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Effects of shear flow and annealing on the morphology of rapidly precipitated immiscible blends of polystyrene and polyisoprene

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Binary blends of polystyrene (PS) and polyisoprene (PI) were prepared by rapidly precipitating a homogeneous solution, consisting of PS, PI and toluene, into methanol under vigorous agitation. In this study, a series of PSs and PIs were synthesized via anionic polymerization in our laboratory. Portions of the as-precipitated blend were annealed at 110°C for different periods up to 12 h and the rest was extruded at 160 or 180°C using a capillary die. The extrudates were also annealed for different periods up to 12 h. Then, the morphology of the as-precipitated blend with and without annealing, and the extrudate with and without annealing, was investigated using transmission or scanning electron microscopy. We found that: (1) the as-precipitated blend had a co-continuous (or quasi co-continuous) morphology, often observed in two-phase polymer mixtures which have undergone spinodal decomposition; (2) annealing or extrusion transformed the initially co-continuous (or quasi co-continuous) morphology of the as-precipitated blend into a well-defined dispersed two-phase morphology; (3) during annealing, the elongated droplets in an extrudate specimen recoiled considerably, the extent of which depended upon the duration of annealing. The effects of blend composition and the viscosity ratio of the constituent components on two-phase blend morphology are discussed. Copyright © 1996 Elsevier Science Ltd.

(Keywords: polymer blends; phase morphology; rapid precipitation)

INTRODUCTION

Today it is well established that the mechanical properties of a two-phase polymer blend depend on its morphology, which in turn depends on: (i) the extent of miscibility between the constituent components; (ii) the surface energy associated with the interfacial tension; (iii) the rheological properties of the constituent components in the molten state; (iv) blend composition; (v) processing conditions, e.g. extrusion rate, temperature, etc.[1-4]. In the processing of two-phase polymer blends, two steps are involved: the first step is the melt-blending of two polymers using a batch mixer (e.g., Banbury) or a continuous mixer (i.e., twin-screw extruder) and the second step is the shaping and solidification of the melt-blended stream using fabricating equipment (e.g. an injection moulding machine). The first step may be termed as 'compounding' and the second step as 'fabrication'. Invariably, the morphology of the blend generated during compounding will further be changed during fabrication. This then suggests that the morphological state of a two-phase polymer blend in the respective steps be monitored in order to obtain consistent mechanical/physical properties of the fabricated product. Although during the past decades numerous experimental studies have been reported in the literature which dealt with two-phase polymer blends (there are too many references to cite them all here)[1-4], our understanding of the fundamental mechanisms associated with morphology development in two-phase polymer blends is far from complete.

Earlier, in an effort to establish a procedure for controlling the morphology of two-phase polymer blends, Nauman *et al.*[5] prepared blends of polystyrene (PS) and polybutadiene (PB) by flash devolatilization, thereby evaporating rapidly the solvent in a homogeneous solution containing PS and PB. They reported that the resultant morphology of PS/PB blends depended on the rate of solvent evaporation and blend composition. Since the blend prepared by flash devolatilization was not influenced by kinematic variables, Nauman *et al.*[6] discussed the morphology of PS/PB blends from the viewpoint of polymer solution thermodynamics.

Very recently, we prepared binary blends of PS and polyisoprene (PI) by rapid precipitation,[7] in which PS and PI were first dissolved in a common solvent, toluene, and then they were rapidly precipitated out upon contact, under vigorous agitation, with a non-solvent, methanol. Although rapid precipitation is conceptually very similar to flash devolatilization, the former has the advantage over the latter in that, the polymers containing little solvent precipitate out instantly upon contact with a non-solvent. According to Nauman *et al.*[6], in flash devolatilization the solvent in the polymer solution could

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not be removed instantly and considerable amounts of solvent had to be removed in subsequent steps.

Having prepared PS/PI blends by rapid precipitation, we investigated the morphology of the blends by transmission electron microscopy (TEM). We then annealed as-precipitated blends in a vacuum oven at a temperature above the glass transition temperature (T_g) of the PS and then investigated the morphology of the annealed blend. In order to study the effect of kinematic variables on blend morphology, a portion of the as-precipitated blends was extruded using a capillary die and then the morphology of the extrudates with and without annealing was investigated using TEM or scanning electron microscopy (SEM). In this paper we report the highlights of our findings.

EXPERIMENTAL

Materials and blend preparation

The polymers used in this study are monodisperse PS and PI. *Table 1* summarizes the molecular characteristics of the polymers employed in this study. All the polymers, except for PI-170 which was supplied by Dr A. Halasa at Goodyear Tire & Rubber Company, and PI-32 which was supplied by Shell Development Company, were synthesized via anionic polymerization in our laboratory.

Rapid precipitation[7] was employed to prepare blends of PS and PI. Specifically, PS and PI were dissolved in toluene at room temperature to form a homogeneous solution (2 wt% polymer), which was then stirred for at least 24 h. *Table 2* shows the blend combinations investigated along with the compositions. Note that *a priori* calculation confirmed that the polymer concentration utilized had guaranteed a homogeneous solution for all blend combinations investigated.

Figure 1 gives a schematic of the rapid precipitation setup employed in this study, which is comprised of a six-blade turbine centrally placed in a perforated draft tube. The impeller rotation speed was controlled by a variable speed motor, and the system was maintained at −72°C by a mixture of dry ice and ethanol. Such a low temperature was necessary in order to fix the PI phase upon phase separation. Initially, the tall form beaker containing both the draft tube and the rotating shaft was charged with methanol, 6/1 methanol/polymer solution, by volume. While rapidly stirring to create turbulence and intimate mixing, the polymer solution was slowly poured into the draft tube. Immediate precipitation of the polymers was observed upon the polymer solution's contact with the circulating methanol pool. Except for the PS-76/PI-170 blend, all other precipitates were dried in the following manner: (i) the suspension of the precipitated polymers in a liquid mixture of toluene and methanol was filtered at room temperature; (ii) the precipitates were then vacuum-dried in an oven at 40°C for at least 24 h; (iii) the dried blends were then stored in the freezer to minimize morphological changes. Hereafter, the precipitates dried in this manner will be referred to as 'oven dried'.

Table 1 Molecular characteristics of polymers employed

Sample code	M_w	M_w/M_n
PS-150	150 000	1.11
PS-76	76 000	1.05
PS-43	43 000	1.05
PI-170	170 000	1.12
PI-118	118 000	1.07
PI-32	32 000	1.03

Table 2 PS/PI blends investigated

Sample code	Blend composition (wt%)
PS-76/PI-170	70/30
PS-150/PI-118	70/30, 50/50, 30/70
PS-150/PI-32	50/50
PS-43/PI-118	50/50

For the PS-76/PI-170 blend (see *Table 2*), a small volume of the suspension from the rapid precipitation step was dried, using a set-up similar to freeze-drying where volatile liquids were removed under high vacuum. The precipitates dried in this manner will be referred to as 'as-precipitates'. During the removal of the toluene and methanol mixture, the suspension was maintained at -50 ± 8°C by a combination of dry ice and pyridine. It was not feasible to run the process at a temperature below the T_g (*ca* −60°C) of the PI, because at such a low temperature both extremely high vacuum and impractical process times would have been required. The rest of the as-precipitates for capillary extrusion was dried at room temperature for at least 10 h under high vacuum. All precipitates were stored in dry ice.

