

# The Effect of Mixing Time on the Morphology of Immiscible Polymer Blends

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## SYNOPSIS

The effect of mixing time on the morphology, with the viscosity ratio and composition as parameters in the mixing process, was studied for two immiscible binary polyblend systems, polyamide/polyethersulfone (PA/PES) and poly(butylene terephthalate)/polystyrene (PBT/PS), by selective dissolution followed by macroscopic and microscopic observations. At a short mixing time, the morphology of each phase depends not only on the composition, but also on the viscosity difference of two phases, shown by the results of PA/PES blends with a viscosity ratio of 0.03. The lower viscous phase (PA) forms particles, fibrils, and layers successively with its increasing content and becomes a continuous one at low concentrations as the minor phase, while the high viscous phase (PES) appears mainly in the form of particles and directly becomes a continuous one at high concentrations. With increasing mixing time, the effect of the viscosity ratio becomes less and the morphology is determined mainly by the volume fraction of each phase. Particles are the final morphology of the minor phase. Only at a viscosity ratio of unity is the morphological development of two phases (PBT and PS) with mixing time the same, and any one of these two components is in the form of particles when it is the minor phase. At the composition near 50/50, fibrillar or continuous structure may coexist for both phases. The composition range of co-phase continuity is decided not only by the viscosity ratio but also by the mixing time. With increasing mixing time, this range becomes narrower and finally occurs at volume fraction of 50/50, no longer affected by the viscosity ratio. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

Polymer blending is an important and attractive route to obtain new polymer materials due to the reduced cost and combined properties of neat polymers. Most polymers are immiscible, so that during processing component polymers form a multiphase system in their blend with a variety of morphologies such as droplets, fibrils, lamellae, and cocontinuous structure. Since the morphology of polyblends is one of the decisive aspects determining the final mechanical properties, it is of great importance to know how these complicated morphologies are formed and will be controlled during processing. Several factors including composition, viscosity ratio, interfacial

tension, shear rate, and mixing time have their own influences in controlling the final morphology of two phases. Up to now, many good results uncovering the relationship between morphology and respective factors have been obtained.<sup>1-12</sup>

Particles are the mostly observed morphology in polyblends. Since this morphology is closely related to the mechanical properties such as impact strength, it has been extensively investigated by researchers. Favis and Chalifoux<sup>1-3</sup> did much work on the size and shape of the dispersed phase in systems of polypropylene/polycarbonate (PP/PC). They studied the influence of the viscosity ratio, composition, and some processing parameters. Their results showed that at low contents of the minor phase, such as 7 and 23%, when the viscosity ratio of the dispersed phase to the matrix ( $\lambda = \eta_d/\eta_m$ ) was in the region of  $\lambda > 1$ , the particle size increased as  $\lambda$  increased. Reduction in the size of the minor phase

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was achieved when  $\lambda < 1$ , with the minimum particle size occurring at  $\lambda = 0.15$ . The composition had a marked effect on the dispersed-phase size, especially as the composition region of dual-phase continuity was approached, and on the size of the particle increased with increasing concentration of the dispersed phase. Processing parameters such as screw speed and volumetric flow rate had no significant effect on the phase size. Wu<sup>4</sup> studied the interfacial and rheological effects on the dispersed phase, using nylon and polyester as matrices and ethylene-propylene rubber as the dispersed phase at a concentration of 15%. He found that the particle size was smaller when the interfacial tension was lower. But his conclusion that the smallest particle size is obtained when  $\lambda = 1$  is inconsistent with Favis' results.

Fibrillar structure is another important morphology in polyblends, which has been found and studied early in flexible polymer blends by some authors and has attracted more attention in recent years, especially in polyblends containing liquid crystalline polymers (LCP). Tsebrenko<sup>5</sup> studied the influence of the viscosity ratio of melt components of a polyoxymethylene (POM)/ethylene and vinyl acetate copolymer (EVAC) mixture on the process of fiber formation in extrudates. He found that ultrathin fibers were the sole type of structure when the viscosity ratio  $\lambda$  was close to unity. If  $\lambda$  exceeded unity, the extrudates contained short fibers, high-dispersity powder, and defective fibers. If  $\lambda$  was lower than 1, films were formed along with the fibers. No composition was specified in this system. Borisenkova et al.<sup>6</sup> analyzed some literature data of polymer pairs containing 30% of the second component and concluded that at the condition of  $\lambda = 1$  fibrillar structure was pronounced, while at  $\lambda < 0.2$ , these fibers transformed into layers. All these results seem contradictory with that of the minimum droplet formation mentioned above. Min and co-workers<sup>7</sup> studied three polyblends of polyethylene/polystyrene, polyethylene/polycarbonate, and polyethylene/nylon 6. They concluded that when the dispersed phase had a lower viscosity than that of the continuous phase droplets were elongated by the shear stress and formed fibrils. Recently, for polyblends containing LCP, some researchers<sup>8,9</sup> found that the viscosity ratio of LCP to the matrix resin below unity favored the formation of LCP fibrils. He et al.<sup>9</sup> studied four polyblends containing LCP with different viscosity ratios and compositions and found that at low LCP contents long LCP fibrils could be obtained only when the viscosity ratio was far below unity.

