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In situ formed copolymers as emulsifier and phase-inversion-aid in reactive polysulfone/polyamide blends

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Abstract

Reactive blending of dissimilar polymers involves in situ reactions of functionalized components to form a block or graft copolymer at the interface between phases. The copolymer is believed to play a role of the emulsifier to prevent particle coalescence and to improve interfacial adhesion. A mixture of non-reactive polysulfone (PSU) and small amount of reactive PSU, phthalic anhydride-terminated PSU (PSU–PhAH), was melt-blended with polyamide (PA) at 65/35 (PSU/PA) wt ratio using a miniature mixer. When the molecular weight of PSU–PhAH was high (comparable with non-reactive PSU), PA particles were dispersed in PSU matrix and the particle size was much smaller than non-reactive system, suggesting the typical emulsifying effect caused by the in situ formed block copolymer. On the other hand, when the molecular weight of PSU–PhAH was much smaller than the non-reactive PSU, phase inversion took place; i.e. at early stages of mixing, PA particles were dispersed in PSU matrix; however, at later stages the PSU particles were dispersed in PA matrix. TEM observation showed a micelle formation in PSU particles. The phase inversion mechanism was discussed in terms of the increase in viscosity of PSU phase caused by the pull-out of the in situ formed block copolymers.

Keywords: Reactive blending; Block copolymer; Emulsifier

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1. Introduction

Reactive blending of dissimilar polymers is attracting great attention to produce high-performance materials [1]. The reactive blending is a process that involves in situ reaction of functionalized components to form a block or graft copolymer at the interface between the phases [2–9]. The copolymer formation is known to be effective for morphology control and for mechanical property improvement.

Theoretical works [10–15] have shown that block copolymers prefer to locate at the interface and reduce the interfacial tension. The copolymers at interface are expected to stabilize morphology against coalescence [16]. In other words, the copolymer is believed to play a role of an emulsifier. However, recent studies [17–19] have shown that behavior of the copolymer during melt processing are more intricate and rather versatile. For example, the in situ formed block copolymer chains are easily pulled out from the interface region by external shear forces during melt blending, whereas the in situ formed graft copolymer chain are hardly pulled out [18]. Their interfacial activities may depend on several factors such as molecular architecture of in situ formed copolymer (graft or block), coupling reaction kinetics, and processing conditions.

In this paper, a different interfacial behavior of in situ formed block copolymers and the effects on morphology development is demonstrated in contrast with the emulsifier activities. A mixture of non-reactive polysulfone (PSU) and small amount (1–10 wt%) of reactive PSU, phthalic anhydride-terminated PSU (PSU–PhAH), was melt-blended with polyamide (PA) at 65/35 (PSU/PA) wt ratio using a miniature mixer. Morphology development and stability were investigated by light scattering (LS) and transmission electron microscopy (TEM).

2. Experimental section

The PSU and PA used were commercial polymers of BASF-AG, Ultrason S1010 and Ultramid T, respectively. PSU is a condensation product of Bisphenol-A and 4,4′-dichlorodiphenyl sulfone. PA is a partially aromatic polyamide consisting of units derived from caprolactam, hexamethylene diamine, and terephthalic acid. Number-average molecular weight (M_n) and weight-average

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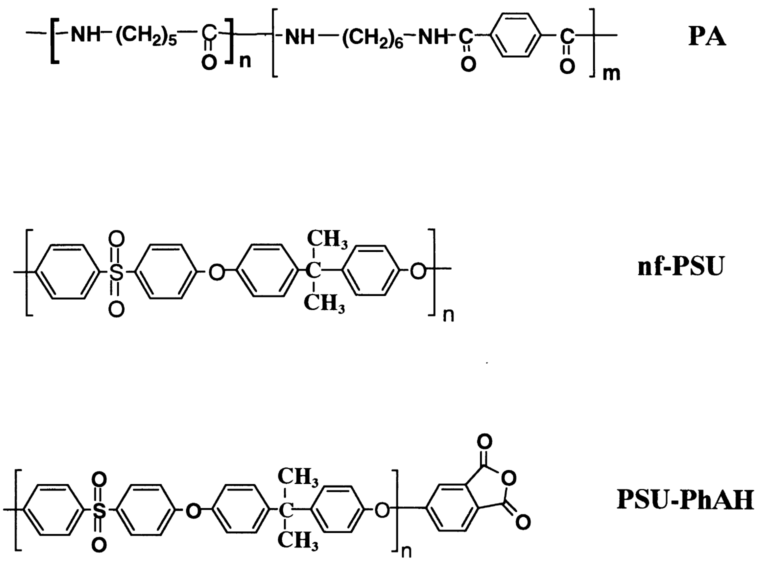