Preparation of extrudate

An Instron capillary rheometer (Model 3211, Instron Company) with a capillary diameter of 0.15 cm and a length-to-diameter ratio of 28.5 was utilized to extrude the as-precipitated blends. Initially, all the precipitates were vacuum-compression moulded at room temperature to pack the blends such that void formation would be minimized during the extrusion process. Except for the PS-76/PI-170 blend which was extruded at 160°C and

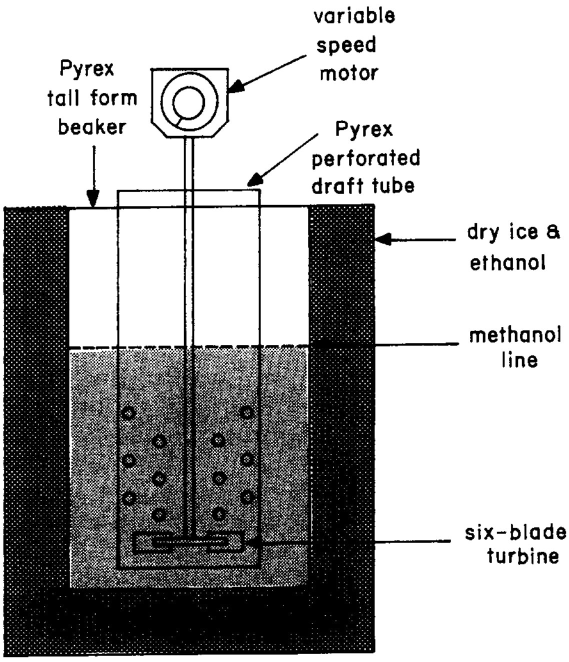

Figure 1 Schematic describing the apparatus used for rapid precipitation

shear rates ($\dot{\gamma}$) of 1.3 and 8.7 s^{-1}, all other blends were extruded at 180°C and $\dot{\gamma} = 1.3\,\mathrm{s}^{-1}$. Such low shear rates were used because of insufficient amounts of as-precipitated blends available. All blends remained in the rheometer barrel at the extrusion temperature for a maximum of 20 min since the residual packing pressure created by the sample purge had to be relaxed before extrusion. All extrudates were cooled at room temperature and then stored in the freezer.

Isothermal annealing

All annealing was performed, due to its precise and accurate temperature control, using a Rheometrics Mechanical Spectrometer (RMS 800, Rheometrics Inc.). The PS-76/PI-170 as-precipitates were annealed at 110°C for 2 min, 6 min, $\frac{1}{2}$ h, and 12 h. The PS-76/PI-170 extrudates were annealed at 110°C for $\frac{1}{2}$, 2 h, and 12 h. Upon removal from the RMS fixture, all extrudates and precipitates were immediately quenched in liquid nitrogen to freeze-in the existing morphology.

Rheological measurement

The PS sample was prepared in the following way for rheological measurements: PS powder was initially dried in a vacuum oven at 100°C for about 1 week to completely remove any volatiles left over from polymerization. The dried PS was then vacuum-compression moulded at 160°C into 25-mm diameter disks. Sample preparation for PI was carried out in the following manner: PI was dissolved in toluene with an antioxidant (Irganox 1010, Ciba-Geigy Corp.; 0.1 wt% of polymer) to make a 10 wt% polymer solution. The solution was stirred overnight and then the solvent was slowly evaporated in a fume hood for a week. Subsequently, the sample was placed in a vacuum oven for 4 days at room temperature and for three days at 40°C. Finally, the oven temperature was raised to 110°C (10°C h^{-1}), and the weight of the sample measured thereafter, until constant mass was reached. Such careful steps were necessary to guarantee complete absence of the solvent.

For the PS-76/PI-170 blend, rheological properties of the constituent homopolymers were measured with a cone-and-plate rheometer (RMS 800, Rheometrics Inc.) in the steady-state mode under a nitrogen atmosphere at 160°C. Shear viscosity (η) and the first normal stress difference (N_1) were measured over a range of $\dot{\gamma}$ from 0.01 s^{-1} to *ca* 1 s^{-1}.

Microscopy

A TEM (JEM 1200EX II, JEOL) was used to take micrographs of as-precipitates and annealed precipitates for all the PS/PI blend specimens investigated. As-precipitates and annealed precipitates were first embedded in an epoxy (EPON 828) and cured at room temperature using a 10 wt% triethylenetetramine. Complete curing took about 24 h. For TEM the embedded samples were then cryo-ultramicrotomed using a Reichert Ultracut S (Leica) microtome equipped with glass knives. Sections 0.05 μm thick were obtained at −100°C and stained with osmium tetroxide vapour for 5 min. Except for the PS-76/PI-170 extrudates, all of the extrudates were prepared in a manner similar to that of as-precipitates and annealed precipitates. Sections 0.05 μm thick were obtained at −100°C both perpendicular and parallel to the extrusion direction and stained with osmium tetroxide vapour for 15 min. Sections were then examined using TEM.

The PS-76/PI-170 extrudates were polished at −100°C to create a flat surface using a Reichert Ultracut S (Leica) microtome equipped with glass knives. Extrudates were trimmed both perpendicular and parallel to the extrusion direction to obtain a three-dimensional image. The dispersed PI phase was chemically extracted using *n*-pentane. The extrudates were then silver coated and micrographs of the extrudates were taken using a SEM (ISI SX-40 International Scientific Instrument Inc.).

RESULTS AND DISCUSSION

The morphology of as-precipitated PS/PI blends

The primary mechanism of phase separation in rapid precipitation is considered to be spinodal decomposition for the reason that the nucleation and growth mechanism is a slow rate process compared to spinodal decomposition[8,9]. Note that in rapid precipitation, the time elapsed by the solution in the metastable region is extremely short for any appreciable nucleation and growth to occur before the solution enters the unstable region wherein phase separation takes place by spinodal decomposition. Thus the expected morphology of a blend obtained by rapid precipitation is a modulated, interconnected, periodic structure typical of a system which has undergone spinodal decomposition[8]. The rapid precipitation process can best be illustrated by using a ternary phase diagram[10–12], such as the one shown in *Figure 2*, for ternary mixtures consisting of PS having the molecular weight (M_W) of 7.6×10^4, PI having M_W of 1.7×10^5, and toluene at 30°C. In *Figure 2*, both binodal and spinodal curves were constructed based on the Flory–Huggins theory, using the values of the Flory–Huggins interaction parameter χ in the literature[13].

Figure 2 illustrates that only a polymer concentration below *ca* 5 wt% does the solution form a single phase. The arrow in *Figure 2* indicates the process path for rapid precipitation. A homogeneous, single phase solution consisting of toluene, PS, and PI is rapidly quenched deep into the unstable, two-phase region via addition of

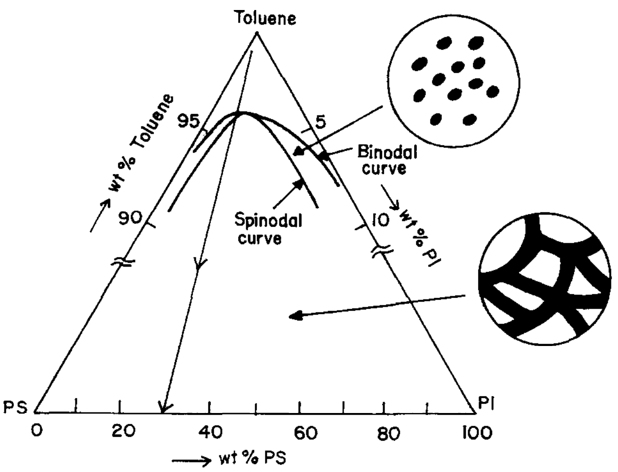

Figure 2 Phase diagram for a ternary mixture consisting of PS having M_w 7.6×10^4, PI having M_w 1.7×10^5, and toluene at 30°C, where the Flory–Huggins interaction parameters used are[13]: $\chi_{\text{PS-PI}} = 0.042$, $\chi_{\text{toluene-PS}} = 0.40$, and $\chi_{\text{toluene-PI}} = 0.37$

the non-solvent, methanol. The excessive amount of methanol, upon contact with the polymer solutions, causes the PS and PI to instantaneously phase separate or precipitate. The high molar mass polymer will precipitate first and from there on, in the order of decreasing molar mass. One can envision precipitation as a reversal of the dissolution process. Notice that upon addition of the non-solvent, the ternary system becomes quaternary, strictly speaking. Although *Figure 2* may indicate that the precipitation process leads to complete removal of the solvent, it actually means that both PS and PI have completely precipitated out of solution.

