Shear effect on the phase behaviour and morphology in oligomer blend of polystyrene/poly(methyl methacrylate)

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Abstract

The phase behaviour of an oligomer mixture of polystyrene/poly(methyl methacrylate) (PS/PMMA), which shows an upper critical solution temperature (UCST) type phase diagram, has been investigated under simple shear flow. The cloud points were strongly affected by the values of the applied shear rate. The phase diagrams under different values of shear rate, indicated shear-induced mixing for all measured compositions, and the magnitudes of the depression of the cloud points under the effect of shear rate were found to be composition dependent. The dramatic decrease of the homogenization temperature was investigated as a function of shear rate ($\dot{\gamma}$), and the normalised shift in the cloud point $\left|\Delta T(\dot{\gamma})/T(0)\right|$ versus $\dot{\gamma}$ was also studied and compared with that of simple liquid mixtures and polymer solutions, as well as high molecular weight polymer blends. The cloud points of this oligomer mixture showed high sensitivity to change under the effect of shear rate; a much higher sensitivity than both simple liquid mixtures and polymer solutions, on the other hand, slightly less sensitivity than the high molecular weight polymer blend (PMMA/poly(styrene-*co*-acrylonitrile)). The morphology of PS/PMMA = 30/70 blend was also studied under different values of shear rate at 35°C below its quiescent cloud point, using the transmission electron microscopy (TEM). The results showed that the shear-induced mixing occurred at a high critical shear rate value (34 s^{-1}), below which the dispersed PS-rich domains were slightly elongated and broken-up into very small domain sizes with very good particle distribution. © 2000 Published by Elsevier Science Ltd.

Keywords: Shear flow; PS/PMMA; Cloud point

1. Introduction

The properties of multiphase materials are greatly influenced by the morphology, which in turn, depends on the equilibrium phase behaviour of the system and the method of preparation. Diverse morphologies can be developed through the use of shear flow and temperature histories, such as those that occur in a typical operation of polymer processing. Even though there is a significant amount of literature on the dispersive and/or homogenising action of the flow fields in multiphase systems (including immiscible polymer blends), little is known about the effect of flow processing on the phase behaviour of miscible or partially-miscible polymer blends.

The effects of flow on the phase behaviour of polymer solution have been recognised for several decades [1–8]. Most polymer solutions exhibit an upper critical solution temperature (UCST) in the temperature ranges that have been studied. Some of the literature reported shear-induced

mixing or demixing; however, others detected shear-induced mixing and demixing within one composition, depending on the experimental conditions and the applied shear rate.

In an early study, Silberbey and Kuhn [1] have observed the shear-induced mixing for a solution of polystyrene (PS) and ethyl cellulose in benzene, the maximum depression of the cloud point was 13°C at a shear rate of up to 270 s^{-1}. In contrast to the observation of Silberberg and Kuhn, Ver Strate and Philipoff [2] found shear-induced demixing for PS solution in di(2-ethyl hexyl) phthalate, and in a mixture of *cis*- and *trans*-decalin. An increase of the cloud point as high as 28°C for sheared solution of PS in dioctyl phthalate (DOP), was detected by Rangel-Nafaile [3]. Kramer and Wolf [4] detected shear-induced mixing and demixing for a solution of PS in *trans*-decalin system depending on particular conditions, polymer molar mass and concentration. Hashimoto et al. [5–8] studied shear effect on the phase behaviour of semidiluted solution of PS and polybutadiene (PB) in common solvent (DOP) by using small angle light scattering (SALS). They observed anisotropic scattering that resulted from the elongation of polymeric domains in

the phase-separated mixture. At a very high shear rate they observed homogenisation; the result was interpreted as shear-induced shifting of the cloud temperature.