Being a special morphology, co-phase continuity remains one of the poorly understood phenomena in polyblends, which may be attributed to the complexity of the microstructure and the lack of characterization methods. Jordhamo et al.<sup>10</sup> proposed a semiempirical expression which related the composition of co-phase continuity with the viscosity ratio of two phases:

$$\frac{\eta_1}{\eta_2} \cdot \frac{\phi_2}{\phi_1} \cong 1$$

where  $\eta_1$  and  $\eta_2$  are the viscosities of phases 1 and 2, respectively, and  $\phi_1$  and  $\phi_2$  are the volume fraction. This equation has been shown applicable for indicating qualitatively the trend of co-phase continuity occurring but does not match well in quantity with results of other researchers.<sup>2</sup> Utracki<sup>11,12</sup> reviewed expressions for predicting phase inversion and proposed two new relations for calculating the concentration of phase inversion,  $\phi_1$ . In his equations, the intrinsic viscosity of the dispersed phase,  $[\eta]$ , was introduced besides the viscosity ratio. All the results above were based on the assumption that the 100% co-phase continuity took place at only one certain value of composition. However, experimental results revealing this kind of microstructure are still small.

Although most morphologies have been studied, it can be seen that these morphologies were investigated isolately and the conditions for their formation in different articles were mostly incomparable. So, the results up to now were not consistent with each other and even were contradictory. From these results, it is difficult to have a general understanding.

Investigating the process of morphology development in polymer blends is an effective way for understanding the mechanism of morphology formation and the effect of processing conditions on the final morphology of polyblends. The processes of breakup and deformation of the dispersed phase in two-phase Newtonian systems and viscoelastic systems were studied by Taylor and other researchers.<sup>13,14</sup> In their results, the viscosity ratio of the dispersed phase to the continuous phase played an important role. But most of their studies were based on the existing, isolated droplets, which was not enough to explain the complicated results in the practical processing of polyblends. Plochocki et al.<sup>15</sup> proposed that the dispersion initially took place by an "abrasion" mechanism, and the elasticity ratio rather than the viscosity ratio of the components would be the most relevant factor. The less elastic component would tend to be stretched out and then

broken off and become the dispersed phase. Sundararaj and Macosko<sup>16</sup> investigated the morphology development in a batch mixer and a twin-screw extruder. They postulated that small particles were created from the breakup of thin ligaments formed by the coalescence of holes in the sheets of the dispersed phase, so the most significant morphology development in the batch mixer occurred within 1 min and in the extruder occurred within 30 mm of the first point of melting. But their results considered only the morphology of the dispersed phase itself, neglecting the role of the other phase, and did not relate the morphology development with the viscosity difference of the two phases. The suitability of their postulation for the two components with different viscosities was not conclusive.

In the present research, the authors systematically investigated the morphology development at different viscosity ratios, compositions, and mixing intervals, especially with a focus on the combining effect of these factors and the inherent relations among various morphologies in polymer blends. The goal was to obtain a deep insight into the regularity of morphology development during processing and to have a basic understanding for predicting and controlling the morphology.

## EXPERIMENTAL

### Materials

Two series of polyblends, polyamide 6/polyethersulfone (PA/PES) and poly(butylene terephthalate)/polystyrene (PBT/PS), were studied in this work. These two blend systems have different viscosity ratios and one of the components could be selectively dissolved. Polyamide 6 (PA), with a relative viscosity of 2.6–2.9, was a product of Heilongjiang Nylon Factory, China. Polyethersulfone (PES), having an intrinsic viscosity of 0.38 dL/g (measured in *N,N*-dimethylformamide at 25°C), was supplied by Jilin University, China. Poly(butylene terephthalate) (PBT, Beijing Municipal Institute of Chemical Engineering, China), had an intrinsic viscosity  $\eta_{IV}$  of 1.0 dL/g (measured in phenol/tetrachloroethane at 25°C) and polystyrene (PS) was PS B1 of Lanzhou Chemical Co., China. Some properties of these polymers measured in this laboratory are given in Table I.

### Mixing

The polymer blending was conducted in a mixer, a Haake Rheomix 600, for convenient sampling at dif-

ferent time intervals of mixing. Before blending, all the polymers were dried in a vacuum at 120°C for at least 8 h. The temperature of mixing was 300°C for PA/PES and 250°C for PBT/PS. After the set temperature of the mixer was reached and the motor started, pellets of two neat polymers were dry-blended and then quickly loaded into the mixer within 20 s. The screw speed was fixed at 50 rpm. During mixing, samples were taken at different mixing time intervals. At every sampling time, the drive was stopped and the loading ram was raised quickly, and a small lump of the sample was taken out from the bulk of the test material near the roller rotors within 10 s. The longest mixing time was confined within 25 min to avoid the decomposition of the polymers. It is found that after 1 min mixing some neat polymer pieces could still be seen for PA/PES, so the first sampling time was set at 2 min for both blends. The details are listed in Table I.

### Rheological Testing

The rheological measurement of the component polymers was carried out in a Goettfert Rheograph 2001 capillary rheometer at their blending temperatures, i.e., 300°C for PA and PES and 250°C for PBT and PS. A capillary die with a diameter of 1 mm and an *L/D* ratio of 30 was used. The viscosities of component polymers and the viscosity ratio of each blend at a shear rate of 57.6 s<sup>-1</sup>, which corresponded approximately to the screw speed of 50 rpm, are listed in Table I. Flow curves are given in Figure 1.