Figure 3 gives micrographs of: (a) an oven dried specimen; (b) the cross; (c) longitudinal sections of an extrudate, for 30/70 PS-150/PI-118 blend, where the dark areas represent the PI phase and the white areas represent the PS phase. Similar micrographs are given in *Figure 4* for 50/50 PS-150/PI-118 blend and in *Figure 5* for 70/30 PS-150/PI-118 blend. The extrudates were obtained by extruding an as-precipitated blend at 180°C at $\dot{\gamma} = 1.3\,\mathrm{s}^{-1}$. The 30/70 PS-150/PI-118 precipitate (see *Figure 3a*) shows a co-continuous or quasi co-continuous morphology with regions of concentrated PI phase. However, the as-precipitates of 50/50 PS-150/PI-118 blend (see *Figure 4a*) and 70/30 PS-150/PI-118 blend (see *Figure 5a*) do not have co-continuous morphology. Instead they have a morphology containing the PI phase (dark areas) dispersed in the PS matrix (white areas) with diffuse interface.

If spinodal decomposition is the sole mechanism for the formation of blend morphology by rapid precipitation, according to the Cahn theory of spinodal decomposition[8], one would expect a highly interwoven, interconnected structure in as-precipitated polymer blends, but such features are not observed in *Figures 4a* and *5a*. The lack of co-continuous morphology in *Figures 4a* and *5a* is attributable to the movements of the PI phase, which took place during the oven drying (at 40°C) of as-precipitates (see Experimental). Considering that the as-precipitates were exposed to a temperature

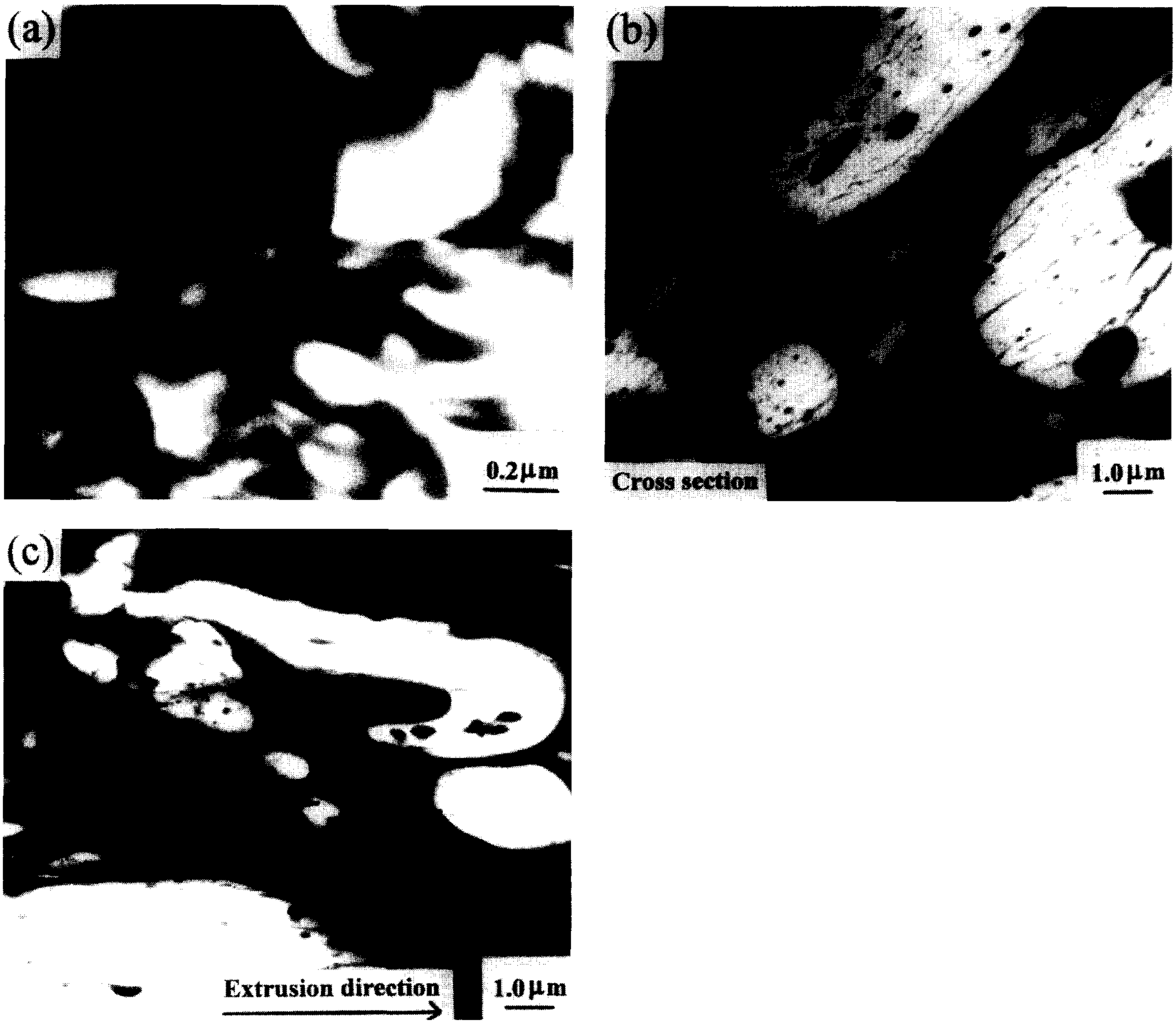

Figure 3 TEMs of: (a) oven dried 30/70 PS-150/PI-118 precipitates; (b) the cross section of an extrudate; (c) the longitudinal section of an extrudate. The extrudate specimen was obtained by extrusion of the precipitate in a capillary die at 180°C and $\dot{\gamma} = 1.3\,\mathrm{s}^{-1}$. The dark areas represent the PI phase and the white areas represent the PS phase