In contrast, experimental studies of the flow effect on liquid–liquid phase behaviour of polymer blends are relatively few. Most investigations have observed shear-induced mixing and/or demixing [9–15], as opposed to the case of small molecular mixture where only shear-induced mixing has been reported. Flow effects on the miscibility of PS and poly(vinyl methyl ether) (PVME) blends, which exhibit a lower critical solution temperature (LCST) behaviour, were first reported by Mazich and Carr [9] who interpreted an abrupt change in the viscosity of a blend under shear flow as a phase transition. They concluded that shear stress could increase the cloud point from 2 to 7°C. Katsaros, Malone, and Winter [10] also reported an increase in the cloud point of PS/PVME blend by as much as 12°C using extensional flow and turbidity measurements. Lyngaae-Jorgensen and Sondergaard observed that a two-phase blend of poly(styrene-*co*-acrylonitrile) (SAN) and poly(methyl methacrylate) (PMMA) forms a homogeneous phase if it is subjected to shear stress that is sufficiently high, in a cone-plate rheometer, using two-dimensional light scattering [11]; but there is no data concerning the phase diagram of the blends as a function of shear rate. The influence of flow on the cloud-point curves for three different binary polymer blends of PS/PVME, poly(ethylene-*co*-vinylacetate)/solution-chlorinated polyethylene (SCPE) and poly(butyl acrylate)/SCPE have been studied by Hindawi, Higgins, and Weiss [14]. They observed lowering and raising of the cloud points under shear for each blend, using a rheo-optical light-scattering device.

In a previous study[15], we also reported shear-induced mixing at 17°C and shear-induced demixing at 35°C for the critical composition of PS/PVME = 30/70 blend under simple shear flow. Therefore, shear-induced demixing and/or mixing could be observed in only single binary polymer blends, depending on the temperature and the applied shear rate value.

Several attempts have been made to investigate theoretically the effect of shear flow on the phase behaviour of polymer solutions and blends. From the thermodynamic point of view a large number of studies [2,3,16–23] introduced an additional term, defined as the energy stored by polymeric materials during flow (ΔE_s) to the Gibbs free energy of mixing under quiescent state (ΔG_m),

$$\Delta G\dot{\gamma} = \Delta G_m + \Delta E_s \tag{1}$$

where $\Delta G\dot{\gamma}$ is the Gibbs free energy under shear flow. This methodology has been successfully used in predicting the effect of shear flow on the phase behaviour of various polymer mixtures. Rangel-Nafaile et al. [3] found that this approach is capable of predicting the change in the cloud point of PS/dioctyl phthalate mixture caused by flow. Very recently An and Wolf [17] calculated the phase diagram of

PS/*trans*-decalin mixture as functions of shear rate, pressure and molar mass. Kammer et al. [18] introduced an interaction parameter in the stored energy and fitted the model predictions to the experimental phase behaviour of SAN/PMMA blends.

Rector et al. [24] developed an expression that predicts the effect of 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, estimated using the elastic dumbbell model. Lyngaae-Jorgensen and Sondergaard [11] developed a semi-theoretical model for the transition from two-phase to one-phase under shear flow. This model predicted the critical shear stress required for the transition.

Onuki [25] reviewed the phase transitions of fluids in shear flow; he also discussed some related problems in polymer blends, gels and surfactant systems, etc. He has found that in near-critical fluids, convective deformations can drastically alter the critical behaviour, spinodal decomposition and nucleation. In this case, the hydrodynamic interaction suppresses the fluctuations and gives rise to a downward shift of the critical temperature (shear-induced mixing). On the contrary, shear flow can bring single-phase polymer solutions and polymer blends into phase separation when the elastic effect plays an important role.

Recently, we investigated the shear effect on the phase behaviour and morphology of a PMMA/SAN-29.5 blend, which showed an LCST-type phase diagram[26]. It has been found that only shear-induced mixing was detected for all the compositions. The PMMA/SAN blends were more sensitive to the shear rate than both simple liquid mixtures and polymer solutions. The morphology of the critical blend composition (PMMA/SAN = 75/25) showed 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. Here, we shall extend our measurements to an oligomer mixture of PS/PMMA, which shows a UCST-type phase diagram [27]. Comparison of the sensitivity of this oligomer mixture to the shear rate effect with other systems, such as the high molecular weight polymer blends (previous work) [26] and polymer solutions, as well as simple liquid mixtures will also be investigated. Furthermore, the morphology under different shear rate values will be studied, to obtain deeper insights into the shear rate–morphology relationship.

2. Experimental

2.1. Materials and sample preparation

The PS sample was obtained from Aldrich Chemical Company, with molecular weight average, $M_w = 2514$ and polydispersity index, $M_w/M_n = 1.034$. The PMMA was obtained from Sumitomo Chemical Company, Japan with $M_w = 6000$ g/mol and $M_w/M_n = 1.3$. The glass
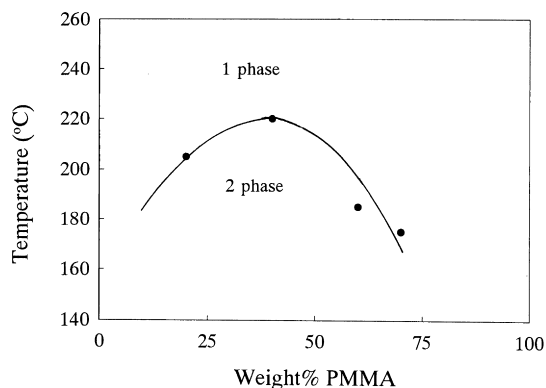
Fig. 1. Quiescent cloud point curve in PS/PMMA blend.

transition temperatures of PS and PMMA are 68 and 78°C, respectively.

