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PII: S0032-3861(97)00212-7

Polymer Vol. 38 No. 26, pp. 6347–6353, 1997

0032-3861/97/$17.00+0.00

Co-phase continuity in immiscible binary polymer blends

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(Received 29 May 1996; revised 1 January 1997)

Methods of microscopic observation and macroscopic characterization have been developed for determining the co-phase continuity in immiscible binary blends. After selective dissolution of the component polymers, the morphologies of microscopic observation are consistent with the results of macroscopic observation and weight percentage determination. By using these methods, the relationship between co-phase continuity, composition and blending time has been explored for two immiscible binary polyblends with different viscosity ratios (λ), polyamide 6/polyethersulfone (PA/PES, $\lambda = 0.03$) and poly(butylene terephthalate)/polystyrene (PBT/PS, $\lambda = 1$). Both blend systems show a similar dependence of co-phase continuity on the composition and mixing time. That is at short mixing time (for example, 2 minutes), the co-phase continuity takes place in a wide composition range. With increasing blending time, the composition range of co-phase continuity becomes narrow, and finally shrinks to one point. After a long enough mixing time the co-phase continuity region will occur only at a volume fraction of 50/50, no matter what the viscosity ratio of the blend is. © 1997 Elsevier Science Ltd.

(Keywords: polyblends; microstructure; co-phase continuity)

INTRODUCTION

Polymer blending is an economical and attractive route to getting new polymer materials at low cost and combining performances of neat polymers. Polymer pairs are mostly immiscible. Their blends will be multi-phase systems where one of the component polymers may have a variety of morphologies such as droplets, fibrils, lamellae and co-continuous structures after melt blending. Since the morphology of polyblends can affect a multiplicity of physical and mechanical properties including impact strength[1–3], elongational properties[4,5], and permeability characterists[6,7], it is of great importance to know how these complicated morphologies are formed *in situ* and will be controlled during processing. Several factors such as compositions, viscosity ratio, elasticity ratio, interfacial tension, shear rate/shear stress 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[8–18].

Co-phase continuity is a special case of morphologies in binary polyblends where both phases maintain their whole continuity. This structure has significant effects on the physical and mechanical properties of polymer blends such as transport properties. However, the complexity of the microstructure brings about difficulties for its characterization and description. Until now, a few studies have been conducted in this area, but co-phase continuity remains one of the poorly understood phenomena in polyblends. Jordhamo *et al.*[17] proposed a semi-empirical expression which related the compostiion of co-phase continuity to the viscosity ratio of two phases:

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

where, η_i is the viscosity and ϕ_i the volume fraction of phase i, respectively. Miles and Zurek[19] suggested that the condition for the formation of co-phase continuity structure should more precisely be

$$\frac{\eta_1(\dot{\gamma})}{\eta_2(\dot{\gamma})}\cdot\frac{\phi_2}{\phi_1} \cong 1 \tag{2}$$

where $\eta_i(\gamma)$ is the viscosity of phase i at the shear rate, $\dot{\gamma}$, used to prepare the blend in the mixing device. Both equations have been shown applicable for indicating qualitatively the trend of co-phase continuity occurring but do not match well in quantity with results of other researchers[9]. Utracki[18] reviewed expressions for predicting phase inversion and proposed two new relations for calculating the concentration of phase inversion, ϕ_I. In his equations the intrinsic viscosity of the dispersed phase, $[\eta]$, was introduced beside the viscosity ratio. All the results above were based on the assumption that 100% co-phase continuity took place at only one certain value of composition. However, experiemntal results revealing this kind of microstructure are still rare.

In the present study, two blend systems with different viscosity ratios have been investigated. Based on macroscopic quantitative characterization and microscopic observation, a procedure for determining the state of co-phase continuity was set up and the relationship among co-phase continuity, composition, and mixing time was investigated.