### Morphological Characterization

In this study, selective dissolution was used for the morphology observation of each phase in the blends. Solvents were carefully chosen for completely dissolving one component without any influence on the other component. *N,N*-Dimethylformamide was used to dissolve the PES phase and formic acid to dissolve PA phase in PA/PES blend. For PBT/PS, PS was easily dissolved in toluene while PBT was resistant to it. Typically, a piece of sample was weighed and immersed in one of the solvents mentioned above. After 24 h dissolving, if the sample kept its original shape with no broken pieces, the solution was poured away and fresh solvent was added. This process was repeated three times (which had been proved enough for separating the two components). Then, the remains were taken out of the solvent, dried, and weighed carefully, followed by SEM observation. If tiny pieces dispersed in the solution or the sample shape changed completely

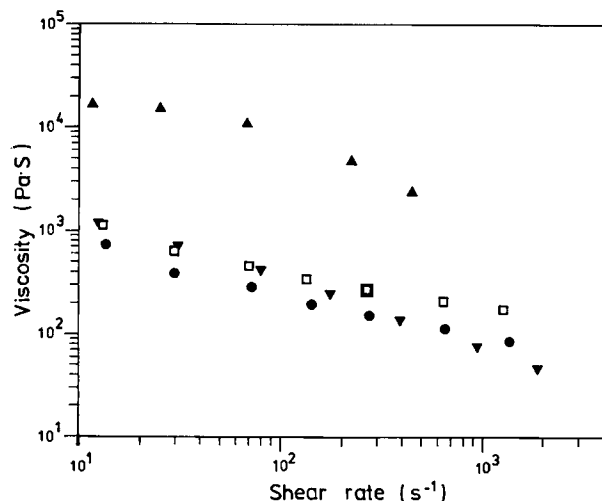
(e.g., it collapsed or became spongy), the remains were separated by centrifuging the solution and decanting off the supernatant liquid. The centrifuged phase was put into fresh solvent, and then the above process was repeated twice more. Finally, a drop of the remaining dispersion was placed directly on an SEM sample holder, evaporated off the solvent, and coated with gold for observation. A scanning electron microscope (SEM), a HITACHI S-530, was used for microstructure observation.

## EXPERIMENTAL

Besides the SEM observation, a method of macroscopic characterization was conducted for determining the continuous or dispersed state of each phase. This method consisted of a macroscopic observation (by naked eyes) of sample shapes and a comparison of weights of a remaining phase and its original fraction in the blend after and before selective extraction. The method is summarized in Table II. It was proved that the results were consistent with the morphology in the SEM observation.

### Morphology Change in PA/PES Blends ( $\lambda = 0.03$ )

In this study, PA/PES blends were scrutinized thoroughly, since each component had its selective



**Figure 1** Viscosity of (▲) PES and (●) PA at 300°C and (□) PBT and (▼) PS at 250°C.

solvent which was a nonsolvent for the other component. The results of the dissolution experiment of blends with different compositions and at different mixing intervals are summarized in Table III. Some typical micrographs of the PA phase after extracting PES and the PES phase after extracting PA are given in Figures 2 and 3, respectively.

In Figure 2, the morphology change of the low viscous phase PA with its content and mixing time

**Table I** Properties of Component Polymers and Processing Conditions of Their Blends

	System			
	PA/PES		PBT/PS	
	Component			
	PA	PES	PBT	PS
Density <sup>a</sup> at 25°C (g/cm <sup>3</sup> )	1.155	1.378	1.308	1.047
Mixing temperature (°C)	300		250	
Viscosity at 57.6 S <sup>-1</sup> at mixing temperature (Pa·S)	$3.532 \times 10^2$	$1.270 \times 10^4$	$5.510 \times 10^2$	$5.792 \times 10^2$
Viscosity ratio ( $\lambda$ )	0.03		$\cong 1$	
Sampling time (min)	2, 3, 6, 10, 16, 21		1, 2, 3, 6, 10, 16, 21	
Weight fraction and volume fraction (in parentheses) at 25°C	15 (17) 30 (34) 40 (44) 42.5 (47) 45 (49) 50 (54) 60 (64) 70 (74)	85 (83) 70 (66) 60 (56) 57.5 (53) 55 (51) 50 (46) 40 (36) 30 (26)	30 (26) 40 (35) 45 (40) 50 (44) 60 (55) 70 (65)	70 (74) 60 (65) 55 (60) 50 (56) 40 (45) 30 (35)

<sup>a</sup> Measured by density gradient method.

**Table II Determination of Phase Morphology in A/B Blend from the Dissolution Test After Dissolving B**

State of Remaining Phase A Compared with the Original Sample		Morphology of Two Phases	
Shape	$W_r$ (Weight percentage)	A	B
No change	$W_r > W_o$	Continuous	Dispersed or partly continuous
No change	$W_r = W_o$	Continuous	Continuous
No change with a little powder	$W_r < W_o$	Mostly continuous	Continuous
Spongy or powdery	Could not be weighted	Dispersed	Continuous

$W_o$  is the original weight percentage of phase A,  $W_r$  is the weight percentage of the remaining phase A after extraction of phase B.

can be clearly seen. At a sampling time of 2 min, the morphology varies greatly with the composition. The micrographs reveal that at a PA content of 15% PA forms fibrils and ribbons with many particles [Fig. 2(a)]. These fibrils have an average diameter about 1  $\mu\text{m}$ . At a PA content of 30%, the PA phase becomes wholly continuous from macroscopic observation. The PA phase appears like winding walls or layers with open cavities among them, showing that the PA phase is really continuous [Fig. 2(b)]. The average thickness of these walls is less than 2  $\mu\text{m}$ . By increasing the PA content to 45%, these cavities (left by removing the PES phase) change from continuous to isolated [Fig. 2(c)], and they gradually become small holes with further increasing PA content.

As the mixing time increases, PA morphology changes further. Micrographs show that at 15% PA the PA phase changes from fibrils at 2 min to spherical particles at 10 min [Fig. 2(d)]. After a 10 min mixing, the morphology of 30% PA becomes very thin layers with many particles [Fig. 2(e)] and cav-

ities for 45% PA become shorter and more spherical [Fig. 2(f)] than those at 2 min.