The PS and PMMA blends were prepared by dissolving the corresponding weights of the two polymer components in tetrahydrofuran. The blend solutions were then put in a petri dish and left to dry at room temperature for about three days; after that, complete drying of the blends was performed until a constant weight was accomplished under vacuum for another three days at 60°C. About 0.5 g of the blend was taken to prepare a disk like film specimen with 0.5 mm thickness and 40 mm diameter for the shear measurements; another specimens of 1 mm thickness and 25 mm diameter for the pure polymer components were also prepared for the viscosity measurements.

2.2. Measurements

The details of the shear apparatus have been described elsewhere [15]. The sample is located between two parallel glass plates, the top one is fixed and the bottom one is rotated by different speeds, controlled by the motor and the gear mechanism. The simple shear flow is generated by applying constant rotation speeds to the sample, which was preheated to a temperature lower than the quiescent cloud point by about 45°C. After that the sample was heated at a constant heating rate (1°C/min) under a constant rotation speed, to be 10°C above the quiescent cloud point. Under this condition, the phase dissolution takes place at

a certain region, dependent on the values of the applied shear rate. For the parallel plate measurements, the shear rate is a linear function of the radius

$$\dot{\gamma} = \Omega r/h \tag{2}$$

where h is the sample thickness, r is the radius, and Ω is the rotation speed (rad/s). The shear rate is a maximum at the outer edge of the disk ($r = R$) and decreases to zero at the centre of the disk ($r = 0$). Once the measurement was taken, the two plates with the sample could be released very quickly to allow rapid quenching in a water bath for the transmission electron microscope (TEM) analysis. For the TEM analysis, the specimens at different shear rate values were microtomed to an ultrathin section of 70 nm thickness, using a Reichert-Jung ultracryomicrotome with a diamond knife, and then they were stained with RuO_4 vapour. The structure in the section was observed under TEM, JEM 100CX (100 kV).

The complex dynamic viscosities ($\eta *$) of the pure polymer components were measured by a Rheometerics dynamic mechanical spectrometer using two parallel plates, having a diameter of 25 mm, at a stain rate $\leq 10\%$ to keep the linear viscoelastic properties. The measurements were carried out at frequencies in the range of 0.1–100 rad/s at a constant temperature (135°C).

3. Results and discussion

3.1. Phase behaviour under shear

Fig. 1 shows the cloud point curve of the PS/PMMA blend under a quiescent state. A typical UCST-type phase diagram was obtained by heating the samples from two-phase to one-phase at a 1°C/min heating rate, which is identical to the experimental condition under shear flow.

Fig. 2 shows the schematic representations of the cloud region in the PS/PMMA = 40/60 blend under a constant rotation speed (0.85 rad/s) in three temperatures. At 140°C (45°C below the quiescent cloud point) under a constant rotation speed (Fig. 2a), the outer edge of the sample turns transparent indicating shear-induced mixing. The transparent area increases gradually with increasing temperature to 170°C (15°C below its quiescent cloud point), as shown in Fig. 2b. Every region of the sample disk turns completely
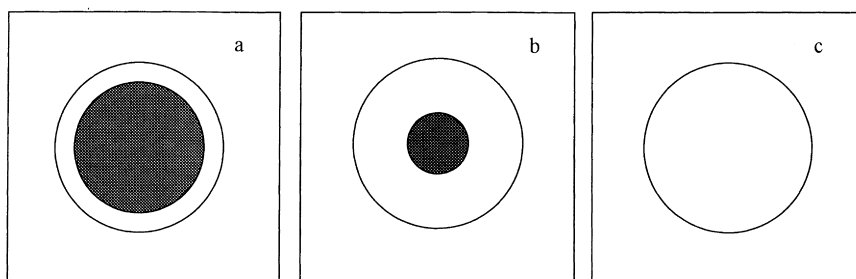