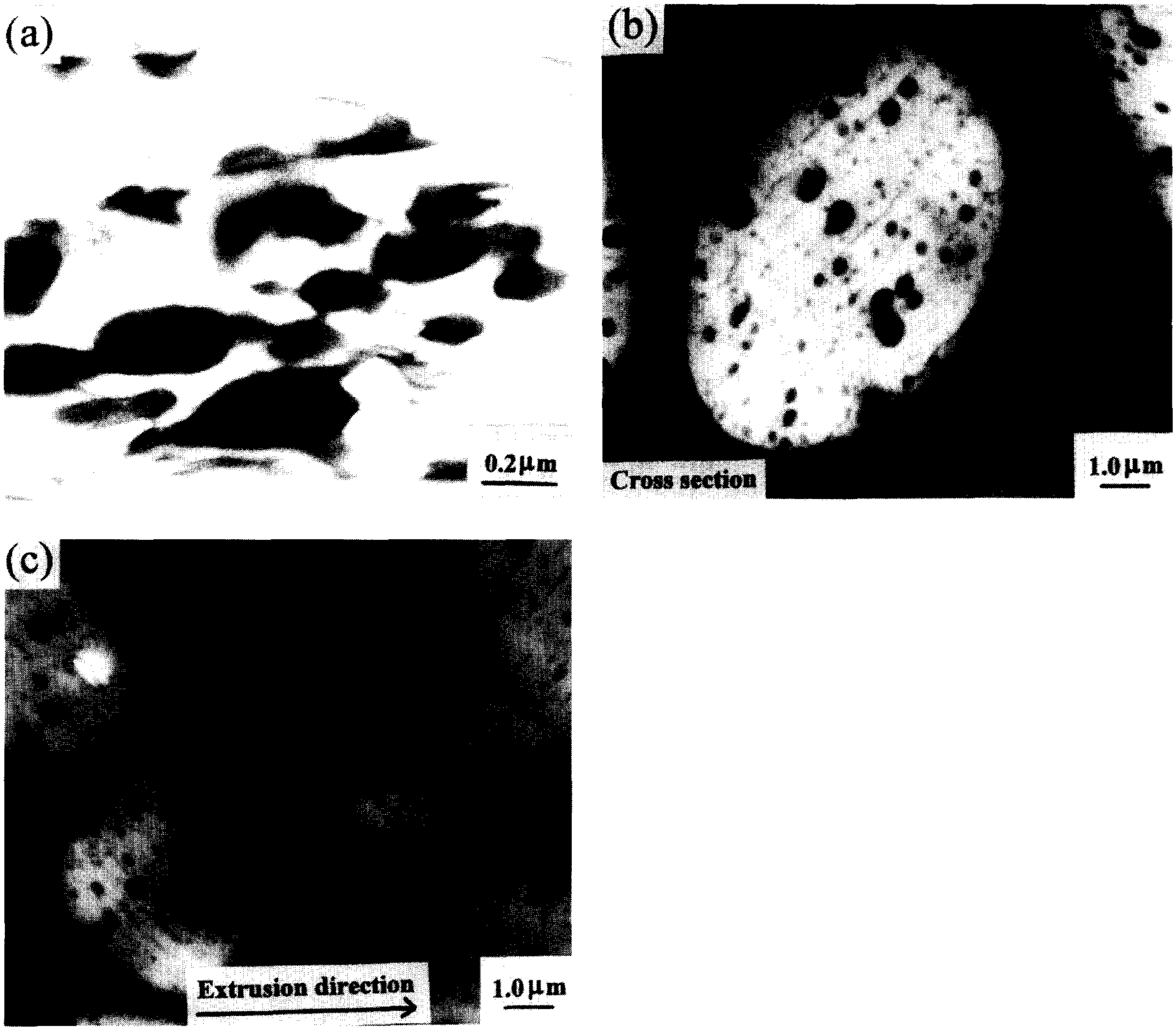

Figure 4 TEMs of: (a) oven dried 50/50 PS-150/PI-118 precipitates; (b) the cross section of an extrudate; (c) the longitudinal section of an extrudate. The extrudate specimen was obtained by extrusion of the precipitate in a capillary die at 180°C and $\dot{\gamma} = 1.3\,\mathrm{s}^{-1}$. The dark areas represent the PI phase and the white areas represent the PS phase

where the PI phase was mobile, the once co-continuous PI phase might have been destroyed. If the movement of the PI phase is possible, then coalescence, leading to a breakup of the co-continuous structure and formation of discrete domains, is inevitable[14,15]. Previously Vasishtha and Nauman[16] conducted computer simulations of a binary blend system undergoing spinodal decomposition and concluded that, without flow, a co-continuous structure remains intact, whereas under flow, co-continuity breaks down to form a dispersed-type morphology.

Effect of shear flow on the morphology of as-precipitated PS/PI blends

When an oven dried PS-150/PI-118 blend was extruded in a capillary die at 180°C, we obtained a dispersed two-phase morphology. Specifically: (1) in *Figures 3b* and *3c* we observe the PS phase dispersed in the PI matrix for 30/70 PS-150/PI-118 blend; (2) in *Figures 4b* and *4c* we observe also the PS phase dispersed in the PI matrix for 50/50 PS-150/PI-118 blend; but (3) in *Figures 5b* and *5c* we observe the PI phase dispersed in the PS matrix for 70/30 PS-150/PI-118 blend. In *Figures 3* and *5* the minor component forms the dispersed phase and the major component forms the continuous phase. In the 30/70 and 50/50 PS-150/PI-118 blends (*Figures 3b* and *4b*) the PS droplets have occlusions of PI phase (dark areas), while such occlusions are not seen in the 70/30 PS-150/PI-118 blend (*Figure 5b*). This difference may be explained as follows: in the 30/70 and 50/50 PS-150/PI-118 blends (*Figures 3* and *4*), the occlusions of PI phase in the PS droplets occurred due to the rearrangement of interfaces between the PS and PI phases during extrusion, whereas in the 70/30 PS-150/PI-118 blend (*Figure 5*) rearrangement of interfaces did not occur.

During the extrusion of oven dried PS-150/PI-118 blend in a capillary die, the viscosity ratio, besides blend composition, might have contributed to a dispersed-type morphology observed in *Figures 3–5*. According to *Table 3*, the viscosity of PS-150 is 27 times higher than

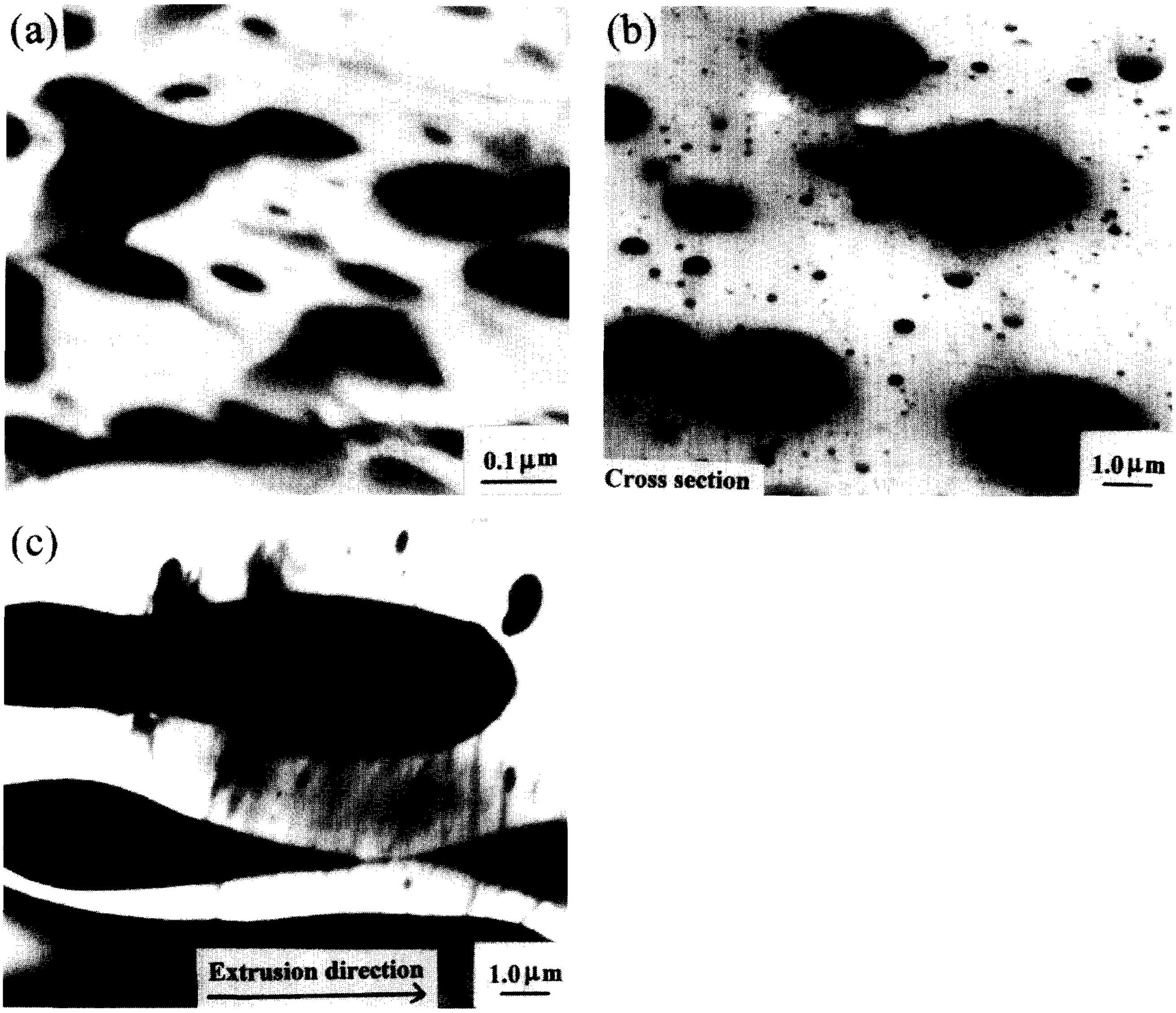

Figure 5 TEMs of: (a) oven dried 70/30 PS-150/PI-118 precipitates; (b) the cross section of an extrudate; (c) the longitudinal section of an extrudate. The extrudate specimen was obtained by extrusion of the precipitate in a capillary die at 180°C and $\dot{\gamma} = 1.3\,\mathrm{s}^{-1}$. The dark areas represent the PI phase and the white areas represent the PS phase

that of PI-118. This observation leads us to conclude that blend composition, not viscosity ratio, played a crucial role in determining the mode of dispersion during the extrusion of oven dried PS-150/PI-118 blend, because the less viscous PI with lower volume fraction formed the dispersed phase (*Figure 5b*) and the more viscous PS with lower volume fraction formed the dispersed phase (*Figure 3b*).