EXPERIMENTAL

Materials

In this study, experiments were preformed with two series of polyblends, polyamide 6/polyethersulfone (PA/PES) and

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Table 1 Properties of component polymers and processing conditions of their blends

System	PA/PES		PBT/PS	
Component	PA	PES	PBT	PS
[a]Density at 25°C (g/cm^3)	1.155	1.378	1.308	1.047
Mixing temperature (°C)	300		250	
Viscosity at 57.6 S^{-1} at mixing temperature (Pa.S)	3.532×10^2	1.270×10^4	5.510×10^2	5.792×10^2
Viscosity ratio (λ)	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 parantheses) at 25°C	15 (17)	85 (83)	30 (26)	70 (74)
	30 (34)	70 (66)	40 (35)	60 (65)
	40 (44)	60 (56)	45 (40)	55 (60)
	42.5(47)	57.5(53)	50 (44)	50 (56)
	45 (49)	55 (51)	60 (55)	40 (45)
	50 (54)	50 (46)	70 (65)	30 (35)
	60 (64)	40 (36)		
	70 (74)	30 (26)		

[a]Measured by density gradient method

poly(butylene terephthalate)/polystyrene (PBT/PS). These blend systems have different viscosity ratios and both or one of the components can be selectively dissolved. Polyamide 6 (PA), with a relative viscosity of 2.6–2.9, was from Heilongjiang Nylon Factory, PRC. Polyethersulfone (PES), having an intrinsic viscosity of 0.38 dl/g (measured in N, N-dimethylformamide at 25°C), was synthesized by Jilin University, PRC. Poly(butylene terephthalate) (PBT), with an intrinsic viscosity of 1.0 dl/g (measured in phenol/tetrachloroethane at 25°C), was obtained from Beijing Municipal Institute of Chemical Engineering, PRC. Polystyrene (PS) was a commercial grade PS B1 of Lanzhou Chemical Co, PRC. Some properties of these polymers are summarized in *Table 1*.

Mixing

Prior to melt mixing, all the component polymers were dried in vacuum at 120°C for at least 8 h in order to minimize hydrolytic degradation of the materials during processing. The melt blending was carried out in a Haake Rheomix 600, a mixer offering convenient sampling at different time intervals of mixing. The temperature of mixing was 300°C for PA/PES and 250°C for PBT/PS. After the set teperature of the mixer was reached and the motor started, dry-blended pellets of two neat polymers were loaded quickly in the the mixer within 20 s. The roller speed was fixed at 50 rpm. During the whole process of mixing, samples were taken at different mixing time intervals. At every sampling time, the drive was stopped and the loading ram raised quickly, a small lump of the sample was taken out from the bulk of the test materials near the roller rotors. The time for sampling was within 10 s. The longest mixing time was confined within 25 min to avoid the decomposition of the ingredient polymers. It was 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 1*.

Rheological testing

The rheological characterization of the component polymers was made in a Goettfert Rheograph 2001 capillary rheometer at their blending temperatues, i.e. 300°C for PA and PES, and 250°C for PBT and PS. The measurement was carried out with a capillary die having a diameter of 1 mm and an L/D ratio of 30. Viscosities of component polymers and the viscosity ratio of each blend at a shear rate of 57.6 s^{-1}, which corresponds approximately to the screw speed at 50 rpm, are listed in *Table 1*. Flow curves are given in *Figure 1*.

Morphology observation

Morphology characterization was carried out in two ways. One was a macroscoopic observation conducted for determining the continuous or dispersed state of each phase. This method consists of a macroscopic observation (by naked eye) of sample shapes and a comparison between the weight percentage of a remaining phase and its original fraction in the blend after and before its selective extraction. The method is summarized in *Table 2*. The other one was a microscopic observation of the remaining phase with scanning electron microscopy (SEM). In this study, selective dissolution was used for the morphology observation of each phase in blends. Solvents were carefully chosen for completely dissolving one component without any influence on the other component. N, N-dimethylformamide was used to dissolve 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 of

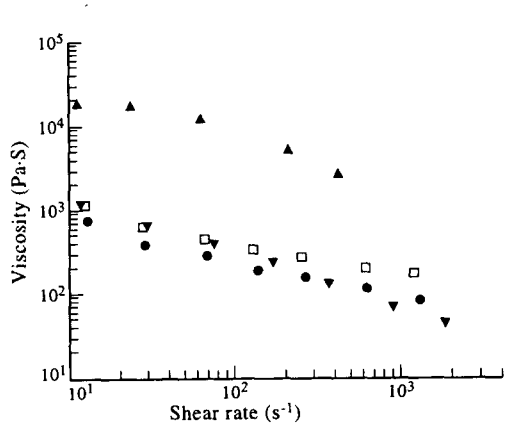

Figure 1 Apparent viscosity of PES (▲) and PA (●) at 300°C, and PBT (□) and PS (▼) at 250°C

