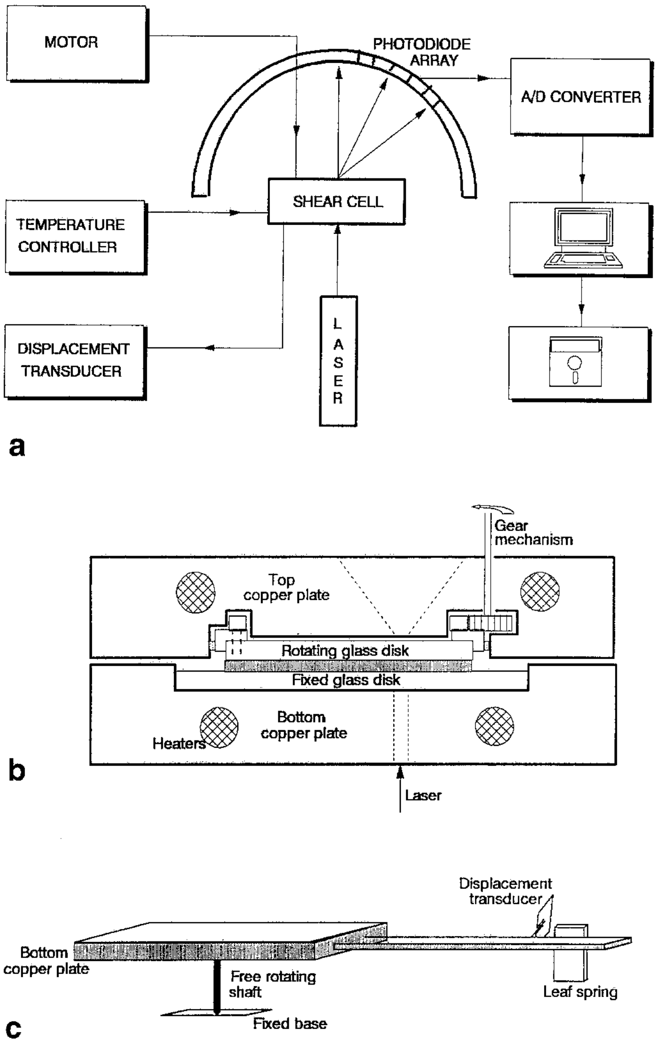

Figure 1 (a) Schematic illustration of the rheo-optical shear apparatus. (b) Side view of the shear cell. (c) Illustration of the method employed to measure torque

was prepared in the same way as SCPE11 but with a slightly higher chlorine content. PS and PVME were obtained from BASF Chemicals. All three blends exhibited an *LCST* behaviour, and the characteristics of each of the polymers are given in *Table 1.*

Clear films of the blends were prepared by solvent casting. Pre-weighed amounts of the two components were dissolved with continuous stirring in a common solvent according to *Table 2.* The solution was then centrifuged and drops of the clear solution were placed on glass slides that were used as the bottom plate of the shear fixture. The slides were placed in covered Petri dishes to ensure slow evaporation of the solvent and to exclude any dust. Samples were initially left at room temperature for 2 days and were then transferred to a vacuum oven at 50°C for a week to ensure full evaporation of the solvent, which was checked by repeated weighing of the glass slide. A constant film thickness of 0.18 mm was used and was controlled by using the same concentration of the casting solution and by placing a constant volume of solution on the glass slide.

Apparatus

A schematic illustration of the rheo-optical apparatus is given in *Figure 1.* The fixture was designed to permit the acquisition of light scattering data from polymeric systems undergoing simple shear flow between parallel glass plates (*Figure 1b*). A temperature-controlled chamber consisting of a fixed upper copper plate and a lower copper plate, which could be moved vertically, surrounded the shear fixture. The bottom glass slide ($76 \times 52\,\mathrm{mm}^2$) rested inside a bed in the lower copper plate, while the rotating glass disc, 46.5 mm in diameter, was fixed inside a copper ring attached to the driving gear. The glass disc was allowed to rotate by a pin fixed to the ring, which fitted inside a notch on the edge of the disc. A thin poly(tetrafluoroethylene) ring was placed on the outside of the copper ring to minimize the friction between the rotating copper assembly. A constant angular speed was applied with an IKA model RW20 motor supplied by Orme Scientific. The shear cell was designed so that, at the completion of a shear experiment, the plates could be quickly released by lowering the bottom copper plate. The glass plates could then be taken out of the cell within 5 to 10 s in order to quench the temperature of the blend and freeze-in the sheared morphology.