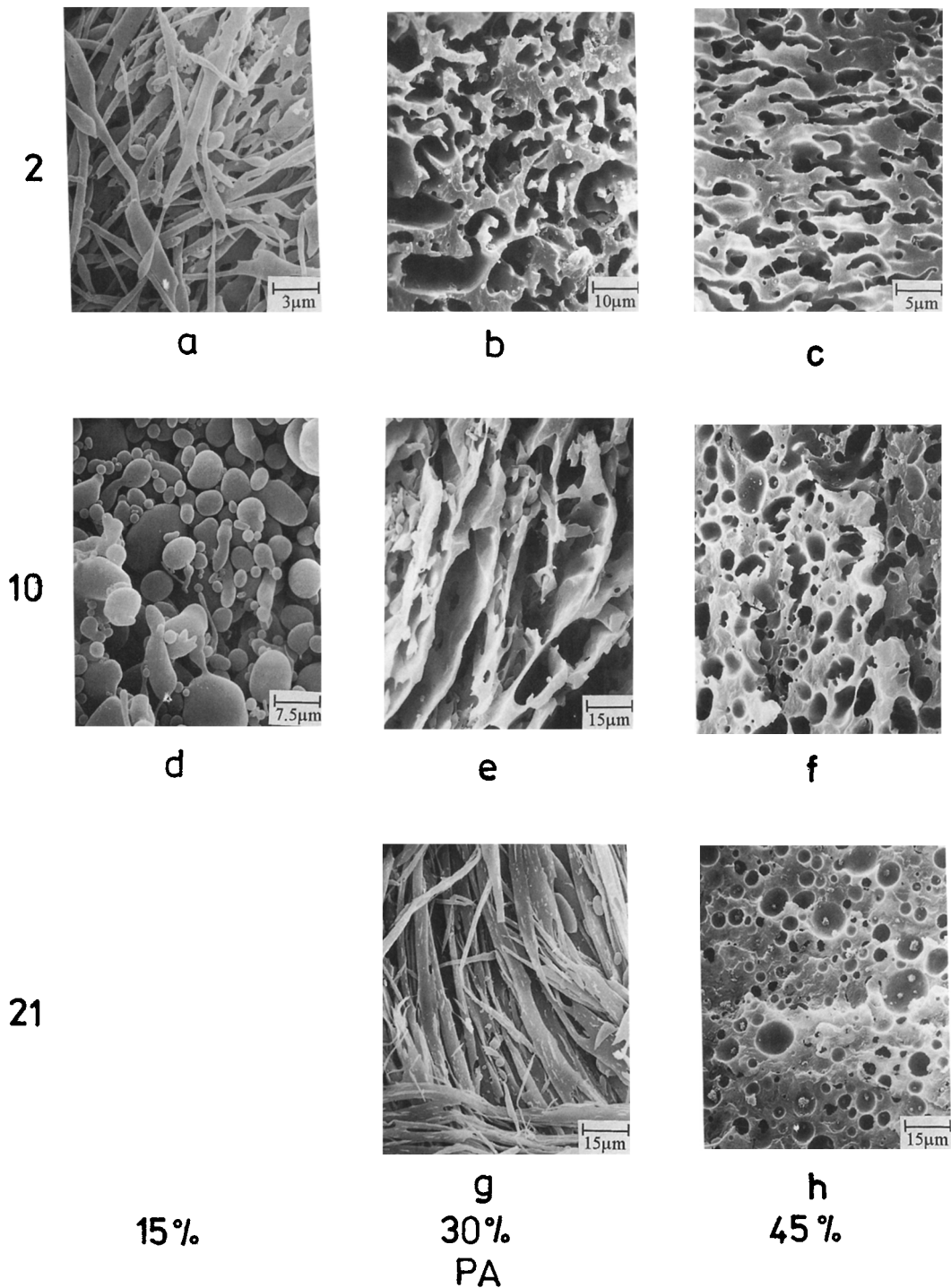
After a 21 min mixing, the continuous thin walls of the 30% PA phase split into dispersed fibers with a large amount of particles [Fig. 2(g)]. At 40% PA, although some powder appears in the PES solution and the weight percentage of PA decreases, the sample shape does not change, which indicates that the PA phase is just near the inversion point from a dispersed to a continuous one. From a PA amount of 45% [Fig. 2(h)], the weight percentage of PA remaining begins to increase with the mixing time, indicating that the dispersed PES phase is occluded within the continuous PA phase so that the former could not be extracted out of the latter.

For the high viscous PES phase, the tendency of morphology change is different from that of the PA phase. At a sampling time of 2 min, the continuity of the PES phase begins to appear at a high content of 55%, while lower than this content, PES is in the form of dispersed particles. The micrograph of PES/PA50/50 after the extraction of PA shows that PES

**Table III The State of the Remaining Phase in PA/PES Blends of Different Compositions After Different Times of Mixing**

Time (min)	Composition (w/w) (PA/PES)							
	15/85	30/70	40/60	42.5/57.5	45/55	50/50	60/40	70/30
2	d	c (29.4%)	c (44.1%)	c (59.0%)	c (54.2%)	d	d	d
10	d	c + d	c- (32.1%)	c (58.9%)	c + d	d	d	d
21	d	d	c- (29.5%)	c (58.7%)	d	d	d	d
	PA phase (PES dissolved)				PES phase (PA dissolved)			