Fig. 2. Schematic representations of the cloud region in PS/PMMA = 40/60 blend between two parallel plates under shear (rotation speed 0.85 rad/s). The shadow region is opaque. (a) 140°C (45°C below the quiescent cloud point); (b) 170°C (15°C below the quiescent cloud point); and (c) 195°C (10°C above the quiescent cloud point).
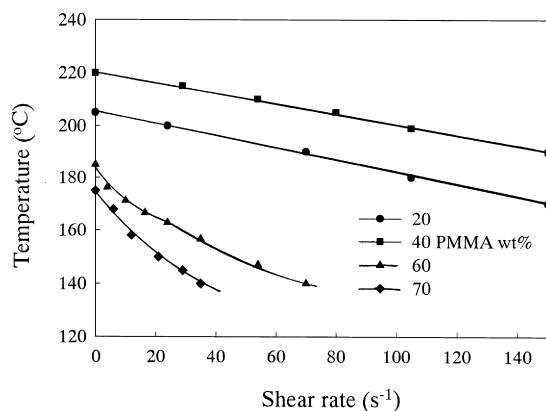
Fig. 3. Shear rate dependence of cloud points for different compositions of the PS/PMMA blend.

Fig. 5. Complex dynamic viscosity of PS and PMMA as a function of shear rate.

transparent at 185°C (the quiescent cloud point). At 10°C above the quiescent cloud point the sample is still transparent even for 3 min under a constant rotation speed (Fig. 2c); no shear-induced demixing could be observed for this blend. It is apparent that, the shear could significantly influence the phase boundary of the blend depending on the experimental temperature and the applied shear rate.

The cloud points under different values of shear rate are shown in Fig. 3. Obviously, the applied shear rate can strongly affect the values of the cloud points. The cloud points decrease with shear rate, i.e. the shear suppresses the phase separation and enlarges the homogeneous region of the blends. The shifts of the phase boundaries with shear rate are quantitatively measured by the cloud points of the blends under simple shear flow.

Fig. 4 shows the phase diagrams under different shear rate values. One can see that the shear flow could shift the cloud points of the phase diagram a few degrees to lower temperatures depending on the values of the applied shear rate and sample compositions. The samples of PMMA-rich composition are much more sensitive to the shear effect than that of PS-rich composition. This may be attributed to the fact that
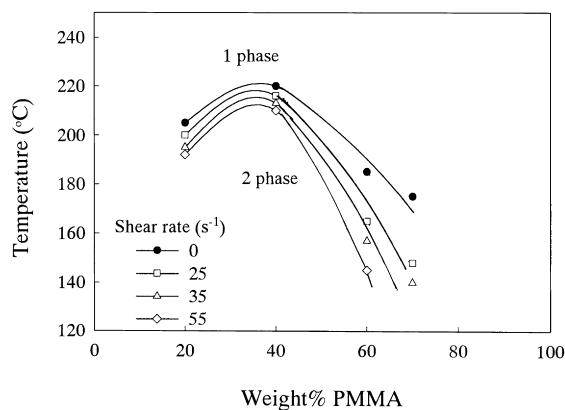
the depression of the cloud points under shear flow greatly depends on the value of the viscosity ratio of dispersed phase for matrix phase. For this reason, the complex dynamic viscosities of the pure polymer components were measured at 135°C. Typical experimental data of the shear rate dependence of the viscosity of the two pure components are shown in Fig. 5. Both materials show Newtonian behaviour over the measured frequency range at the given temperature (135°C), due to the low molecular weight. The viscosities of PS and PMMA were about 250 and 14,000 Pa s, respectively. This gives a viscosity ratio of $56(= \eta_{PMMA}/\eta_{PS})$ when PMMA was in a dispersed phase, while giving $0.018(= \eta_{PS}/\eta_{PMMA})$ when PMMA was a continuos phase. The influence of viscosity ratio on the phase behaviour of a series of blends of PMMA/SAN with different PMMA molecular weight was thoroughly investigated in a previous work [28]. It was found that, the elevation of the cloud points under shear flow is strongly dependent on the value of the viscosity ratio. A maximum elevation of the cloud point was detected at a viscosity ratio near to unity. According to this experimental fact, one can say that, the viscosity ratio plays a dominant role in the

Fig. 4. Changing of the phase diagram of the PS/PMMA blend under different shear rates.