Fig. 1. Chemical structures of polymers used.

molecular weight (M_w) were determined by gel permeation chromatography (GPC) at 25°C. Carrier solvent/standard sample used for GPC were tetrahydrofuran/polystyrene for PSU and hexafluoropropylalcohol/poly(methyl methacrylate) for PA. Two phthalic anhydride terminated-PSUs (PSU–PhAH) with different molecular weights were used as the reactive PSU. They are coded *h*PSU–PhAH and *l*PSU–PhAH. *h*PSU–PhAH has comparable molecular weight with non-reactive PSU and *l*PSU–PhAH has much lower molecular weight than non-reactive PSU. Both PSU–PhAHs were prepared by addition of 4-fluorophthalic anhydride to the as-polymerized solution of polysulfone. The amount of anhydride end-groups was determined by FT-IR. Details of preparation procedure are shown elsewhere [20–22]. Chemical structures of polymers used are shown in Fig.1 and their characteristics are summarized in Table 1.

To remove absorbed moisture, PA pellets were dried under vacuum (10^{-4} mm Hg) at 80°C overnight before blending. Non-reactive PSU, PSU–PhAH, and PA were melt-blended at 65/35 (total PSU/PA) wt ratio using a miniature one gram-scale mixer (Mini–Max Molder, CS-183 MM, Custom Scientific Instruments Inc.) [23] at 310°C. The amount of PSU–PhAH was varied from 0 to 20 wt%. During the mixing, a small amount of mixed melt (40 mg) was picked up by pincette at appropriate intervals and was quickly quenched in ice-water to freeze the two-phase structure in the melt. Thus, we prepared a series of mixed-and-quenched specimen with various mixing times. These specimens were analyzed by light scattering (LS), transmission electron microscope (TEM). The blends and given codes are summarized in Table 2.

The quenched specimen was placed between two cover glasses and melt-pressed to a thin film (ca. 15 μm thick) at 310°C on a hot stage set on light scattering apparatus. After melt pressing, the time-resolved measurement of scattering profiles (angular dependence of scattered light intensity) with a time slice of 1/30 s started. The scattering apparatus consisted of a highly sensitive CCD camera with 576 × 382 pixels, a He–Ne laser of 632.8-nm wavelength and V_v (parallel polarization) optical alignment [24]. Since the two-phase structure in the melt is at a non-equilibrium state, it may coarsen with time after the re-melt. A scattering profile just after the re-melt provides information on the two-phase structure in the mixed-and-quenched blend. In addition, by time variation of light scattering profiles, one can discuss the structure coarsening during isothermal annealing, which may be suppressed by the in situ formed PSU–PA block copolymer.

For TEM observation, the quenched specimen was

Table 1
Characteristics of polymers used

Code	M_n [a]	M_w [a]	η^{*} [b]	Functionality [c]
PA	13 000	35 000	1500	
PSU	12 000	30 000	1700	0
*h*PSU–PhAH	9100	26 000	700	2.2
*l*Psu–PhAH	5500	20 000	150	2.3

[a] By GPC measurement (g/mol).
[b] Complex melt viscosity at 310°C, frequency range 10–50 rad/s (Pa·s).
[c] Content of functional group (wt%).

Table 2
Blend compositions

Code	N1	RH1	R2	RH3	RH4	RL1	RL2	RL3	RL4
PA	35	35	35	35	35	35	35	35	35
PSU	65	62.5	60	55	45	63	61	57	49
*h*PSU–PhAH	–	2.5	5	10	20	–	–	–	–
*l*PSU–PhAH	–	–	–	–	–	2	4	8	16

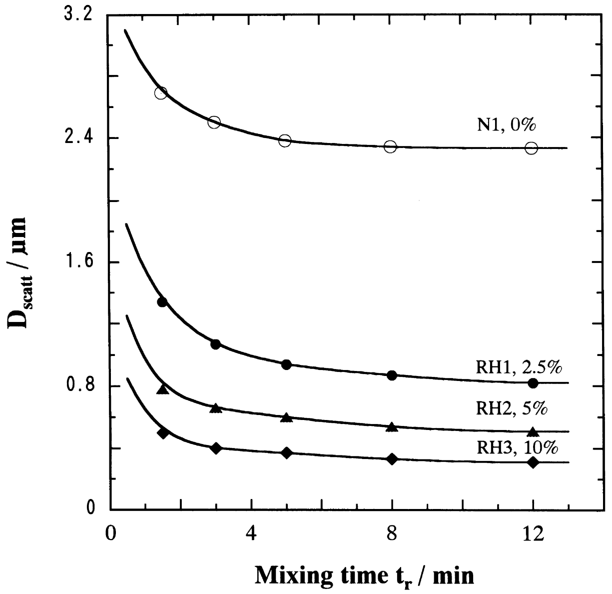

Fig. 2. Time variations of average PA particle diameter D_{scatt} during melt mixing at 310°C.