The bottom copper plate, as show in *Figure 1c*, had an extended arm and was mounted on top of a freely rotating shaft to allow the applied torque to be measured. When flow was imposed, rotation of the bottom glass disc was prevented by the arm impinging aginst a calibrated leaf spring. The displacement of the spring, which depended on its spring constant, was measured with a linearly variable differential transformer (l.v.d.t.) model DFg-1 obtained from Radio Spares.

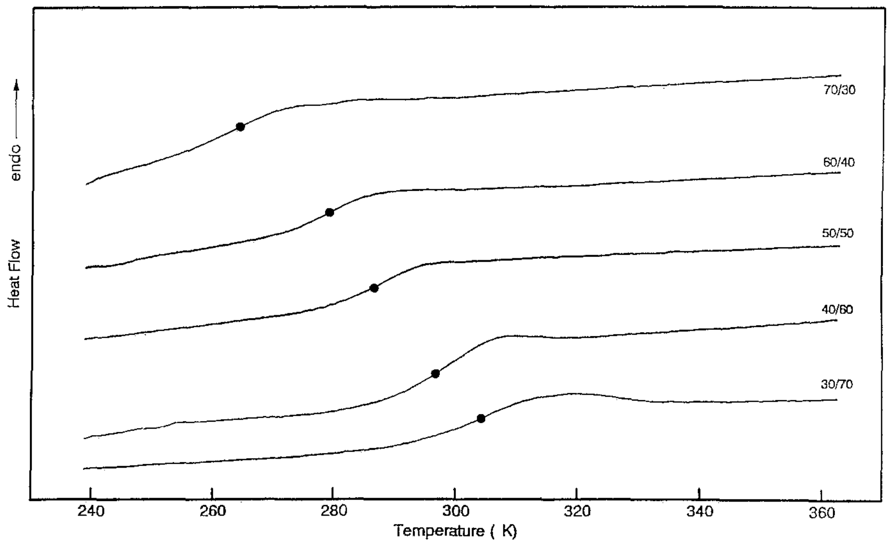

Figure 2 D.s.c. thermograms for the five indicated compositions of the PBA/SCPE12 blend. The glass transition temperatures are indicated by small black circles on the observed transitions

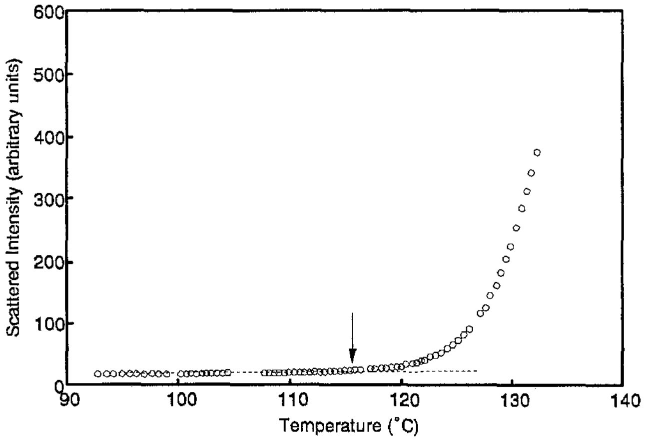

Figure 3 Determining the quiescent cloud point of a (55/45) PBA/SCPE12 blend using the light scattering data. The cloud point is indicated by the arrow

For a fixed separation of the two plates, h, this type of flow exhibits a variation in the tangential velocity with radial distance as the disc rotates at a constant angular velocity Ω. The shear rate $\dot{\gamma}_r$ at a radius r is:

$$\dot{\gamma}_r = \Omega r/h \qquad (1)$$

Therefore, $\dot{\gamma}_r$ is a linear function of the radius and may be written in terms of the shear rate at the outer edge of the blend, $\dot{\gamma}_R$, as:

$$\dot{\gamma}_r = \dot{\gamma}_R(r/R) \qquad (2)$$

Thus $\dot{\gamma}_r$ is a maximum at $r = R$ and zero at the centre of the blend ($r = 0$). Unless specifically stated, the value of the shear rate reported for the experiments corresponded to the maximum or nominal shear rate, $\dot{\gamma}_R$.