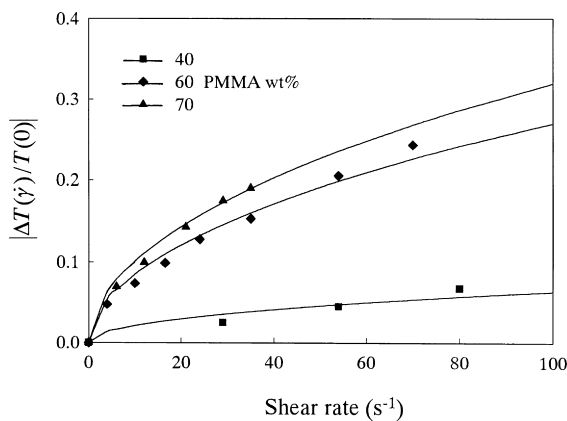Fig. 6. Normalized shifts in the cloud-point curve $|\Delta T(\dot{\gamma})/T(0)|$ as a function of $\dot{\gamma}$ for different compositions of the PS/PMMA blend.

Table 1
Values of fitting parameters to Eq. (3)

PMMA (wt%)	Prefactor, k	Exponent, n
70	0.031	0.501
60	0.027	0.502
40	0.008	0.50
20	0.0075	0.501

phase behaviour of the blend under shear flow and it is apparent that the value of the viscosity ratio must be taken into account, in particular, in understanding the state of the blend during processing. In this PS/PMMA blend, the values of viscosity ratio in both cases of PS and PMMA matrix are far from 1. However, it appears that the magnitudes of the depression of the cloud points when the more viscous PMMA is a matrix ($\eta_{PS}/\eta_{PMMA} = 0.018$) is much higher than when PMMA is in a dispersed phase ($\eta_{PMMA}/\eta_{PS} = 56$). This will be discussed again.

Fig. 6 represents the normalised shift in the cloud points $|\Delta T(\dot{\gamma})/T(0)| = |\{T(\dot{\gamma}) - T(0)\}/T(0)|$ versus shear rate ($\dot{\gamma}$) for different blend compositions. The following relation was given to the experimental data [29–31]

$$|\Delta T(\dot{\gamma})/T(0)| = k\dot{\gamma}^n \tag{3}$$

where k and n are material constants that depend on the composition. The experimental results can fit to this equation by using the non-linear regression method. The constant k and n are used as fitting parameters. Table 1 represents the values of the fitting parameters that are obtained from regression. Obviously, the exponent (n) is constant regardless of the composition of the blend, while the prefactor (k) greatly increases on increasing the ratio of PMMA in the blend. This is due to the fact that the cloud points of the blends of high PMMA content are much more sensitive to change under shear rate than that of lower PMMA content, as discussed above. This result may be attributed to the difference in the relaxation time of the different blend compositions, as we will discuss in the next section. The solid lines in Fig. 6 are computed from the above equation using the parameters listed in Table 1, while the points are experimental.

Table 2
Values of fitting parameters to Eq. (5) for different systems

System	Prefactor, k	Exponent, n
Simple liquid mixture (cyclohexane/ aniline) [30,31]	$(5.9 \pm 0.66) \times 10^{-7}$	0.53 ± 0.03
Polymer solution (PS/PB/ DOP) [6]	$(2.6 \pm 0.6) \times 10^{-3}$	0.5 ± 0.02
Low molecular weight polymer blend (PMMA/PS)	$0.0075 - 0.031$	0.5 ± 0.02
High molecular weight polymer blend (PMMA/SAN) [26]	$0.015 - 0.045$	0.5 ± 0.02

3.2. Comparison with simple liquid mixtures, polymer solutions, and high molecular weight polymer blends

The drop in cloud points as a function of shear rate of the critical temperature in the case of simple liquid mixtures of cyclohexane and aniline was investigated by Beysens et al. [29–31], their experimental data was given by

$$|\Delta T(\dot{\gamma})/T(0)| = (5.9 \pm 0.66) \times 10^{-7}\dot{\gamma}^{0.53 \pm 0.03} \tag{4}$$