Let us further examine the extrudate morphology of two other blends, 50/50 PS-150/PI-32 and 50/50 PS-43/PI-118, given in *Figures 6* and *7*, respectively. Notice in *Table 3* that at 180°C, $\eta_{\mathrm{o,PS}}/\eta_{\mathrm{o,PI}} = 2200$ for 50/50 PS-150/PI-32 blend, and $\eta_{\mathrm{o,PS}}/\eta_{\mathrm{o,PI}} = 0.39$ for 50/50 PS-43/PI-118 blend. We observe that the more viscous PS formed the dispersed phase in 50/50 PS-150/PI-32 blend (*Figure 6*) and the more viscous PI formed the dispersed phase in 50/50 PS-43/PI-118 blend (*Figure 7*), suggesting that at an equal blend ratio, the viscosity ratio appears to have played a crucial role in determining the mode of dispersion.

What must now be answered is how the blend composition (ϕ_1/ϕ_2) and the viscosity ratio (η_1/η_2), neglecting the elasticity ratio for the time being, of the constituent components might interact to determine the mode of dispersion in a two-phase polymer blend. Earlier, an empirical correlation was suggested[17] that: (i) component 1 forms the dispersed phase and component 2 forms the continuous phase when $(\eta_1/\eta_2)(\phi_2/\phi_1) > 1$; (ii) component 2 forms the dispersed phase and component 1 forms the continuous phase when $(\eta_1/\eta_2)(\phi_2/\phi_1) < 1$; and (iii) a co-continuous structure forms when $(\eta_1/\eta_2)(\phi_2/\phi_1) \approx 1$, where η_1 and η_2 are the viscosities of components 1 and 2, respectively, and ϕ_1 and ϕ_2 are the volume fractions of components 1 and 2, respectively. In the present study, we found that such an empirical correlation cannot explain the mode of dispersion observed experimentally in the 70/30 PS-150/PI-118 blend (*Figure 5*) because PI formed the dispersed phase, while PS should have formed the dispersed phase in accordance with the empirical correlation. It is then fair to state that a comprehensive theory, based on first principles, is needed to predict the mode of dispersion in two-phase polymer blends

Table 3 Calculated zero-shear viscosity ratios, $\eta_{o,PS}/\eta_{o,PI}$ at 180°C

Sample code	$\eta_{o,PS}/\eta_{o,PI}$
PS-150/PI-118	27
PS-150/PI-32	2200
PS-43/PI-118	0.39

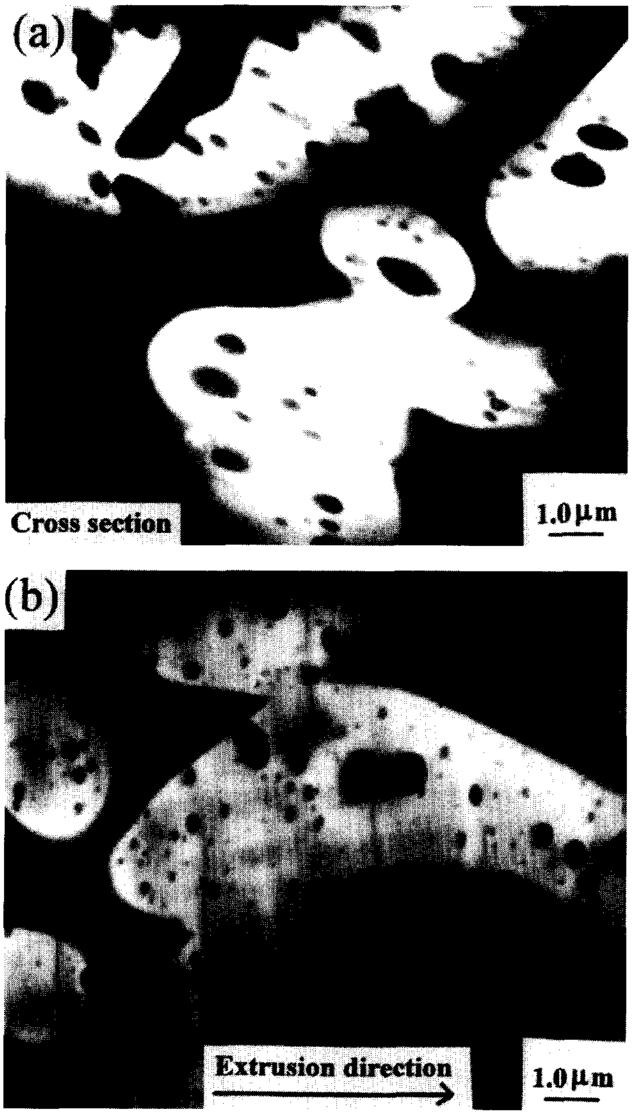

Figure 6 TEMs of an extrudate of 50/50 PS-150/PI-32 blend: (a) cross section; (b) longitudinal section. The extrudate specimen was obtained by extrusion of the precipitate in a capillary die at 180°C and $\dot{\gamma} = 1.3\,s^{-1}$. The dark areas represent the PI phase and the white areas represent the PS phase

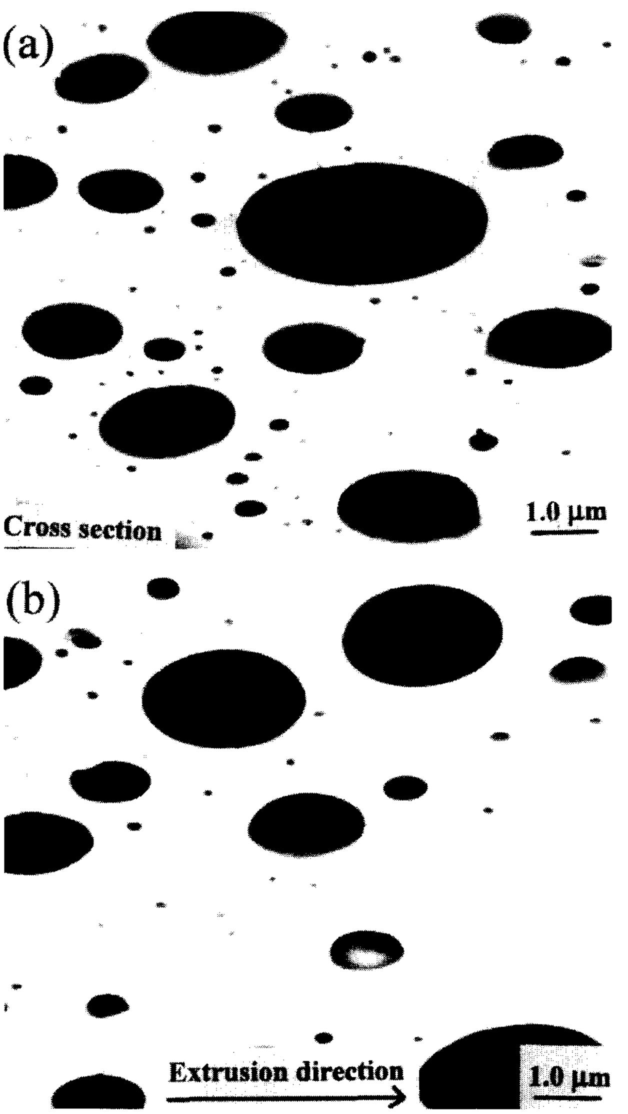

Figure 7 TEMs of an extrudate of 50/50 PS-43/PI-118 blend: (a) cross section; (b) longitudinal section. The extrudate specimen was obtained by extrusion of the precipitate in a capillary die at 180°C and $\dot{\gamma} = 1.3\,s^{-1}$. The dark areas represent the PI phase and the white areas represent the PS phase

in terms of blend composition and the rheological properties of the constituent components.