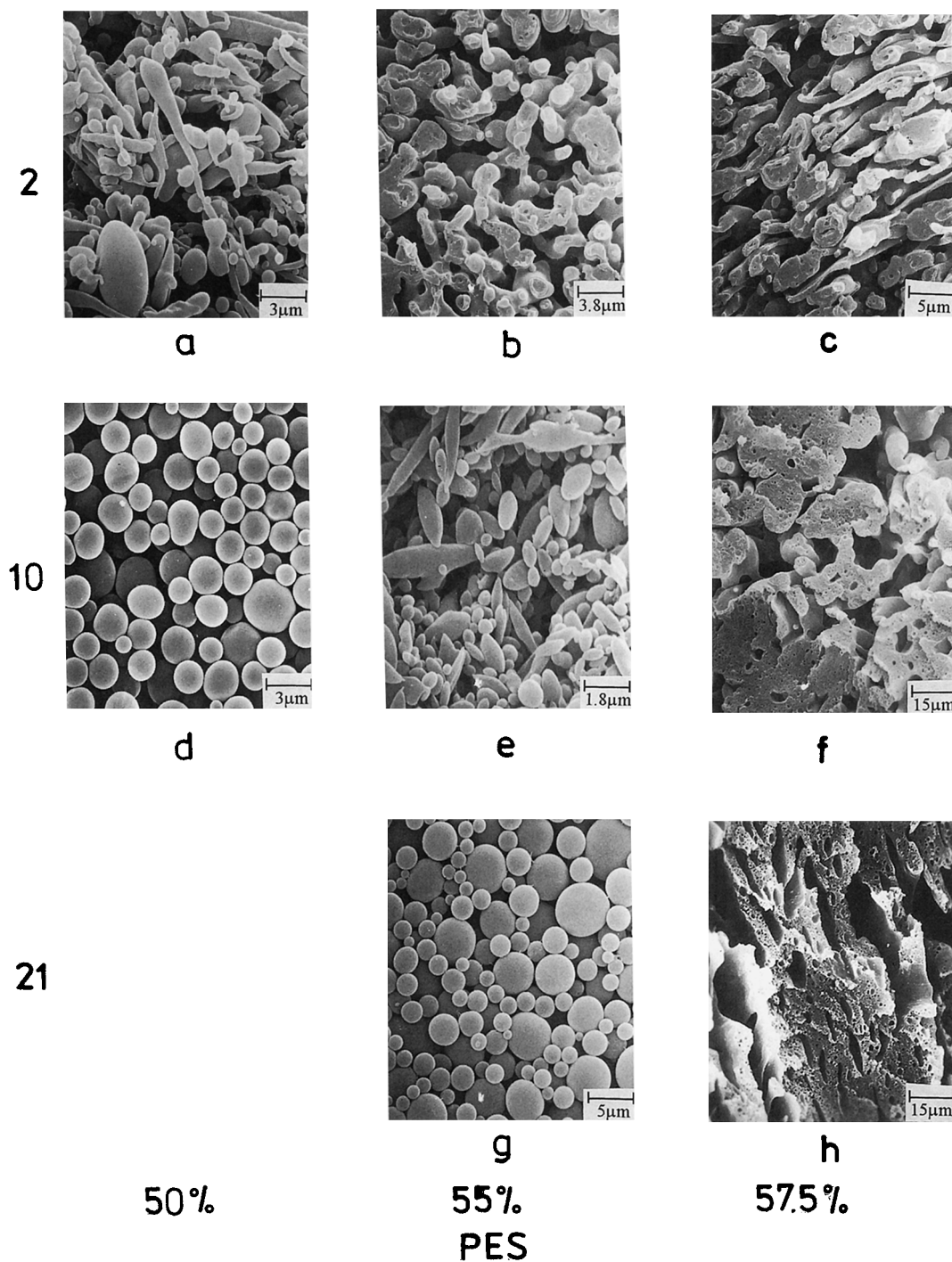
d: dispersed; c: continuous; c + d: partly continuous and dispersed; c-: mainly continuous. Nos. in parentheses are measured weight percentages of the remaining component.



**Figure 2** SEM micrographs of remaining PA phase in PA/PES blends after extraction of PES. Nos. in the left column denote sampling time in minutes.

is in the form of ellipsoidal and spherical particles with some short rods [Fig. 3(a)]. The average diameter of these particles and rods is about 2 μm. At a PES content of 55% [Fig. 3(b)], the continuity of the PES phase can be clearly seen. The PES phase

looks like a network consisting of ellipsoids connected by thin necks. These domains have nearly the same size as that of the particles in PES/PA50/50 and are on the verge of breakup. This microstructure of continuity has some features different from that of



**Figure 3** SEM micrographs of remaining PES phase in PA/PES blends after extraction of PA. Nos. in the left column denote sampling time in minutes.

PA, which could be attributed to higher viscosity of PES and lower viscosity of PA. With further increasing PES content, PES domains become larger but are still not wholly connected [Fig. 3(c)].