Table 2 Determination of phase morphology in A/B blend from dissolution test after dissolving B

State of remaining phase A compared with the original sample		Morphology of two phases	
Shape	Wr (weight percentage)	A	B
no change	Wr > Wo	continuous	dispersed or partly continuous
no change	Wr = Wo	continuous	continuous
no change with a little powder	Wr < Wo	mostly continuous	continuous
spongy or powdery	could not be weighed	dispersed	continuous

Notes: Wo is the original weight percentage of the phase A; Wr is the weight percentage of the remaining phase A after extraction of the phase B

Table 3 The state of remaining phases in PA/PES blends of different compositions after different time of mixing

PA/PES composition (W/W)		30/70	40/60	42.5/57.5	45/55	50/50	60/40
Time (min)							
PA	2	c	c	c	c	c	c
		(29.4)	(44.1)	(40.5)	(49.1)		
	10	c + d	c^-	c^-	c	c	c
			(32.1)	(36.1)	(47.4)		
	21	d	c^-	c^-	c	c	c
			(29.5)	(27.6)	(59.5)		
PES	2	c	c	c	c	d	d
			(55.5)	(59.0)	(54.2)		
	10	c	c	c	c + d	d	d
			(61.0)	(58.9)			
	21	c	c	c	d	d	d
			(61.6)	(58.7)			

Notes: d = dispersed, c = continuous, c + d = partly continuous and dispersed, c^--mainly continuous. Numbers in parentheses are measured weight percentage of the remaining component

dissolving, the solution was poured away and fresh solvent was added, if the sample kept its original shape and remained whole. 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 (for example, 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, the solvent evaporated off and coated with gold for observation. A HITACHI S-530 was used for the microstructure observation.

RESULTS AND DISCUSSION

Co-phase continuity in PA/PES blends ($\lambda = 0.03$)

In this work, the blends of PA/PES have been scrutinized in detail, since each component has its selective solvent which is a non-solvent for the other component. The results of dissolution experiments for blends with different compositions and at different mixing intervals are summarized in *Table 3*. Some typical micrographs of PA phase after extracting PES and PES phase after extracting PA are given in *Figures 2 and 3*, respectively.

Figure 2 shows morphologies of the PA phase and PES phase extracted from PA/PES 45/55 after different mixing times. The two groups of PA and PES micrographs at the same sampling time come from the same sample. The only difference is that the PA micrograph is obtained after PES phase has been extracted and PES micrograph obtained after PA phase extracted. It can be seen that the morpholiges of PA and PES at the same sampling time match quite well with each other. The long shape of PES ellipsoidal droplets at 2 min (*Figure 2b*) just matches the long shape of PA holes at 2 min (*Figure 2a*). In *Figure 2a*, these long holes are connected together and remaining PA phase is in the form of thin winding walls. In *Figure 2b*, these long particles are connected together as well. Both 45% PA and 55% PES phases are continuous, but their shapes are different, resulting from different melt viscosities or surface tensions. At 10 min mixing, the continuous PA holes become isolated (*Figure 2c*) and the continuous PES particles become separated (*Figure 2d*). However, shorter rods of PES (*Figure 2d*) also match the shallow holes of PA (*Figure 2c*). A longer mixing time changes the shape of PA holes and PES particles further; however, spherical PES particles (*Figure 2f*) have almost the same size of spherical holes of the remaining PA phase (*Figure 2e*) even after a 21 min mixing. These well-matched micrographs of one phase after the selective dissolution of the other phase reveal the real morphology of the dispersed or continuous phase and indicate this method to be suitable for the characterization of co-phase continuity in immiscible binary blends.