Light scattering measurements were accomplished by allowing laser light (He–Ne, $\lambda = 633$ nm) to pass through the copper block via a hole of 5 mm diameter at a distance of 11 mm from the centre of the disc. The light source, the photodiode detector, the correction of light scattering, the temperature controller and the heat supply have been fully described previously[23].

Thermal analysis

Glass transition temperatures (T_g) were measured by differential scanning calorimetry using a Perkin–Elmer DSC-2 and a heating rate of 20°C min^{-1}. The T_g was defined as the midpoint in the change of the specific heat.

RESULTS AND DISCUSSION

A single T_g was taken as evidence for miscibility of the cast films. Typical thermograms for PBA/SCPE12 blends are shown in *Figure 2*. A single T_g was observed for each indicated composition. The cloud-point curves of the blends were determined from turbidity measurements using the shear apparatus described above, but with no flow. A heating rate of 1°C min^{-1} was used and the start of phase separation was identified as the temperature at which the measured intensity of scattered light began to deviate from the baseline, as shown in *Figure 3*. The uncertainty of the cloud point was ±2°C since the deviation from the baseline was not usually sharp and clear owing to the low diffusion rates of most polymers. The measured cloud-point curves of the EVA/SCPE11 and PBA/SCPE12 blends are shown in *Figure 4*. For the PS/PVME blend, only one composition (30/70) was studied and this had a cloud point of 92°C.

Quantitative measurements of the shift of the phase boundaries with shear were determined by measuring the cloud point of the blend during simple shear flow at a constant angular speed, i.e. a constant shear rate. Measurements of the scattered light intensity were begun at a temperature within the one-phase region, and the intensity was continuously monitored as the temperature was raised at 1°C min^{-1}. The results obtained for a single composition of PBA/SCPE12 (55/45) for various shear rates are illustrated in *Figure 5*. The shear rates indicated in the figure are as determined at a radius of 11 mm, the point where laser light was allowed to pass through the sample. Similar results were obtained for other compositions and the other blends. The scales used for the different curves in *Figure 5* were the same, but the curves were shifted for the sake of comparison. The magnitude of the scattered light intensity for the blend within the one-phase region was similar for all runs. *Figure 5* shows that, for this particular sample, the cloud