It is worth noting that the prefactor value is much smaller than in the present case (PS/PMMA, see Table 1), but the value of the exponent is almost the same. Therefore, one can say that the observed drop in the cloud points of PS/PMMA blends is larger than that observed for simple liquid mixtures by about 4–5 orders of magnitude [30–31]. A similar comparison can be made for the cases of high molecular weight polymer blends and polymer solutions. Table 2 summarises the values of the prefactors and the exponents of the four different systems. It is clear that all the systems are given by the following relation

$$|\Delta T(\dot{\gamma})/T(0)| = k\dot{\gamma}^{0.5} \tag{5}$$

where the values of exponent n are almost constant (0.5) in all cases, regardless of the type of system under shear. However, the values of k greatly depend on the system under consideration; k values decrease from high molecular weight polymer blends (PMMA/SAN) to simple liquid mixtures. This may be attributed to the fact that, the effect of shear on the cloud points is much more sensitive in the high molecular weight polymer blends, whereas the sensitivity decreases in the simple liquid mixtures. According to this result one can say that the sensitivity of the cloud points to the effect of applied shear rate in the different systems moves with the same order as the prefactor value in the different cases, with a greater value of the prefactor giving greater sensitivity of the cloud points to the application of shear rate. These reported results are in good agreement with a renormalisation group theory of Onuki and Kawasaki [32–34] who predicated the following equation for small molecular system

$$|\Delta T(\dot{\gamma})/T(0)| = p\dot{\gamma}^{1/3\nu} \tag{6}$$

where the prefactor p is given by

$$p = 0.0832\epsilon\tau_\xi^{1/3\nu} \tag{7}$$

and $\epsilon = 4 - d_s$, $1/3\nu = 0.5$. ν is a universal constant that depends on spatial dimensionality d_s. τ_ξ is the characteristic relaxation time for the fluctuations in the concentration of the mixture. Eq. (7) predicted that the larger the characteristic time (τ_ξ) for the fluctuations in the concentration, the larger the change in the cloud point. This general principle can be applied also to a polymeric system (polymer solution [6] and low and high molecular weight polymer blends [26]), since the relaxation time decreases from high molecular weight polymer blends to simple liquid mixtures and becomes very small. Therefore, the large difference in the
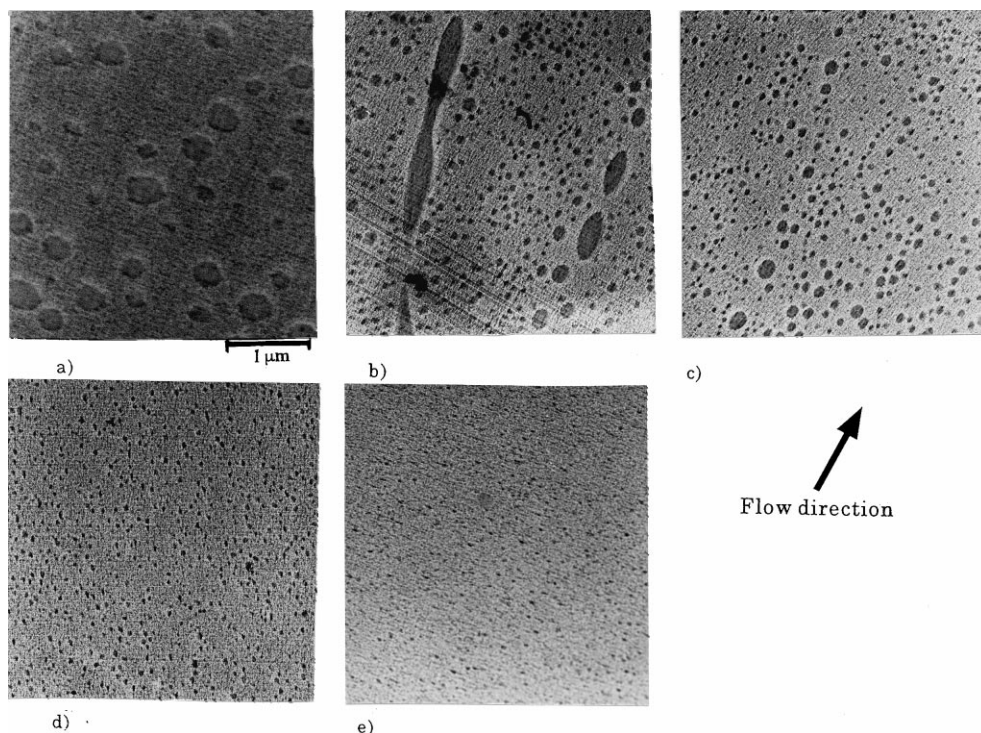
Fig. 7. TEM pictures of PS/PMMA (30/70) samples that were sheared at 140°C (35°C below their quiescent cloud point) at 0.85 rad/s for 3 min and then quenched in a water bath. Samples were then taken from different radial positions at different shear rates: (a) $\dot{\gamma} \approx 0 \text{ s}^{-1}$; (b) 4.25 s^{-1}; (c) 12.75 s^{-1}; (d) 21.25 s^{-1}; (e) 29.75 s^{-1}.

prefactor values, which reflects the sensitivity of the different systems to shear rate, is not surprising at all.