The results of the macroscopic observation and weighing method after selective dissolution are listed in *Table 3*. The accuracy of the weighing method after selective dissolution can be judged by the sum of weight percentages of the two remaining components. For example, after a 2 min mixing, the weight percentage of the remaining PA phase in the PA/PES 40/60 blend is 44.1%. This Wr, a little larger than the Wo, 40%, means the PA phase is continuous. A Wr larger than Wo is a result of some inclusion of the extracted phase

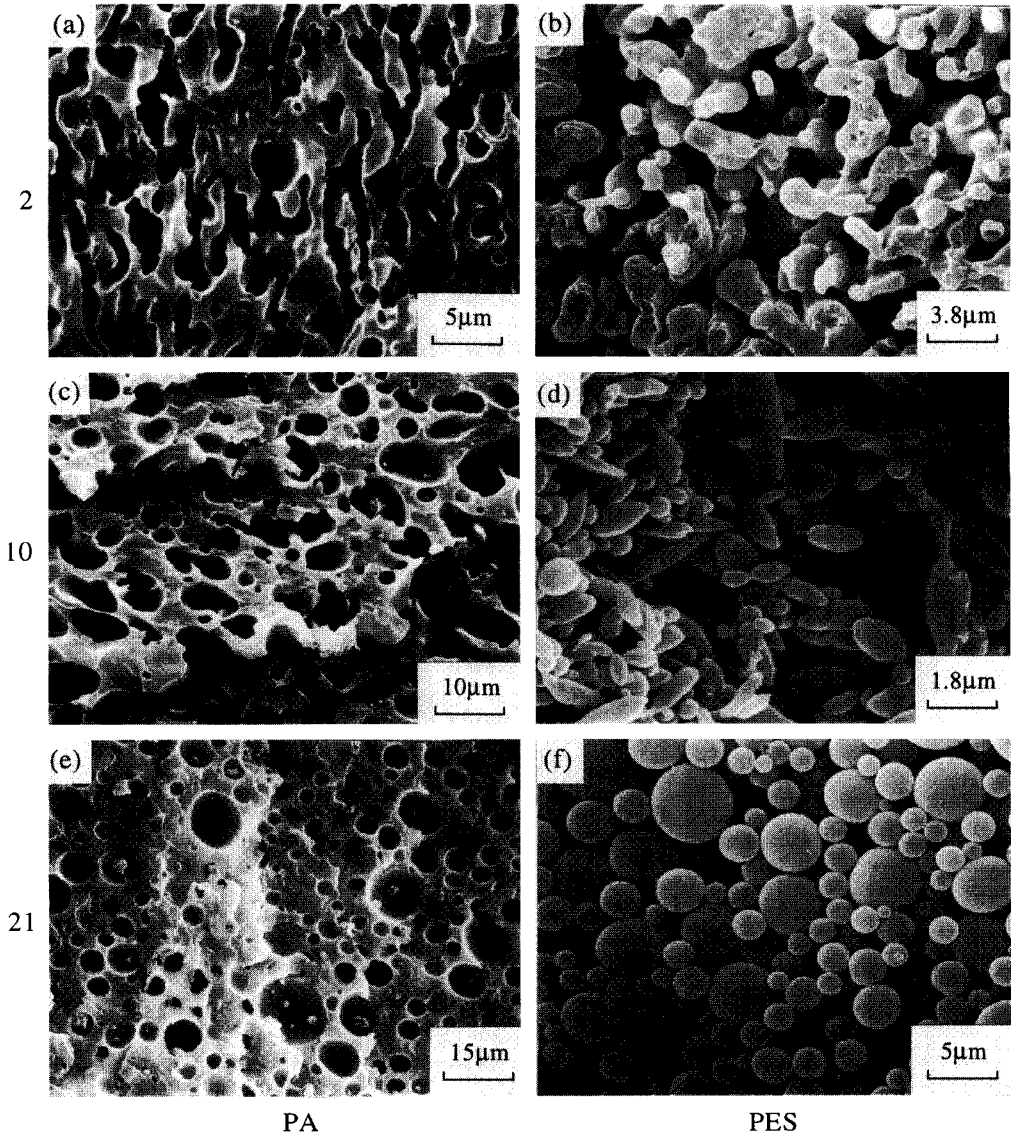

Figure 2 SEM micrographs of remaining PA phase after PES extraction and PES phase after PA extraction in PA/PES 45/55 blends. Numbers in left column denote sampling times in minutes