Since the PES phase at a portion less than 50% (by weight) has formed particles in a 2 min mixing,

increasing mixing time only makes the particles more spherical due to interfacial tension [PES/PA50/50 in Fig. 3(d)]. At 55% PES, a 10 min mixing breaks the continuous PES at 2 min [Fig. 3(b)] into ellipsoidal particles [Fig. 3(e)] and a 21 min mixing into spheres [Fig. 3(g)]. It is surprisingly

**Table IV** The State of Each Component in PBT/PS Blends of Different Compositions After Different Times of Mixing

Time (min)	Composition (w/w) (PBT/PS)					
	30/70	40/60	45/55	50/50	60/40	70/30
2	d	c (39.2%)	c (44.9%)	c [c] (46.9%)	c [c] (60.1%)	c [d]
10	d	c + d	c (44.0%)	c [c] (51.5%)	c [c + d] (67.5%)	c [d]
21	d	d	c + d	c [c] (54.0%)	c [d] (79.2%)	c [d]
PBT (PS dissolved)						

d: dispersed; c: continuous; c + d: partly continuous and dispersed. Nos. in parentheses are measured weight percentages of the remaining PBT component. Results in square brackets are the state of PS phase judged from the weight fraction of PBT.

seen that by increasing the PES fraction to 57.5% the weight percentage of PES remaining is constant (the same as its original content before dissolving PA) or becomes a little larger with mixing time (Table III), indicating that the PES phase remains continuous with blending time at PES concentrations higher than 57.5%. Micrographs of the PES phase show that PES domains transform from particles in PES/PA55/45 into a complete continuity in PES/PA57.5/42.5 after the same mixing time, i.e., a 10 min and a 21 min mixing [Fig. 3(f) and (h)]. The large amount of tiny columnar holes reveals that some PA domains are in the form of tiny cylindrical droplets, although the PA phase is mostly continuous at this content.

Since the degree of continuity of each phase was more accurately determined, the composition range in which both phases were completely continuous could be clearly determined (Table III). After a 2 min mixing, a co-phase continuity occurs in a wide composition range from PA/PES30/70 to PA/PES45/55. As the mixing time increases, this range becomes narrower. After a 21 min mixing, the co-phase continuity region occurs at about one composition between PA/PES42.5/57.5 and PA/PES45/55 by weight (i.e., PA/PES47/53 to 49/51, by volume).

#### Morphology Change in PBT/PS Blends ( $\lambda \approx 1$ )

From the flow curves (Fig. 1), it is shown that PBT and PS melts have nearly the same apparent viscosity at a shear rate of 57.6 1/S, i.e., their viscosity ratio is close to unity. Toluene can dissolve PS easily without any influence on PBT, but it failed to find a chemical being a solvent for PBT and a nonsolvent

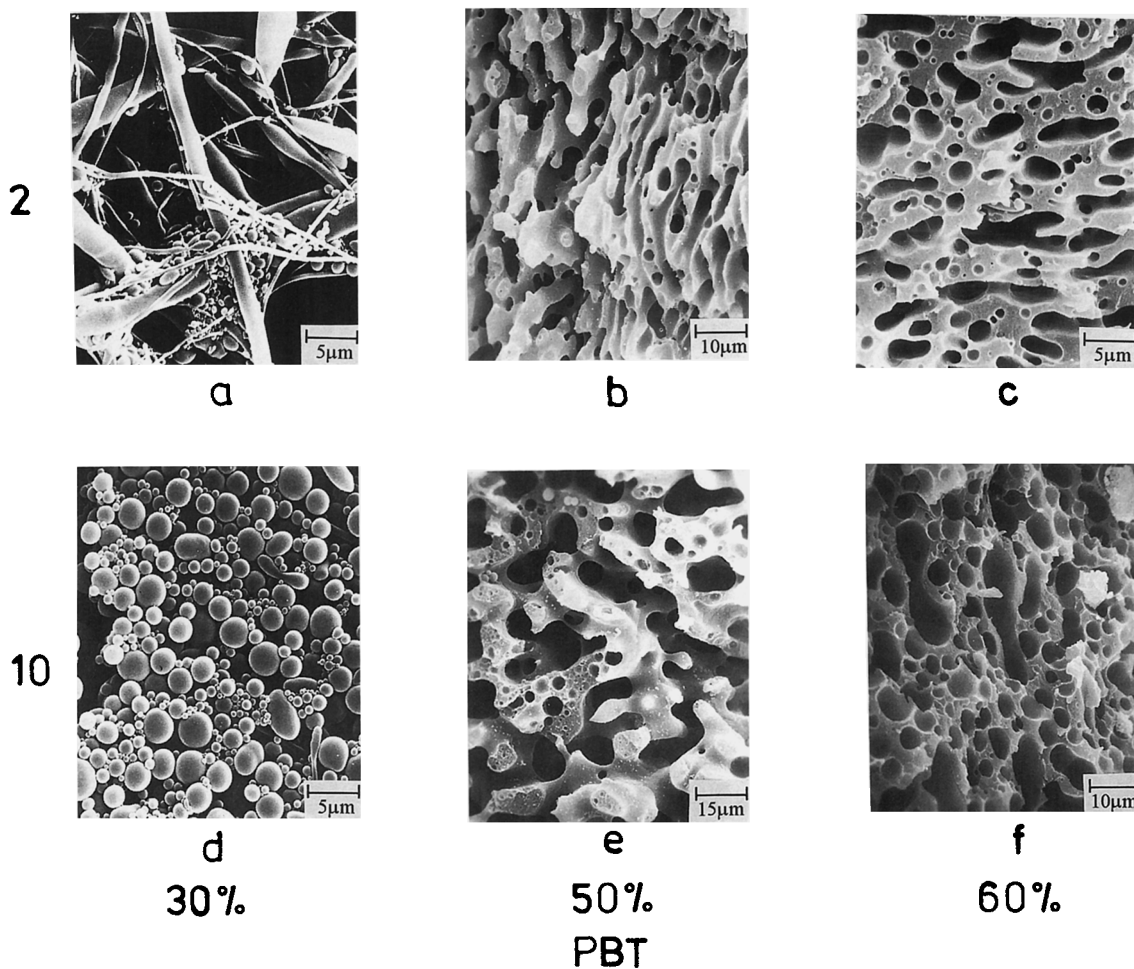
for PS. So, the microstructure of PS was judged only by results of the selective dissolution and the microstructure observation of the PBT phase (Table IV). Some micrographs of the PBT phase after extraction of PS are given in Figure 4.