Let us now discuss the shape of the deformed dispersed phase (i.e. droplets) in the extrudates, displayed in *Figures 3–7*. There is hardly any deformation in the dispersed PS droplets in the 30/70 PS-150/PS-118 blend (see *Figures 3b* and *3c*), in the 50/50 PS/150/PI-118 blend (*Figures 4b* and *4c*), and in the 50/50 PS-150/PI-32 blend (see *Figure 6*). This can be explained by the viscosity ratio of the constituent components given in *Table 3*, i.e. the viscosity of the dispersed PS droplets is too high to bring any noticeable deformation during extrusion. In *Figure 5c*, however, PI droplets are deformed considerably along the flow direction. This can be explained by the fact that the viscosity of PI-118 is much lower than that of PS-150 in the PS-150/PI-118 blend. The extrudate morphology given in *Figure 7* for the 50/50 PS-43/PI-118 blend is quite different from that of the other blends in that, the droplet sizes are much smaller than those in the other blends given in *Figures 3–6*. Notice in *Table 3* that the viscosity ratio of PS-43 and PS-118, $\eta_{o,PS}/\eta_{o,PI}$, at the extrusion temperature of 180°C is 0.39, thus the viscosity of the dispersed PI-118 is 2.67 times the viscosity of PS-43 forming the matrix. According to the literature[18–21], the finest dispersion in two immiscible liquids may occur when the viscosity ratio of the dispersed phase (component 1) to the continuous phase (component 2), $\eta_{o,1}/\eta_{o,2}$, lies between *ca* 0.1 and *ca* 3.4. Therefore we should expect much finer dispersion of droplets in the

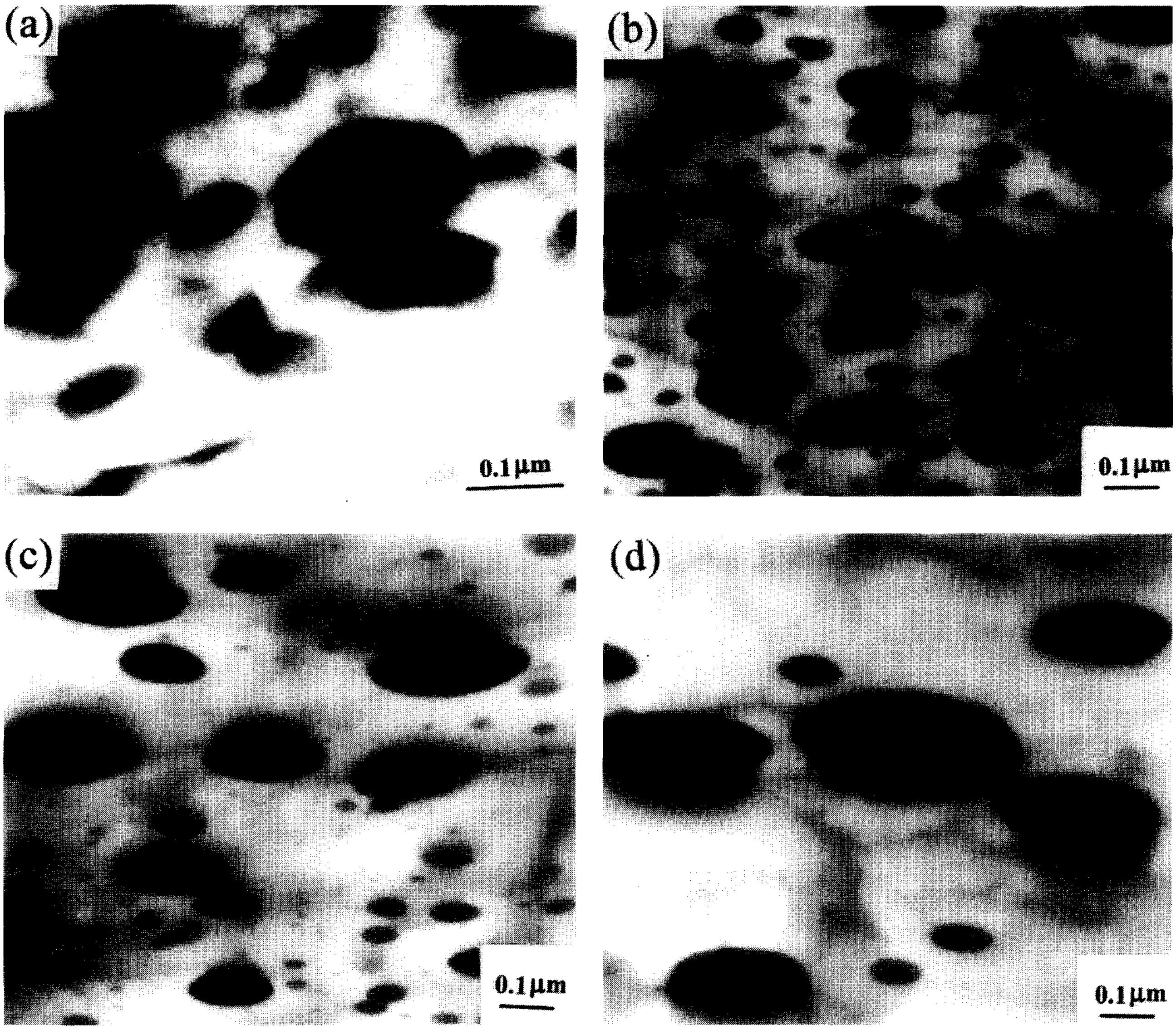

Figure 8 TEMs of 70/30 PS-76/PI-170 blend: (a) as-precipitated; (b) annealed at 110°C for 6 min; (c) annealed at 110°C for 30 min; (d) annealed at 110°C for 12 h. The dark areas represent the PI phase and the white areas represent the PS phase

50/50 PS-43/PI-118 blend than in the other blends, because the $\eta_{0,1}/\eta_{0,2}$ ratio is much larger than 3.4 for the 30/70 PS-150/PI-118, 50/50 PS-150/PI-118, and 50/50 PS-150/PI-32 blends, and the $\eta_{0,1}/\eta_{0,2}$ ratio is much less than 0.1 for the 70/30 PS-150/PI-118 blend. There are too many references to cite them all here which discuss the effect of viscosity ratio of the constituent components on the deformation and breakup of droplets in dispersed two-phase flow, and readers are referred to a series of papers by Han and coworkers[22-25] and his monographs[1,2]. Although many references appeared in the literature since the publications of Han's monographs, the essential features described therein have not changed.

Effect of annealing on the morphology of as-precipitated PS/PI blends

The effect of annealing on the morphology of as-precipitated 70/30 PS-76/PI-170 blend was investigated. For this we varied annealing temperature and the duration of annealing. The purpose of this investigation was to monitor the time evolution of blend morphology during isothermal annealing without external force (i.e. without shear flow).