In the case where the dynamics of the concentration fluctuations is governed by hydrodynamic interactions, for example, the characteristic relaxation time τ was given by the following equation [25],

$$\tau = 6\pi\eta\xi_0^3/k_B T \qquad (8)$$

where η is the mixture viscosity, k_B is the Boltzmann constant and ξ_0 is the microscopic length, which is often expressed by $\xi_0^2 \sim R_g^2/3$ for the polymer unperturbed chain, R_g being radius of gyration. Though τ in Eq. (8) does not strictly correspond to τ_ξ in Eq. (7), Eq. (8) can be used to explain the character of τ_ξ qualitatively. From Eq. (8) it is understood that the value of τ increases from simple liquid mixtures to high molecular weight polymer blends because the values of both η and ξ_0 increase. Consequently, the prefactor p expressed by Eq. (7) increases from simple liquid mixtures to high molecular weight polymer blends, as shown in Table 2. However, for the system with a high concentration of the polymer, it is expected that the contribution of the hydrodynamic interactions become less important because the viscoelastic effects play an important role. Therefore Eq. (8) may not be applicable for polymer blends; a more quantitative analysis about τ_ξ, including its dependence on the degree of polymerisation N and η, will be in the next step of this study.

At the same time, it is well known that the shear can reduce the characteristic relaxation time of concentration fluctuations τ_ξ only when it has enough time to distort them, i.e. when $\dot{\gamma}^{-1} < \tau_\xi$. In general there are two different situations that can be obtained depending on the shear rate value and the relaxation time of the concentration fluctuations [29]: (1) when $\dot{\gamma}\tau_\xi < 1$ the shear has no effect on the critical properties, i.e. nothing changes during shear flow; and (2) when $\dot{\gamma}\tau_\xi > 1$ the shear could suppress the concentration fluctuations and the shear-induced mixing may occur, as in the present case. Therefore, this result can be attributed to the difference in the relaxation times of the four different systems; the greater the relaxation time, the greater will be the effect of the shear rate.

According to the above discussion, the shear effect can be attributed to the difference in the prefactor values, which are listed in Table 1, for PS/PMMA oligomer mixture of different compositions depending on the relaxation times of the concentration fluctuations. The melt viscosity of PMMA is much higher than that of PS at the experimental temperature (see Fig. 5). Thus, the blends of high content of PMMA are much more viscous than those with low PMMA content, which leads to in turn to very long relaxation times for blends of PMMA-rich composition and consequently high sensitivity of the cloud points to change under shear flow. According to this experimental fact, one can say that the phase behaviour of blend under shear flow can be changed with blend composition due to the difference in relaxation

time, which reflects different sensitivity of the cloud point to change under shear flow.

3.3. Morphology under shear rate

The morphology of the two-phase region under flow field has also attracted considerable attention in recent year. The morphology of this system was analysed under different shear rates by TEM. A sample of PS/PMMA = 30/70 was sheared by a constant rotation speed (0.85 rad/s) at 140°C (35°C below its equilibrium cloud point) for 3 min (enough time to obtain a quasi-equilibrium state, i.e. no change in the morphology for a long time). After that the two glass plates with the sample were taken out of the shear apparatus and rapidly quenched in a water bath. Six pieces were taken from different radial positions of the disk (different shear rates), and their morphologies were examined by TEM using ultramicrotomic slices cut parallel to the flow direction.