It is shown that after a mixing time of 2 min the morphology of PBT changes from particles in PBT/PS15/85 into fibrils and ribbons in PBT/PS30/70 [Fig. 4(a)] and becomes continuous in PBT/PS40/60, while for PS dissolution results indicate that PS becomes completely continuous at a 40% concentration (i.e., in PBT/PS60/40 in Table IV), which is confirmed by the continuous cavities in the PBT phase [Fig. 4(c)]. At concentrations lower than 40%, PS exists as the dispersed phase.

As mixing time increases, the PBT phase becomes spherical in PBT/PS30/70 after a 10 min mixing [Fig. 4(d)] and the PS phase is still continuous. The continuous PBT phase occludes some PS in PBT/PS50/50 [Fig. 4(e) and Table IV], indicating that a part of PS has become dispersed particles. From a PBT fraction of 60%, percentages of remaining PBT phase increase with mixing time, i.e., more PS is occluded in the PBT phase. From PBT/PS50/50 to PBT/PS60/40, continuous cavities become isolated holes [Fig. 4(f)]. Only at PBT/PS 50/50 do both phases remain continuous and the morphology changes little with mixing time [Fig. 4(b) and (e)].

A comparison of PBT/PS blends with PA/PES blends shows that the trend of morphology development of both phases in immiscible binary blends is nearly the same. The co-phase continuity occurred in a wide composition range after a 2 min mixing, but it shifted to the middle of the composition range from PBT/PS40/60 to 60/40 after a 10 min mixing





**Figure 4** SEM micrographs of remaining PBT phase after extraction of PS. Nos. in the left column denote sampling time.

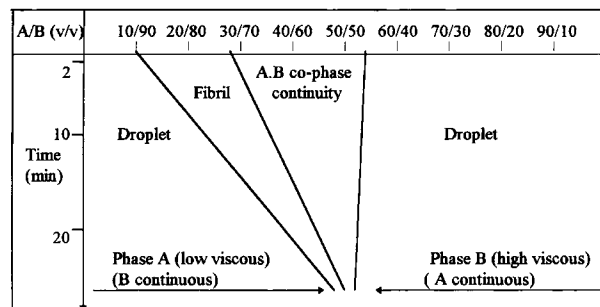
and to about PBT/PS50/50 (i.e., PBT/PS 44/56 by volume) after a 21 min mixing.

## DISCUSSION

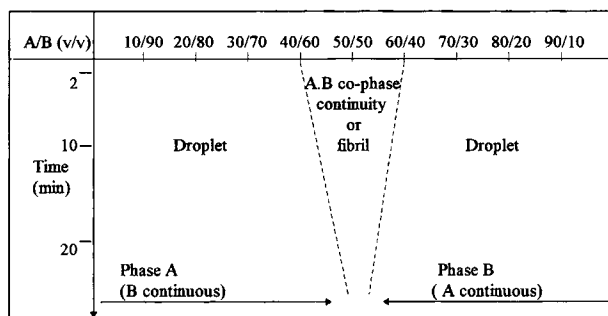
The relationship between morphology and composition was widely studied by Favis and Chalifoux.<sup>2</sup> However, in their study, only the dependence of the phase size on composition of both phases was observed. In the present study, it is seen that the morphology changes not only with the composition but also correlates with the viscosity difference of the two phases. The results shown above are illustrated schematically in Figure 5. Figure 5(a) shows the microstructure development of each phase with the composition and mixing time in a blend A/B with a viscosity ratio about 0.03. Figure 5(b) shows the development in a blend A/B with a viscosity ratio about unity. The development of various morphol-

ogies with viscosity ratio, composition, and mixing time can be clearly seen.

For immiscible binary polyblends with short blending times, generally 2 min, morphologies such as droplets, fibrils of low viscous phase, and co-phase continuity appear consecutively with increasing concentration of the low viscous phase. But the composition at which value a certain morphology of one phase forms depends on the viscosity ratio of two phases and the viscosity of this phase. For polyblends with a large viscosity difference, the high viscous phase can always form particles even at its concentration above 50% and will change from particles into continuity directly with its further increasing concentration. Within this composition range, the morphological development with increasing mixing time is just the decrease of particle size. But for the low viscous phase, it will form particles, fibrils, and layers (continuity) successively with its increasing concentration below 50%. As the viscosity



a



b

**Figure 5** Diagram of microstructure development of each phase in blend A/B with viscosity ratio, composition, and mixing time: (a)  $\lambda = 0.03$ ; (b)  $\lambda = 1$ .

ratio becomes lower, the fraction for the occurrence of each morphology will shift to a lower value of the concentration of the low viscous phase.

Only when the viscosities of two phases are about equal, the morphological change with fractions of two phases will be the same. Each phase will form droplets so long as it is the minor phase, while at composition near 50/50, both phases may form fibers or become continuous.