in the remaining phase. The percentage of 55.5% for the remaining PES phase, less than 60%, indicates that the PES phase is partly continuous. The sum of remaining PA and PES phases is 99.6%. For PA/PES 42.5/57.5 at 2 min sampling time, the measured percentages of remaining PA and PES phases are 40.5% and 59.0%, giving a sum of 99.5%. For PA/PES 45/55, a percentage sum of measured PA and PES remains is 103.3% (49.1% + 54.2%). A sum a little larger than unity means some occlusion occurred in the blend sample, which resulted from some dispersed particle of one phase, surrounded by the other phase and could not be dissolved by the solvent for the other phase. As for the PA/PES 40/60 after different mixing times the weight percentage of remaining PA phase decreases from 44.1% at 2 min through 32.1% at 10 min to 29.5% at 21 min, which indicates that the PA phase gradually becomes partly continuous. While the weight percentage of remaining PES phase increases from 55.5% at 2 min through 61.0% at 10 min to 61.6% at 21 min, resulting from part continuity at 2 min and some occlusion of continuous PES phase at 21 min. From the micrographs in *Figure 2* and the data in *Table 3*, it is undoubted that the results of these two methods, macroscopic and microscopic characterization, are quite consistent. The judgment of morphology development from the macroscopic and microscopic characterization methods is reliable.

Now from microscopic observation (*Figures 2 and 3*) and macroscopic characterization (*Table 3*), it is found that in PA/PES blends the co-phase continuity occurs in the composition range from 30/70 to 45/55 after a 2 min mixing. With increasing mixing time, the composition range for co-phase continuity becomes narrower. The higher viscosity phase PES forms the dispersed phase at concentrations larger than 50%, especially after a longer mixing.

In summary, the region of co-phase continuity (both continuous phases) has been precisely determined in this study (*Table 4*). It is really surprising that the co-continuity occurs in a rather wide composition range after a short time of mixing. This phenomenon suggests that this co-continuity may not be the same as a phase inversion which occurs at a point of composition. This may be a reason 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, microstructures such as layers can usually be observed. As the mixing