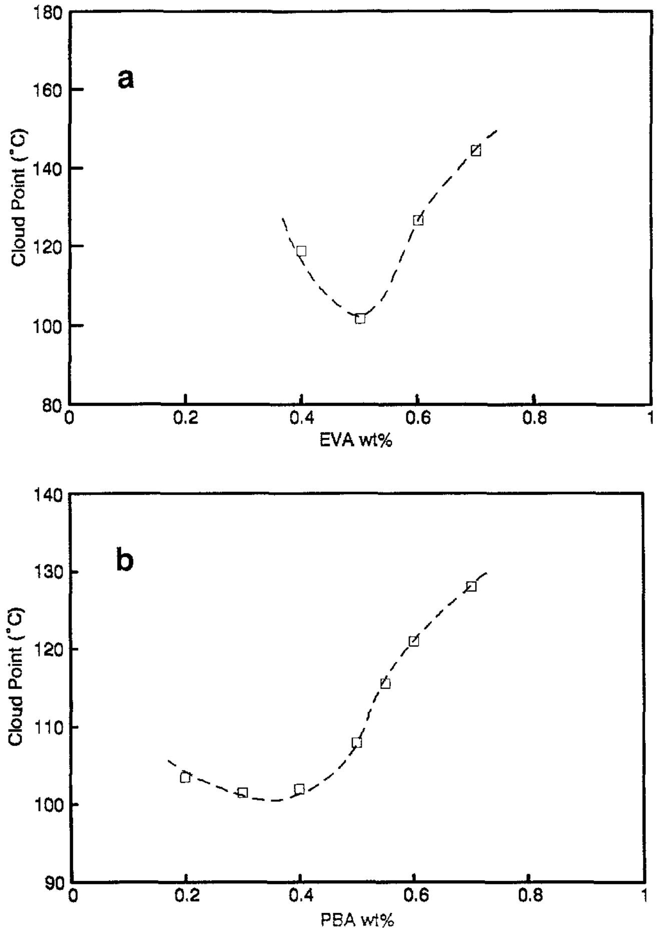

Figure 4 Cloud-point curves for (a) EVA/SCPE11 blend and (b) PBA/SCPE12 blend

point decreased, i.e. flow induced demixing, and exhibited a minimum between a shear rate of 1 and 4.6 s^{-1}. Above the critical shear rate, the cloud point increased, though for all shear rates in *Figure 5*, the dynamic cloud point was lower than the quiescent cloud point. For other blends and compositions, however, it was not uncommon also to observe dynamic cloud points higher than the quiescent cloud point, which corresponded to shear-induced mixing of the blend. The change in the cloud point as a function of shear rate for various compositions of all three blends is illustrated in *Figure 6*, and the corresponding cloud-point curves for the EVA/SCPE11 and PBA/SCPE12 blends are shown in *Figure 7*.

It is useful to examine other explanations for the turbidity differences at different shear rates for the blends and to evaluate the relative merit *vis-à-vis* the conclusion of phase changes. Several phenomena can affect the measured scattered light intensity under shear, including deformation and/or break-up of droplets of the dispersed phase or viscous heating. The likelihood of the first two influencing the results was minimized by approaching the cloud point from the one-phase region. Still, however, the sensitivity of locating the cloud point, i.e. the deviation of the scattered light intensity from the one-phase baseline, may be affected by deformation of the minor phase as phase separation began. The likelihood of particle deformation or break-up being important was assessed from viscosity measurements of the polymers.

Viscosities of the component polymers, shown in *Table 3*, were measured from the torque data obtained with the rheo-optical device at 95°C and a nominal shear rate of 0.8 s^{-1}. The operation of the instrument was checked by comparing viscosity values obtained for polystyrene with data obtained with a Bohlin rheometer at 60°C and shear rates between 1.5 and 6 s^{-1}. The values corresponded within 5%.

Consider first the right side of the phase diagrams in *Figure 7*, that is blends where SCPE is the minor component. If one estimates the viscosities of the two phases by the viscosity of the major component in the phase, the viscosity ratio η_d/η_c (where η_d is the viscosity of the dispersed phase and η_c is the viscosity of the continuous phase) for the two systems varied from 13 to 64 000. Taylor[28] proposed that droplet break-up takes place when viscous forces exceed interfacial forces between the droplet and the continuous phase. The important parameters that determine the ultimate droplet size are the viscosity ratio η_d/η_c and the Weber number, $We = \dot{\gamma}\eta_c r/\sigma$, where r is the droplet size, σ is the interfacial tension and $\dot{\gamma}\eta_c$ is the viscous stress exerted on the drop. The critical values of We and η_d/η_c required for droplet break-up to occur have been derived and experimentally verified by a number of research groups[29]. When η_d/η_c exceeds 3.5, droplet break-up does not occur. Therefore, it is highly unlikely that droplet break-up occurs in the PBA/SCPE12 blend and probably not in the EVA/SCPE11 blend when SCPE is the minor component. Similar arguments rule out particle deformation as being significant in these systems.