The morphology is determined also by the interfacial tension. The particle size of the dispersed phase will be smaller when the interfacial tension is lower.<sup>4</sup> In the comparison of the two immiscible

**Table VI** Calculated Interfacial Tension for Amorphous Polymer Interfaces

Polymer Pair	Interfacial Tension $\gamma$ (mN/m)			$-d\gamma/dT$ (mN/mK)
	20°C	250°C	300°C	
PA/PES	3.99		4.13	-0.0005
PBT/PS	1.88	1.29		0.003

systems investigated here, i.e., PA/PES and PBT/PS, the effect of the interfacial tension in these blends has been taken into consideration. Table V lists the surface tension and polarity of PA, PES, PS, and poly(butylene isophthalate). The surface tension for the amorphous surface of poly(butylene terephthalate) cannot be found, so values of poly(butylene isophthalate) is used in the calculation of the interfacial tension. By using the harmonic-mean equation,<sup>19</sup> the calculated interfacial tension for amorphous interfaces are as follows: 3.99 mN/m at 20°C and 4.13 mN/m at 300°C for PA/PES, and 1.88 mN/m at 20°C and 1.29 mN/m at 250°C for PBT/PS (Table VI). The difference between interfacial tensions of these two blends is not large, so that the difference between the particle size of the dispersed phase in these blends is not large, which is shown by a comparison between Figures 3(d) and 4(d).

The region of co-phase continuity (both continuous phases) has been precisely determined in this study. It is really surprising that the co-continuity occurrence in a rather wide composition range after a short time mixing suggests that this phenomenon may not be the same as a phase inversion which occurs at a point of composition. This can be a reason for that Jordhamo's empirical equation fails to predict the composition value of co-phase continuity, although it describes the tendency correctly.

In the region of co-phase continuity, the microstructure such as layers can usually be observed. But

**Table V** Surface Tension and Polarity for Amorphous Polymer Surfaces

Polymer	Surface Tension (mN/m)			$-d\gamma/dT$ (mN/mK)	Polarity ( $x^p$ )	Ref.
	20°C	250°C	300°C			
PA6	38.4	—	35.8	0.009	0.188	17
PES	41	—	27.9	0.047	0.390	18
Poly(butylene isophthalate)	47.8	29.4	—	0.080	0.270	17
PS	40.7	24.2	—	0.072	0.168	17

Values for 250 and 300°C are calculated by the authors.

the fibrous morphology reached after a 2 min mixing is not an equilibrium state. As mixing time increases, the fibrous or continuous morphology of the lower viscous phase will keep on breaking into particles so long as it is the minor phase, and the composition region of co-phase continuity becomes narrow. With increasing mixing time, the effect of the viscosity ratio on the morphology becomes less. After a long time mixing, the co-continuity region will shrink to one point of the composition, and the spherical particle will be the final morphology of the minor phase due to the interfacial tension of the melt. By considering the error caused by using the density at 25°C instead of the density at the mixing temperature, the volume fractions of the co-phase continuity of PA/PES and PBT/PS after a 21 min mixing should be 50/50. So, it is predicted that after a long enough time mixing the final morphology is determined only by the volume fraction rather than by the viscosity ratio. The co-phase continuity region will occur only at a volume ratio of 50/50, and the minor phase will be in the form of spheres at other compositions.

Favis studied the influence of mixing time on dispersed-phase particles and found the most deformation/disintegration processes took place within 2 min of mixing. Increasing the time of mixing from 2 to 20 min had little effect on the size of the dispersed phase.<sup>3</sup> Sundararaj and Macosko<sup>16</sup> investigated the morphology development during the mixing process, which also showed that most of the significant morphology development occurred within 1 min in the mixer. However, it should be noticed that in all these studies the dispersed phase was the high viscous phase (at least of equal viscosity with the other one) and the content was low (7 and 20%, respectively). These results could be taken as special cases in the present study and were confirmed by the present study, i.e., both PES and PBT of higher viscosity formed particles in their respective blends within 2 min mixing. But results of the present study also show that a more significant morphology development will occur for the lower viscous phase.

The phenomenon described above could not be explained by the existing mechanisms. It is suggested that the process of morphology development for immiscible binary blends, especially those of two components with different viscosities, might be as follows: Due to a low viscosity, the lower viscous phase in melt blending flows more quickly than the higher viscous phase does, so the former can enter the space between domains of the high viscous phase and the

wall of the mixer easily and encapsulate the high viscous phase. This causes the high viscous phase in the form of dispersed particles even at high concentrations above 50%, while the lower viscous phase is more likely in the form of fiber, layer, and continuity even at low contents below 50%. This tendency may be related to the process of energy dissipation during mixing. As mixing time increases, the energy input increases and the flow of the higher viscous phase becomes stronger, so that the effect of viscosity becomes less while the role of the volume fraction becomes significant. The authors think some theoretical research considering these parameters is eagerly needed.

## CONCLUSIONS

For immiscible binary polyblends, there is an inherent relationship among various morphologies such as particles, fibrils, layers, and co-continuity structure, which are controlled by a combining effect of viscosity ratio, composition, and mixing time. At a short mixing time, the morphology of each phase depends not only on the composition, but also on the viscosity difference of the two phases. The lower viscous phase will form particles, fibrils, and layers successively with its increasing content as the minor phase and can become continuous at low contents such as 30% (by weight), while the high viscous phase appears mainly in the form of particles as the minor phase and directly becomes continuous at high contents. Only at a viscosity ratio of unit ( $\lambda = 1$ ) is the morphological change of the two phases with their concentrations the same and both phases will exist as particles so long as they are the minor phase. At a composition near 50/50, the fibrillar structure may appear for both phases.

As the mixing time increases, the effect of viscosity ratios become less and the morphology will be determined mainly by the volume fraction of each phase. Particles will be the final morphology of the minor phase.

The composition range of the co-phase continuity is determined not only by the viscosity ratio but also by the mixing time. There is a rather wide composition range in which both phase are completely continuous after a short time mixing. This range will shift from compositions where the low viscous phase is the minor phase to compositions around 50/50 by volume. After a long enough time mixing, the co-phase continuity is no longer affected by the viscosity ratio and occurs at a certain composition, i.e., 50/50 by volume.

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