cryomicrotomed at −65°C by ultramicrotome (Reichert Ultracut-Nissei). The thin section of ca 60 nm thickness was mounted on 200-mesh copper grid and exposed to the vapor of ruthenium tetroxide (RuO_4) for 20 min. The two-phase morphology was observed by transmission electron microscope, JEM-100CX (JEOL), at an accelerating voltage of 100 kV. TEM picture was digitized using a scanner (EPSON GT-8500). The area of individual particle a_i was directly determined using a software (NIH Image Analysis System). The diameter of dispersed particles D_i was calculated by $D_i = 2(a_i/\pi)^{1/2}$, assuming the shape of particle to be circular. The average was obtained by

$$D_{\mathrm{TEM}} = \sum_{i=1}^{N} D_i^3 / \sum_{i=1}^{N} D_i^2 \tag{1}$$

where N was 100–300 in a TEM picture. The average by Eq. (1) may be appropriate for comparison with that by light scattering, because the particle size by light scattering is based on the surface area per unit volume, which corresponds to the ratio of volume-average diameter (numerator in Eq. (1)) and surface-average diameter (denominator in Eq. (1)).

The complex dynamic viscosity η^* was measured at 310°C by Dynamic Stress Rheometer at parallel-plate mode (plate radius 12.5 mm, gap 1.0 mm).

In a differential scanning calorimeter (DSC), Seiko EXSTRAR600, neat polymer or blend specimen packed in aluminum pan was heated at a heating rate 10°C min^{-1} under nitrogen atmosphere. The melting temperature and enthalpy of fusion were obtained from the maximum and the area of the endothermic peak, respectively. The relative crystallinity X_c was calculated by: $X_c = \Delta H^*/\Delta H^0_{\mathrm{PA}}$, where ΔH^* is the enthalpy of fusion per gram of the blend and ΔH^0_{PA} is the enthalpy of fusion per gram of 100% crystalline PA [= 40 J/g] [25].

3. Results and discussion

3.1. *In situ formed block copolymer as emulsifier*

For all the re-melted blend specimens, the intensity of scattered light monotonically decreased with increasing scattering angle. The mean diameter of the dispersed particle D_{scatt} was obtained by Debye–Bueche plot [26,27]. More details of data analysis have been given elsewhere [6,9,17]. Fig. 2 shows the mean PA particle size by light scattering as a function of mixing (reaction) time. One can see systematic size reduction process and the effect of reactive component (*h*PSU–PhAH) on the particle size. TEM micrographs after 8 min mixing are shown in Fig. 3. In these micrographs, the darker phase is PSU, stained more deeply by RuO_4. TEM results agree well with those from light scattering analysis. From Figs. 2 and 3, one can see that all reactive systems (RH1, RH2, and RH3) yielded smaller particles than the non-reactive system. Since the reactive system is known to generate the PSU–PA block copolymer, which would play a role of emulsifier to provide entropic repulsion between neighboring particles and hence prevent particle coalescence during melt mixing. The effect of loaded amount of *h*PSU–PhAH on the dispersed particle size could be also demonstrated in Fig. 4. The higher amount of *h*PSU–PhAH leads to the smaller particle size, demonstrating clearly the emulsifying effect of the in situ formed block copolymer.

The time variations of D_{scatt} during static annealing at 310°C are shown in Fig. 5. One sees that in the non-reactive system (N1), D_{scatt} increases with annealing time, t_a. It suggests that structure coarsening took place during annealing. By contrast, D_{scatt} of the reactive system containing large amount of *h*PSU–PhAH (≥5%) remains constant, suggesting that the in situ formed PSU–PA block copolymer prevents coalescence. Such morphology stabilization mechanism is already set up in short mixing time ($t_r =$ 1.5 min).

As a measure of coalescence rate, we estimated a slope α of D_{scatt} versus t_a plot in Fig. 5. The slope α is plotted as a function of mixing time in Fig. 6. It can be seen that, even in a low *h*PSU–PhAH content system (RH1, –●–, 2.5 wt%), a nice stabilization mechanism is established after mixing for 8 min ($t_r = 8$ min), suggesting sufficient coverage of the interface by the in situ formed block copolymers. When the *h*PSU–PhAH content is higher, the stabilization mechanism is set up in shorter time.