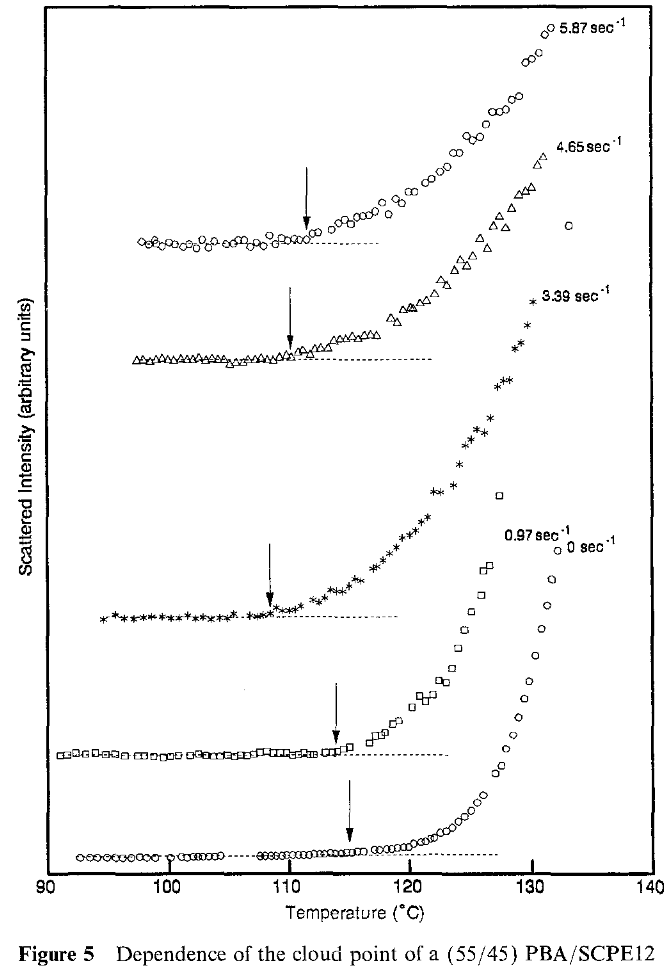

Figure 5 Dependence of the cloud point of a (55/45) PBA/SCPE12 blend on the applied shear rate. The cloud point is indicated by an arrow on each curve

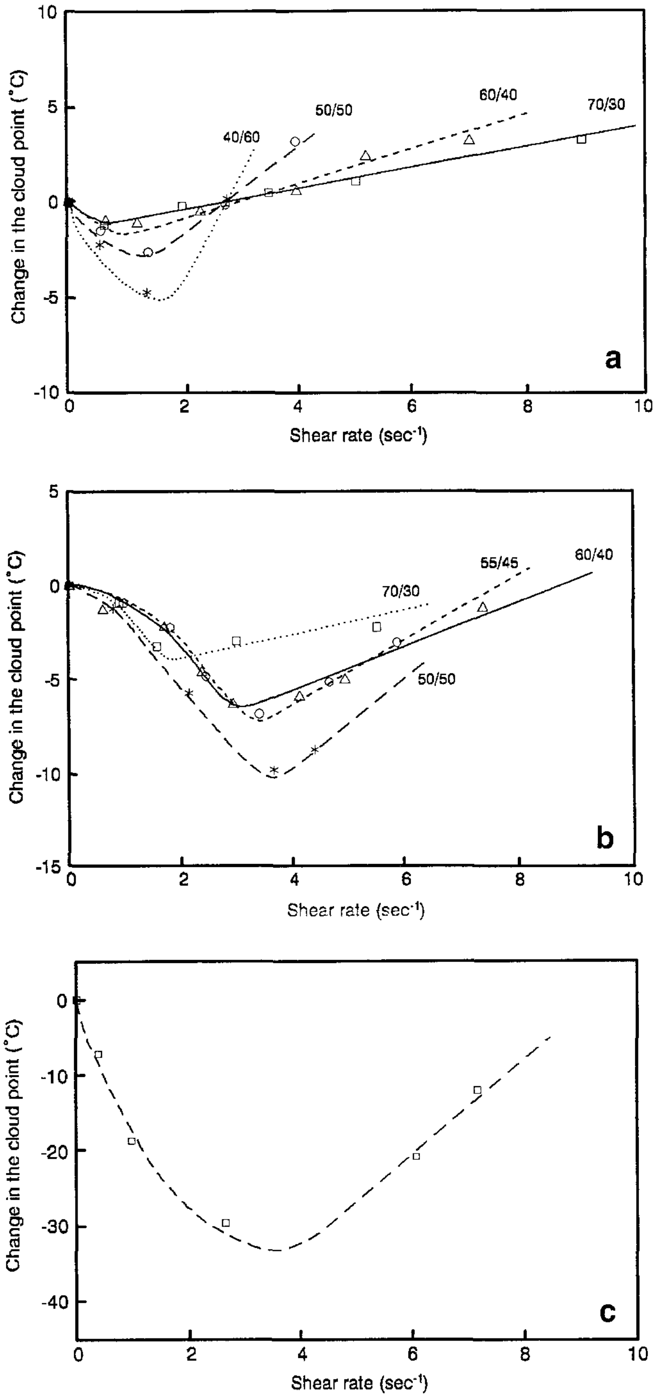

Figure 6 Change in the cloud point as a function of shear rate for (a) EVA/SCPE11 blend, (b) PBA/SCPE12 blend and (c) PS/PVME blend. Compositions are as shown in the figure

As to left of the phase diagrams in *Fiugre 7*, where SCPE is the continuous phase, one cannot *a priori* rule out droplet break-up or deformation. However, one would expect these phenomena to become more important as the shear rate increased, i.e. increasing *We*. In that case, it is difficult to reconcile why the cloud point should first decrease and then increase as the shear rate was raised.