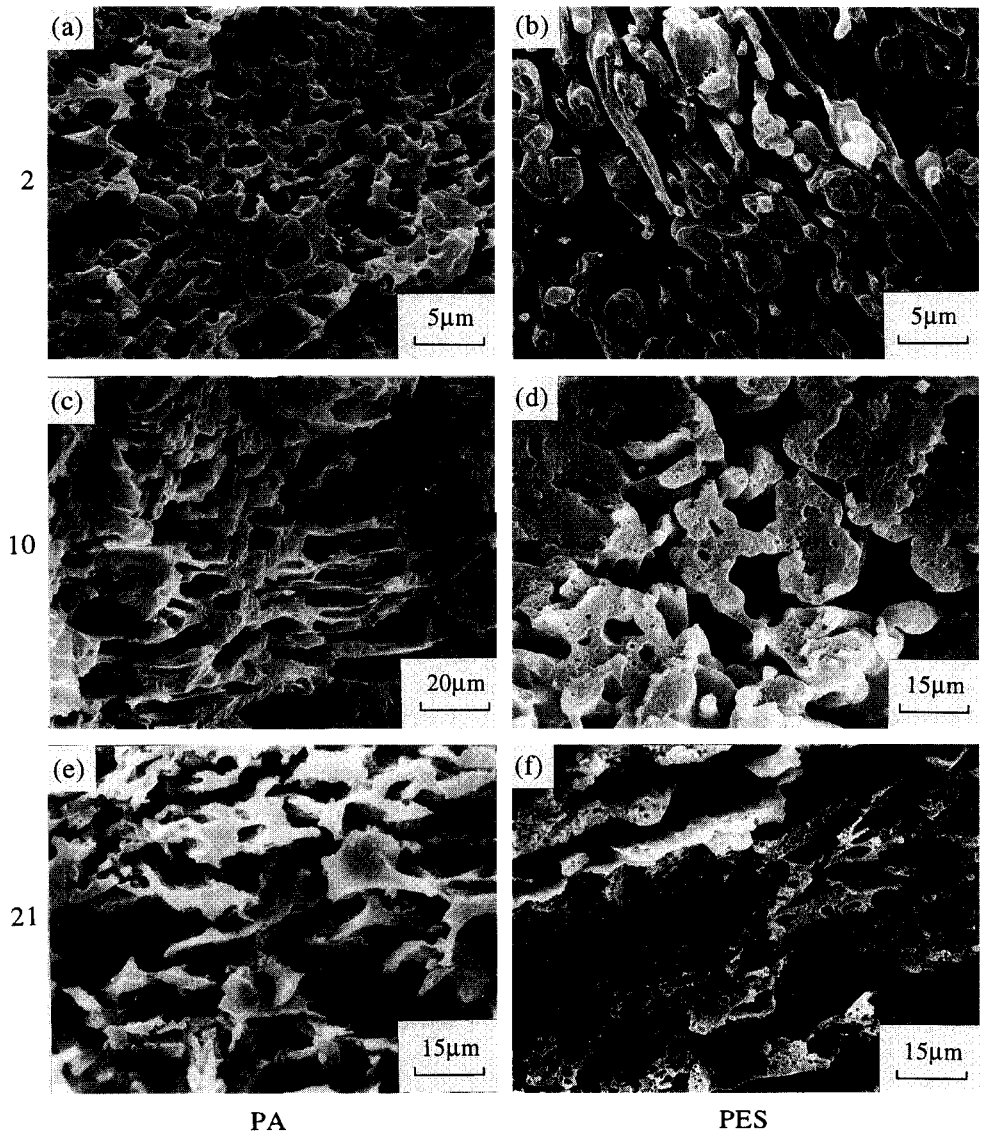

Figure 3 SEM micrographs of remaining PA phase after PES extraction and PES phase after PA extraction in PA/PES 42.5/57.5 blends. Numbers in left column denote sampling times in minutes

Table 4 The state of the remaining PBT phase in PBT/PS blends of different compositions after different time of mixing

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

Notes: d = dispersed, c = continuous, c + d = partly continuous and dispersed, c$^-$ = mainly continuous. Numbers in parentheses are measured weight percentage of the remaining component. Results in square brackets are the state of PS phase judged from the weight fraction of PBT

time increases, the continuous morphology of the lower viscosity phase will keep on breaking into fibres or 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 viscosity ratio on the morphology becomes smaller. After a long time mixing, the co-continuity region will shrink to one point of 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 mixing temperatures, the volume fraction of PA/PES co-pahse continuity after a 21 min mixing should be 50/50. So it is predicted that after a long enough mixing time, the final morphology is

determined only by the volume fraction rather than by the viscosity ratio. The co-phase continuity will occur only at a volume ratio of 50/50, and at other compositions the minor phase will be in the form of spheres. For practical polymer processing such as extrusion, the blending time is usually relatively short. This result is important for predicting and controlling the phase morphology of the blends in processing.

Although both PA and PES phases can be in continuous forms in some blends, the features of their morphologies are different. The continuous PES phase looks like a network consisting of ellipsoids connected by thin necks (*Figure 2b*) and seems on the verge of breakup. The continuous PA phase looks like winding thin walls. This could be attributed to a higher viscosity of PES and a lower viscosity of PA. A melt having a high viscosity is more difficult to flow and spread.

Co-phase continuity in PBT/PS blends ($\lambda = 1$)

Melts of PBT and PS have nearly the same apparent viscosity at the shear rate of 57.6 l/s (*Figure 1*), so their viscosity ratio is close to unity. Toluene can dissolve PS easily without any influence on PBT. However a solvent being a solvent for PBT and a non-solvent for PS could not be found. In the present study, the microstructure of the PS phase is judged only by results of the selective dissolution of the PS phase, followed by weight percentage determination and microstructure observation of the PBT phase (*Table 4*). Some micrographs of remaining PBT phase after extraction are given in *Figure 4*.

The PBT phase in a PBT/PS 50/50 blend is continuous after a 2 min mixing (*Figure 4a*). Judged from this micrograph, the PS phase is continuous, too. When the mixing time increases to 10 min, the remaining PBT phase is still a continuous one (*Figure 4b*). The weight percentage of the remaining PBT phase is 51.5%, a little larger than 50% (*Table 4*). Some isolated holes disperse in the PBT phase. It is clear that the continuous PBT phase occludes some PS and a part of PS has become dispersed particles. For a PBT/PS 60/40, the dissolution result indicates the PS phase has a complete continuity at a concentration of 40% (*Table 4*), which is confirmed by continuous cavities in the PBT phase (*Figure 4c*). For the PBT/PS 60/40, the increased percentage of the remaining PBT phase with mixing time (*Table 4*) means more PS occluded in PBT phase. This is also shown by the change from continuous cavities at 2 min to isolated holes at 10 min (*Figure 4c* and *d*). All these results hint that a wide composition range for a co-phase continuity exists after a short mixing time and a narrow range after a long mixing time. Both phases keep continuous only at PBT/PS 50/50 with a 21 min mixing and the morphology changes little with further mixing. This morphology development is the same as the blend system of PA/PES with the viscosity ratio of 0.03.