Figure 8 gives micrographs of (a) as-precipitated specimen, and specimens annealed for (b) 6 min, (c) 30 min, and (d) 12 h at 110°C for 70/30 PS-76/PI-170 blend. The as-precipitated specimen (see *Figure 8a*) does not have a co-continuous morphology, as it should from the viewpoint of spinodal decomposition. Notice, however, in *Figure 8a* that the phase boundaries are diffuse. Bear in mind that the annealing temperature (110°C) employed in obtaining the specimens, the micrographs of which are given in *Figures 8b–8d*, is slightly above the T_g of PS phase, which is *ca* 100°C and all micrographs represent the average domain size. As expected, the average PI domain size increased and its size distribution broadened with increasing annealing time. These results are in agreement with previous findings[26,27]. Comparison of the micrograph of the specimen after annealing for 6 min (*Figure 8b*) with the micrograph of as-precipitated blend (*Figure 8a*) indicates that the average domain size of the dispersed PI phase is about the same, but the

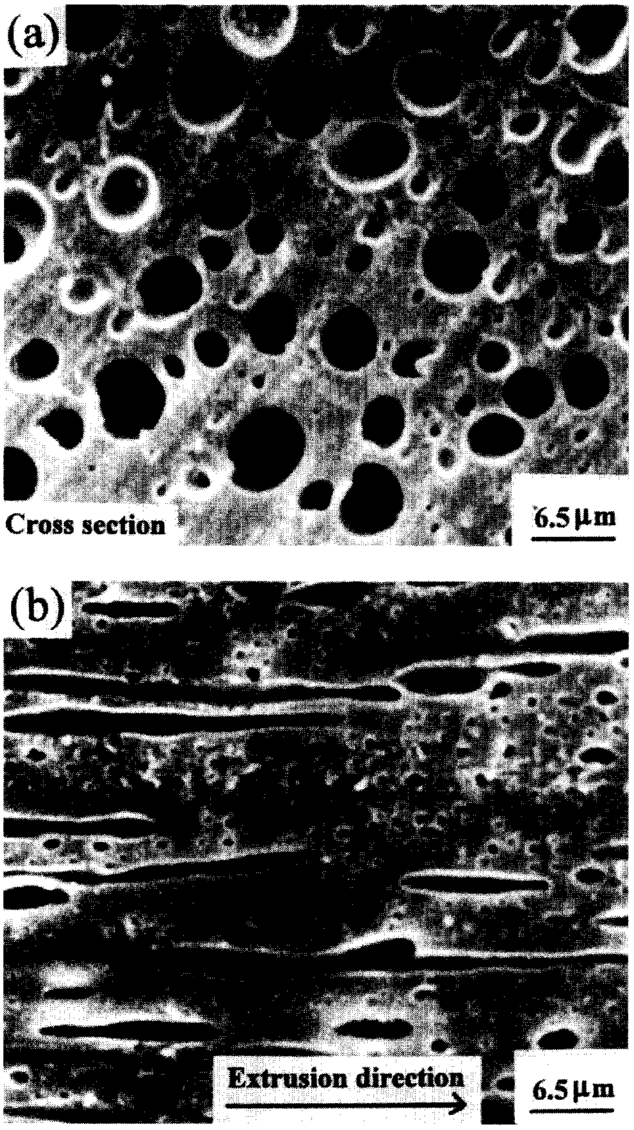

Figure 9 SEMs of an extrudate of 70/30 PS-76/PI-170 blend: (a) cross section; (b) longitudinal section. The extrudate specimen was obtained by extrusion of the precipitate in a capillary die at 160°C and $\dot{\gamma} = 1.3\,\mathrm{s}^{-1}$. The dark areas represent the PI phase and the white areas represent the PS phase

annealed precipitates have a broader size distribution compared to the as-precipitates. Notice that the magnifications of the micrographs between *Figure 8a* and *Figure 8b* are different. Also, the shapes of PI domains in the annealed precipitates are more or less spherical or ellipsoidal. As the annealing continued to 30 min and to 12 h, from *Figures 8c* and *8d* we observe that the domain size increased considerably, suggesting that smaller PI droplets coalesced during annealing. In other words, annealing induced growth of the dispersed phase by coalescence. With thermal energy as the force behind the droplet motion dispersed PI droplets of smaller sizes must have migrated towards others in the blend since the smaller droplets are more mobile. Upon droplet coalescence, interfacial tension will tend to resist droplet breakup. Intuitively speaking, with increasing annealing time, the probability of droplet motion and coalescence will increase, thus causing both the growth of the average domain size and broadening of its size distribution.

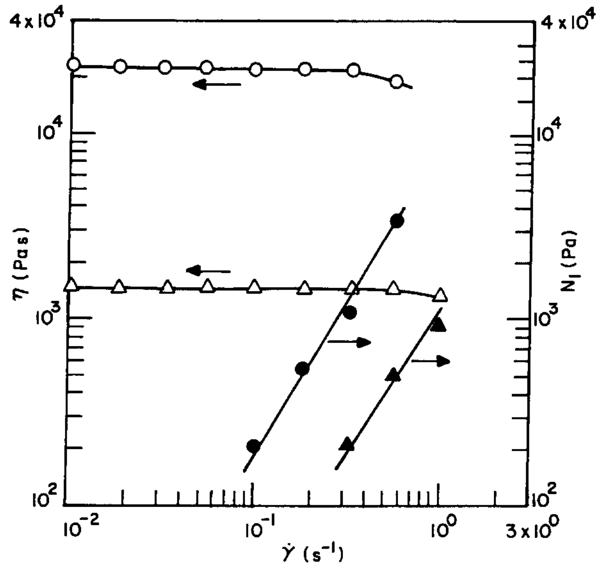

Figure 10 Plots of log η *versus* log $\dot{\gamma}$ and log N_1 *versus* log $\dot{\gamma}$ for PS-76 and PI-170 at 160°C: (○, ●) PS-76; (△, ▲) PI-170

Effect of annealing on the morphology of extruded PS/PI blends

Figure 9 gives micrographs of 70/30 PS-76/PI-170 blend extruded at 160°C and $\dot{\gamma} = 1.3\,\mathrm{s}^{-1}$. The morphology of the extrudate's cross section (*Figure 9a*) shows regularly shaped PI droplets dispersed in the PS matrix, while the morphology of the extrudate's longitudinal section (*Figure 9b*) shows PI droplets elongated along the extrusion direction. As mentioned in Experimental, the precipitates were kept inside the rheometer reservoir at 160°C for a maximum of 20 min before extrusion began. Therefore, it is reasonable to speculate that a considerable amount of annealing must have taken place before the extrusion actually began.

In order to assess the effect of the rheological properties of the constituent components on the blend morphology given in *Figure 9*, we measured steady-state shear viscosity (η) and first normal stress difference (N_1)