As for viscous heating, it would be manifest as an apparent decrease in the cloud point. That is, if the melt were actually at a higher temperature than the set point due to viscous dissipation, one would observe the cloud point prematurely. The magnitude of the temperature rise due to viscous heating was calculated using the cone-and-plate estimation procedure[30] for the blend of EVA/SCPE11 (40/60) at a shear rate of 15 s^{-1}, and a value of 1.1°C was obtained. This value was much smaller than the observed decrease in the cloud point shown in *Figure 6*. Viscous heating could, therefore, be eliminated as the explanation for the reduction in the cloud point at the lower shear rates.

One is left, then, with one possible explanation for the cloud-point curve behaviour shown in *Figure 7*: shear-induced mixing and demixing can occur for a single binary polymer blend depending on the shear rate.

Measurement of the glass transition temperature was used as a second means for assessing changes in the miscibility of the flowing blends. A blend of PS/PVME (30/70) was sheared at 80°C and $\dot{\gamma}_R = 8.8$ s^{-1}. The flow was stopped and the glass plates with the sandwiched blend were quickly taken out of the shear cell and

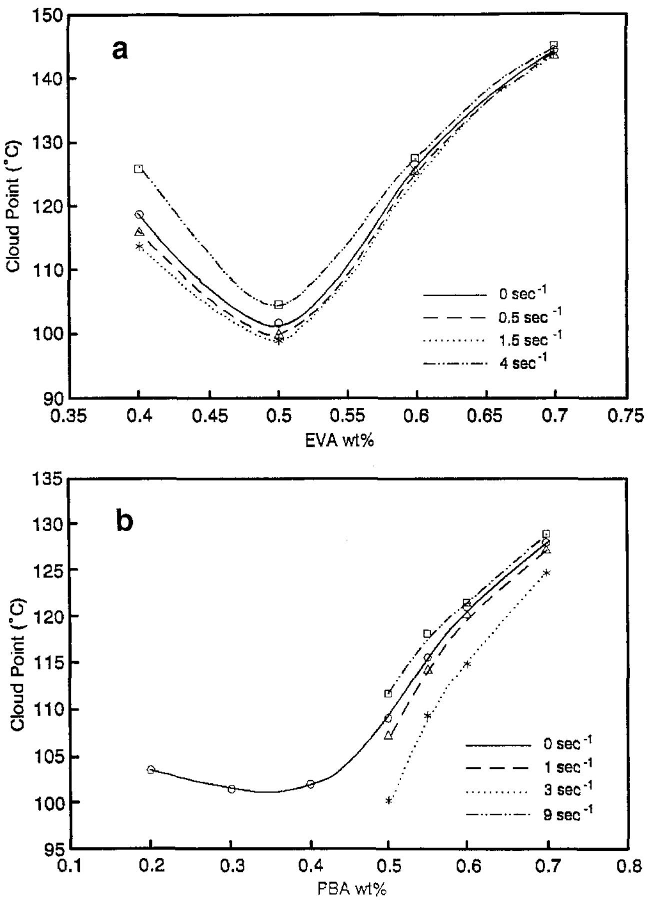

Figure 7 Dependence of the cloud-point curve on the applied shear rate for (a) EVA/SCPE11 blend and (b) PBA/SCPE12 blend. Data at 9 s^{-1} in (b) were obtained by extrapolation

Table 3 Viscosities of the polymers used in three blends as measured at 95°C and 0.8 s^{-1}

Blend	Polymer	Viscosity (Pa s)	Viscosity ratio
EVA/SCPE11	SCPE11	2.1×10^5	1.3×10^1
	EVA	1.6×10^4	
PBA/SCPE12	SCPE12	6.4×10^5	6.4×10^4
	PBA	1×10^1	
PS/PVME	PS	Glass	∞
	PVME	1.8×10^2	