The typical morphology observed in the different pieces at different shear rate values is represented in Fig. 7. The dark region corresponds to the PS-rich phase and the bright matrix to the PMMA-rich phase. It is very clear that, at the centre of the sample (nearly zero shear rate) a well-defined phase separation of the blend is obtained with large PS-rich domains dispersed in the PMMA-rich matrix. Under the shear, the PS-rich domains are slightly elongated and oriented in the direction of the flow, then they are broken-up into very small particle sizes at a high shear rate. At shear rates of 4.25 and 12.75 s^{-1}, the TEM results showed that the bigger PS-rich domains were broken-up into small particles, characterised by slight elongation and orientation in the flow direction. At higher shear rates, i.e. 21.25 and 29.75 s^{-1}, the PS-rich domains were broken-up gradually to give a very small domain size with a good distribution, in which the detection of the flow direction becomes very difficult. No TEM result was detected at 34 s^{-1} indicating shear-induced mixing at this critical shear rate value (34 s^{-1}). From these results one can classify the change of morphology into three regimes, according to the value of the applied shear rates. In regime I, at nearly zero shear rate (centre of the disk) the sample phase-separated into two phase-structures: PS-rich domains and PMMA-rich matrix. In regime II at shear rates smaller than the critical shear rate, the morphology showed that the larger PS-rich domains were broken-up into small particles, which were characterised by slight elongation and orientation in the flow direction. Finally, in regime III at a shear rate higher than the critical shear rate no morphology can be observed by TEM. It is noted here that the morphologies under shear in Fig. 7 are located in the strong shear rate region, i.e. $\dot{\gamma}\tau_\xi > 1$ (The characteristic relaxation time for concentration fluctuations τ_ξ for PS/PB/DOP mixture has been evaluated by Hashimoto et al. [5,6]. The value of $\tau_\xi \sim 6$ s was calculated by the growth rate of the intensity at the peak wave number $q_m(0)$, in the early stages of spinodal decomposition after cessation of the strong shear. Accordingly, one can expect that the value of τ_ξ for our system

must be at least higher than Hashimoto's value due to the high sensitivity of PS/PMMA to the shear effect than polymer solutions, as explained in the previous section.). At this region, the structure of the critical fluctuations is expected to be strongly suppressed, i.e. the shear rate could enlarge the homogenous region.

These results are in close agreement with a previous study [26] of the morphology of PMMA/SAN = 75/25 under shear. It was observed that the shear-induced mixing occurred at a critical shear rate value, below which the two phases were highly oriented and elongated in the flow direction. Three regimes of different morphologies were also detected, depending on the applied shear rate values. In regime I, at nearly zero shear rate (centre of the disk) a well-defined phase separation co-continuous of two SAN-rich and PMMA-rich phases took place. Regime II corresponds to the modest shear rate values (up to 7 s^{-1}); the morphology indicated a highly elongated two-phase occurrence with a high degree of orientation parallel to the flow direction and a large decrease in the periodic distance. Finally, in regime III at 10 s^{-1} no morphology was observed as a result of shear-induced mixing at the critical shear rate value (10 s^{-1}). The highly elongated morphology of the PMMA/SAN blend is due to the fact that, the viscosity of the two components are very close to each other and the viscosity ratio is almost unity. However, on other hand, the morphology of the PS/PMMA blend is not as highly oriented as a PMMA/SAN blend under shear flow due to the very small value of its viscosity ratio (0.018). Thus, it is highly unlikely that the deformation and orientation of the two phases in the blend occurred under shear. According to these experimental facts, one can say that under shear flow the macroscopic phase separation cannot occur. At the critical shear rate, the macroscopic phase boundary is broken into pieces with small domains, which can be elongated and oriented in the direction of flow, decreasing the concentration fluctuations of the blend and consequently enhancing the mixing of unlike segments.

4. Conclusions

Shear-induced depression of the cloud points of the UCST-type phase diagram in an oligomer mixture of PS/PMMA has been observed. The magnitudes of the depression of the cloud points were found to be composition dependent. A comparison of this system under shear rate with high molecular weight polymer blends and ternary mixture of polymer solutions, as well as simple liquid mixtures, indicated that the cloud points of this system were much more sensitive to the shear rate than those of both polymer solutions and simple liquid mixtures and slightly less sensitive than high molecular weight polymer blends. This result was attributed to the difference in relaxation times for the concentration fluctuations of the four systems, where the larger the relaxation times the larger the change in the cloud points. This is in good agreement

with the renormalisation group theory of Onuki and Kawasaki [32–34].

The morphology of the PS/PMMA = 30/70 blend under different shear rate at 35°C below its quiescent cloud points, showed different morphologies (three regimes) depending on the values of the applied shear rate. At nearly zero shear rate (centre of the disk, regime I), a well-defined phase separation of PS domains in PMMA matrix was observed. At modest shear rate values (regime II), the PS domains were broken-up and were slightly elongated, parallel to the flow direction. Finally, in regime III no morphology was detected due to shear-induced mixing at a shear rate higher than the critical shear rate (34 s^{-1}).

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