In the previous paragraphs, co-phase continuity has been

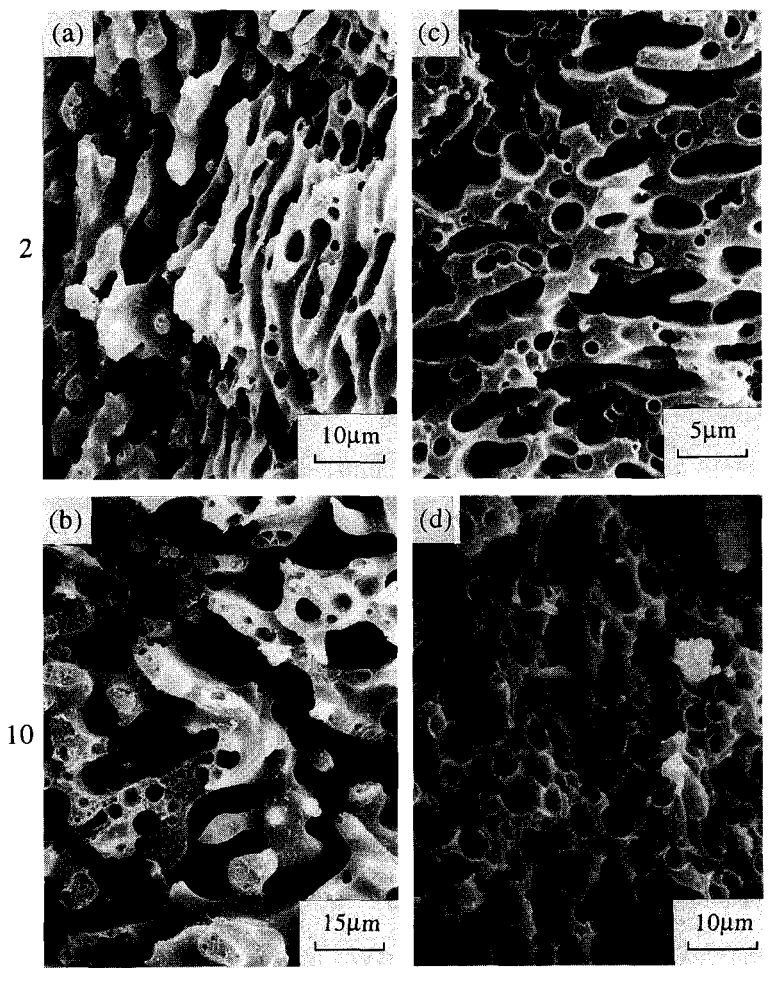

Figure 4 SEM micrographs of remaining PBT phase after PS extraction in PBT/PS 50/50 and 60/40 blends. Numbers in left column denote sampling times in minutes

discussed. It is controlled by the mixing time, together with the composition and the viscosity ratio. However, the morphology development in immiscible binary blends is determined also by the interfacial tension. Based on the published results in the literature, the authors have listed the surface tension of these component polymers and calculated the interfacial tension in these blends[20]. The interfacial tensions 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. The difference between interfacial tensions of these two blends is not large, so that no significant differences are found in the co-phase continuity.

CONCLUSIONS

Methods of microscopic observation and macroscopic characterization have been developed for co-phase continuity in immiscible binary blends, especially in PA/PES blends. After selective dissolution of the component polymers, morphology observed in the micrographs agrees well with the results of macroscopic observation and weight percentage determination. The results show that these methods are reliable, accurate and effective. Based on the micrographs and weight percentages of the remaining phase, it is found that co-phase continuity occurs in a wide composition range at a short mixing time. With increasing mixing time, the composition range of co-phase continuity gets narrow and finally shrinks to one point.

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