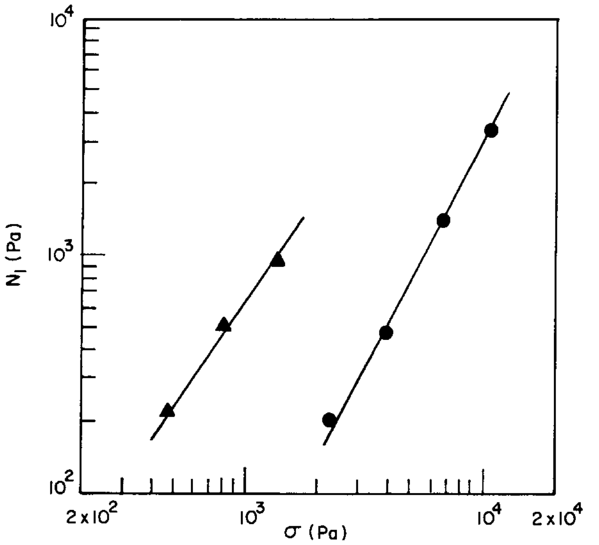

Figure 11 Plots of log N_1 *versus* log σ for PS-76 (●) and PI-170 (▲) at 160°C

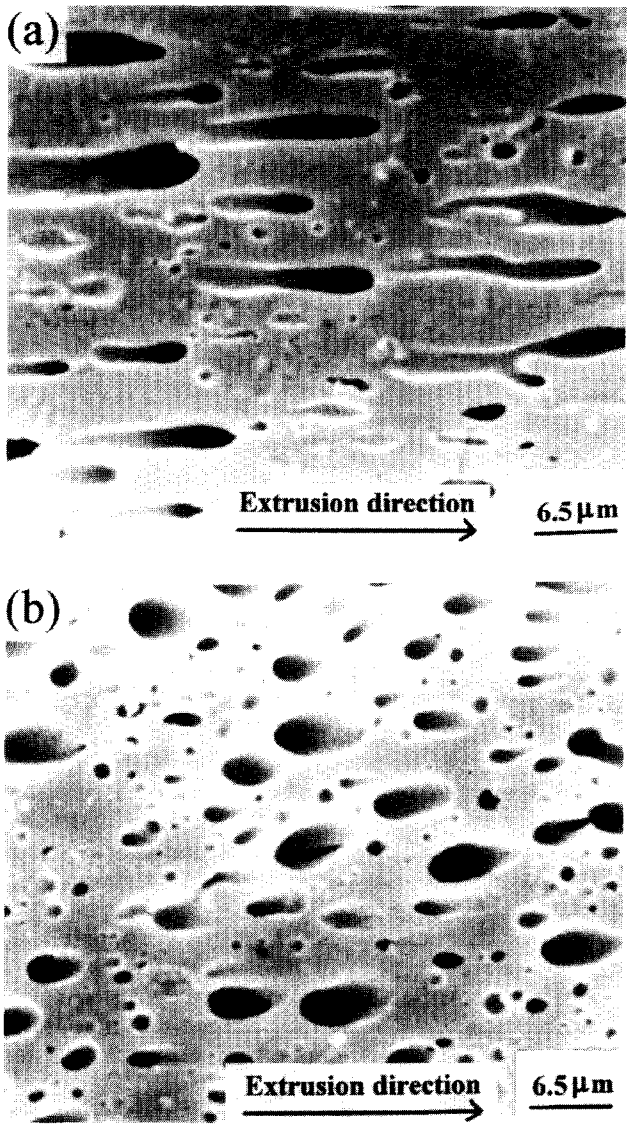

Figure 12 SEMs of the longitudinal section of extrudates of 70/30 PS-76/PI-170 blend, which were obtained by extrusion of the as-precipitated in a capillary die at 160°C and $\dot{\gamma} = 1.3\,\mathrm{s}^{-1}$. The specimen was later annealed at 110°C for (a) 30 min and (b) 12 h. The dark areas represent the PI phase and the white areas represent the PS phase

as functions of shear rate ($\dot{\gamma}$) for homopolymers PS-70 and PI-170, using a Rheometrics Mechanical Spectrometer (Model 800). *Figure 10* gives plots of log η *versus* log $\dot{\gamma}$ and log N_1 *versus* log $\dot{\gamma}$ for PS-76 and PI-170 at 160°C, showing the viscosity ratio of PS-76 to PI-170, $\eta_{0,\mathrm{PS}}/\eta_{0,\mathrm{PI}}$, to be about 15 at $\dot{\gamma} = 1.3\,\mathrm{s}^{-1}$. This means that the viscosity of PI-170 is only 6.7% of the viscosity of PS-76. This now explains why in *Figure 9b* the PI droplets are elongated considerably along the direction of extrusion.

We will now examine which of the two polymers, PS-76 or PI-170, is more elastic than the other. From *Figure 10* one may be tempted to conclude that PS-76 is more elastic than PI-170 because over the range of $\dot{\gamma}$ investigated, the values of N_1 for PS-76 are greater than those of PI-170. However, when values of N_1 are plotted against shear stress (σ), as given in *Figure 11*, we observe that over the range of σ investigated, the values of N_1 for PI-170 are greater than those of PS-76, leading us to conclude that PI-170 is more elastic than PS-76. Which of the two interpretations is correct is very important for correct assessment of the role of melt elasticity, relative to the melt viscosity, to the formation of blend morphology displayed in *Figure 9*. Han[1,2] suggested that plots of log N_1 *versus* log σ, instead of plots of log N_1 *versus* log $\dot{\gamma}$, be used to assess the significance of fluid elasticity. Based on this interpretation, we conclude that PI-170 is more elastic than PS-76. This conclusion leads us to state that, with reference to *Figure 9*, the less elastic PS phase encompasses the more elastic PI phase, which is contrary to the theory by van Oene[28]. Such discrepancy seems to suggest that the blend composition and the viscosity ratio of the constituent components might have a greater influence on the mode of dispersion in two-phase polymer blends than the elasticity ratio of the constituent components.

Figure 12 gives micrographs of the longitudinal section of extrudates, which were annealed at 110°C for (a) 30 min and (b) 12 h, for 70/30 PS-76/PI-170 blend. Comparison of *Figure 12a* with *Figure 9b* reveals that after annealing for 30 min at 110°C, the length of the elongated droplet became shorter and as a consequence, the droplet's breadth became wider, indicating that the elongated PI droplets recoiled somewhat. As can be seen in *Figure 12b*, after annealing for 12 h, a remarkable change in the shape of PI droplets occurred, namely, the elongated PI droplets recoiled almost completely, yielding spherical or ellipsoidal shapes.

We speculate that due to the annealing temperature of 110°C employed, at which the PS matrix was much more viscous than the dispersed PI phase, coarsening of the dispersed phase was minimized for the 70/30 PS-76/PI-170 blend. It should be mentioned that a deformed Newtonian droplet suspended in a Newtonian medium recoils exclusively due to the interfacial tension, whereas a deformed viscoelastic droplet suspended in a viscoelastic medium recoils, upon removal of the applied stress, mainly due to its elasticity rather than the interfacial tension.

CONCLUSION

In the present study, we investigated the morphology of rapidly precipitated binary blends of PS and PI. In rapid precipitation, spinodal decomposition is believed to be the prevailing mechanism of phase separation, based on the assumption that the time spent by the solution in the metastable region is very short for any noticeable nucleation and growth to occur before the solution enters the unstable region. However, we found that none of the precipitates showed a co-continuous morphology. This is attributable to the fact that as-precipitates were dried at a temperature much higher than the T_g of the PI phase, thus leading, after a sufficiently long time, to a transformation of the co-continuous morphology into a dispersed-type morphology.

The effects of blend composition and viscosity ratio on morphological development were investigated by applying shear flow to as-precipitated blend samples. We found that the blend composition played a crucial role in determining the mode of dispersion in the PS/PI blends, although there is a general consensus among researchers that the component with the higher viscosity and lower volume fraction would form the dispersed phase. We found that the extrudate morphology parallel to the extrusion direction was highly dependent on the viscosity ratio and applied shear rate. When the dispersed phase was less viscous than the matrix, elongation of the dispersed phase along the extrusion direction was observed.

Annealing of the precipitates increased the domain size and broadened its size distribution. Although not presented in this paper, we observed that annealing at a higher temperature induced a much more rapid rate of domain growth. With increasing annealing time or annealing temperature, the probability of droplet motion and coalescence may increase, giving rise to both the growth of the average domain size and broadening of its size distribution. When annealed for a sufficiently long time, the elongated droplets completely recoiled, yielding spherical or ellipsoidal shape.

The major difficulty encountered with the PS/PI blends, prepared by rapid precipitation in this study, was that owing to the very low T_g of the PI phase, it apparently moved within the blend during the oven drying at *ca* 40°C, giving rise to a dispersed-type morphology.

More experimental study is needed to fully understand how blend composition and viscosity ratio might interact to determine the morphology of two-phase polymer blends. To date, there exists no theoretical model that predicts the morphology of immiscible polymer blends. This subject requires urgent attention by polymer researchers, in order to be able to develop polymer blends of practical significance.

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