3.2. *In situ formed block copolymer as phase-inversion-aid*

When the *l*PSU–PhAH, having smaller molecular weight than the non-reactive PSU, was introduced to the blends,

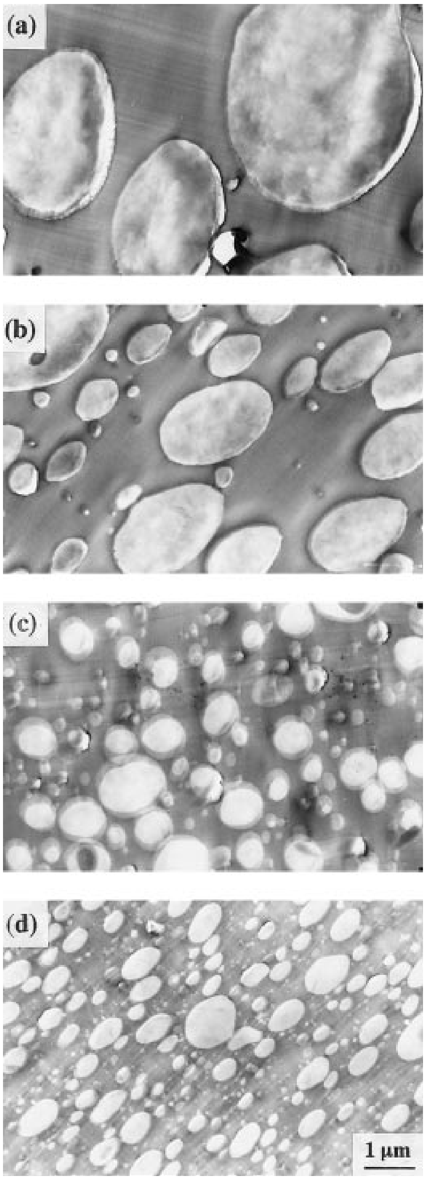

Fig. 3. TEM micrographs of blends melt-mixed at 310°C for 8 min: (a) N1 (non-reactive system); (b) RH1; (c) RH2 and (d) RH3.

phase inversion took place. The phase inversion process is shown in Fig. 7. At early stage ($t_r = 1.5$ min), the major component (PSU) is the matrix (dark phase). At a later stage ($t_r = 8$ min), the minor component (PA) is the matrix (bright phase). The phases are clearly inverted from PA particles/PSU matrix to PSU particles/PA matrix. Fig. 7b ($t_r = 3$ min) may correspond to a transient point. In Fig. 7c, PSU particles occlude tiny PA particles. The occlusion of PA particles should be caused by the phase inversion. Much finer PA domains (~40 nm) are also occluded (see Appendix A). They should be formed by the micelle formation caused by pull-out of in situ formed block copolymers from the interface [18]. Micelle-rich particles are shown by a higher magnification TEM in Fig. 8. Taking account of the micelle formation, the phase inversion could be interpreted as follows.

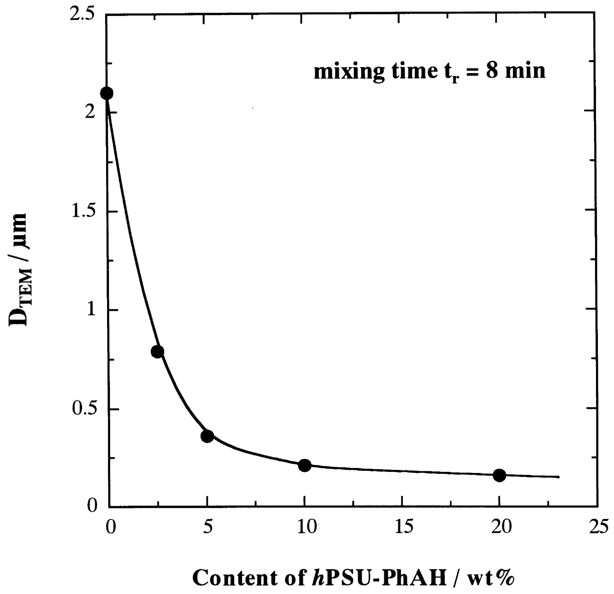

Fig. 4. Average particle size diameter D_{TEM} as a function of the loaded amount of *h*PSU–PhAH.