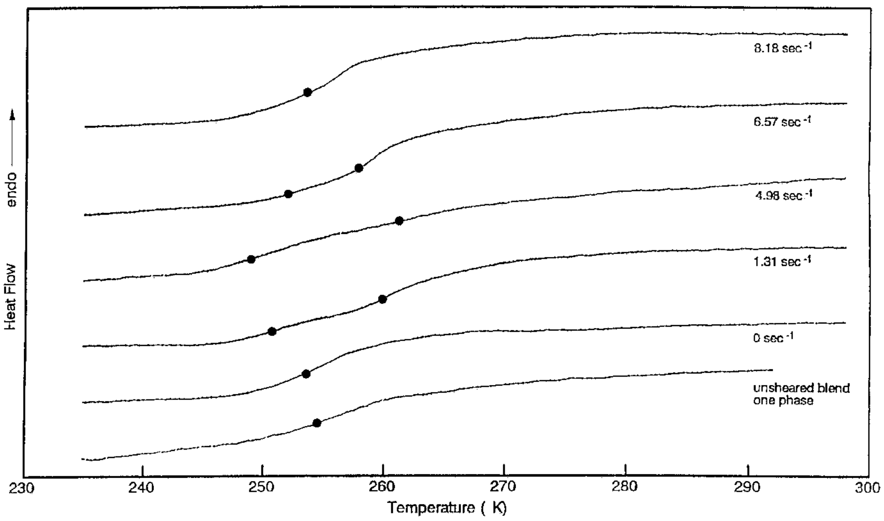

Figure 8 D.s.c. thermograms for five samples taken from different radial locations of a PS/PVME (30/70) blend sheared at $\dot{\gamma}_R = 8.8\,\mathrm{s}^{-1}$. The glass transition temperatures are indicated by small black circles on the observed transitions

quenched in liquid nitrogen. Five samples were then taken from different radial positions of the disc and their glass transitions were measured. The d.s.c. thermograms obtained for the five samples are given in *Figure 8*. At 80°C, the blend was below the quiescent cloud point. At $r = 0$ ($\dot{\gamma} = 0\,\mathrm{s}^{-1}$) a single T_g was observed as expected. At $r = 3.5$ mm ($1.31\,\mathrm{s}^{-1}$), the blend phase separated as evidenced by two T_g values in the d.s.c. thermograms. At $r = 13.2$ mm ($4.98\,\mathrm{s}^{-1}$), the two T_g values were further apart, indicating more demixing. At $r = 17.4$ mm ($6.57\,\mathrm{s}^{-1}$), the two T_g values moved closer together, indicating less demixing. And at $r = 21.6$ mm ($8.81\,\mathrm{s}^{-1}$) only a single T_g was observed, indicating that the blend formed a single phase. These results are consistent with the turbidity data discussed above.

No T_g measurements were performed for the PBA/SCPE12 and EVA/SCPE11. It was difficult to quench the PBA/SCPE12 blend after cessation of flow before any changes took place. For the EVA/SCPE11 blend, the EVA copolymer was partially crystalline and its wide melting region interfered with observation of the glass transition of the blend.

CONCLUSIONS

The influence of flow on the cloud-point curves for three different binary polymer blends exhibiting *LCST* behaviour was studied using a custom-built rheo-optical instrument that allowed angular-resolved light scattering measurements during simple shear flow of a polymer melt. Both lowering and raising of the cloud point by shear were observed for each blend. At low shear rates, the cloud-point curves were shifted to lower temperatures, which indicates that flow-induced phase separation took place. This behaviour reversed at a critical shear rate, above which the cloud-point curves increased in temperature, indicating flow-induced phase mixing.

Particle deformation and break-up and viscous heating were discounted as explanations for the observed changes in the cloud-point curves during flow.

Based on these results, it does appear that, as with polymer solutions, flow can induce both phase separation and mixing. The fact that both were observed in the same blend suggests that competing effects occur during flow. For example, one hypothesis that would tend to promote phase mixing is that deformation of the chains results in an increase in the concentration of intermolecular sites. This would tend to reduce the effective interaction parameter, χ, in expressions for the free energy. On the other hand, Helfand[25] and Onuki[26] suggest that elastic deformation may act to enhance some concentration fluctuations, promoting the uphill diffusion that occurs in phase separation. Alternatively, as discussed by Wolf[31], elasticity contributions to the free energy can conceivably change the shape of the free-energy curve and give rise to either phase mixing or separation. As yet, however, no adequate theory exists to explain all of the experimental observations. It is hoped that the generation of a more complete database on phase changes due to flow of polymer blends will stimulate new advances in theory.

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