In non-reactive blends of dissimilar polymers, major component (1) usually tends to be the matrix, while minor one (2) the dispersed phase. In a symmetrical blend (50/50), the lower viscosity component tends to be the matrix. The situation is empirically described using the parameter λ:

$$\frac{\eta_1}{\eta_2}\frac{\phi_2}{\phi_1} = \lambda \tag{2}$$

i.e. the component 2 likes to be the matrix for $\lambda > 1$, where η_i is the viscosity of component i and ϕ_i its volume fraction

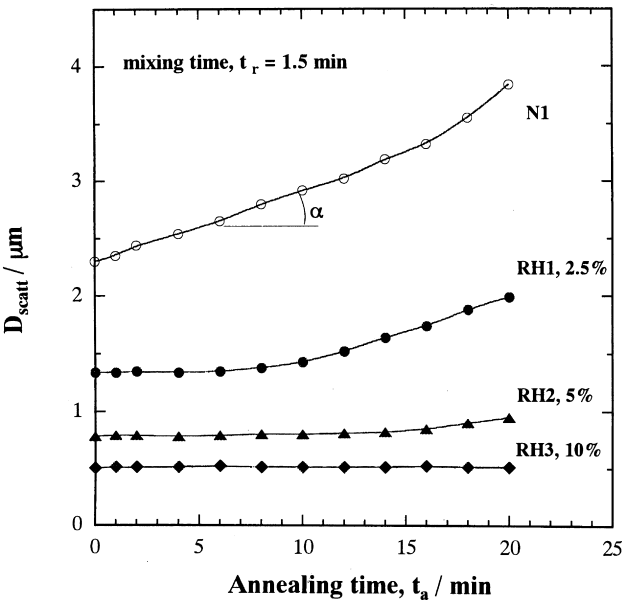

Fig. 5. Time variation of average PA particle diameter D_{scatt} during static annealing at 310°C after melt mixing for 1.5 min. Slope α may be the coalescence rate (symbols are the same as in Fig. 2).

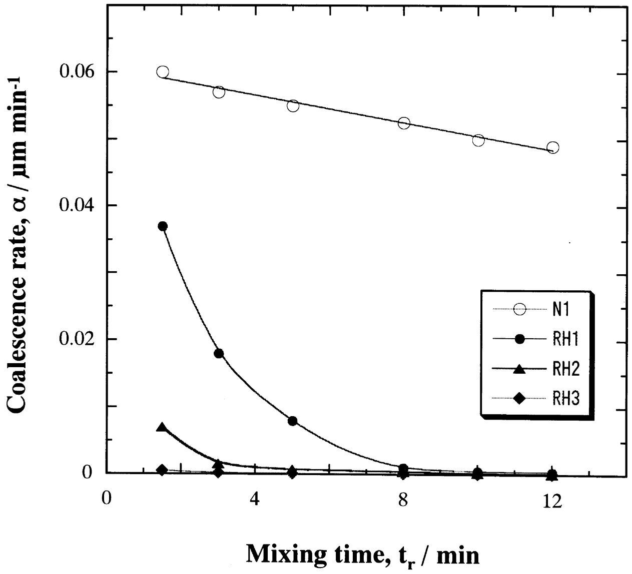

Fig. 6. Coalescence rate α versus residence time in mixer t_r (symbols are the same as in Fig. 5).

[28–30]. Let us define phase 1 is PSU and phase 2 is PA. The complex melt viscosity at a frequency range of 10–50 rad/s at 310°C was 1700 Pa·s for PSU (η_1) and 1500 Pa·s for PA (η_2). Then, the λ value for non-reactive system is 0.63 (assuming $\phi_1 = 0.65$ and $\phi_2 = 0.35$), hence PSU (major component) should be the matrix. In the reactive system, however, the micelle formation takes place so that the melt viscosity of PSU phase (η_1) increases with time of mixing (see below). Then, λ becomes larger than unity and the phase inversion can take place. This process is schematically shown in Fig. 9.

To confirm the increase of melt viscosity by micelle formation, we separately prepared a model blend (PSU/*l*PSU–PhAH/PA: 82/6/12) and measured the viscosity as a function of mixing time. Note that the small amount of PA apparently would be stoichiometrically enough for coupling reaction with *l*PSU–PhAH but it would not be enough for phase inversion. The results are shown by a broken line in Fig. 10. Employing this time variation as an alternative of the $\eta_1(t_r)$ in real system, λ vs. mixing time curve was generated, as shown by a solid line in Fig. 10. λ crosses over 1 at $t_r \approx 3$ min. Thus, the phase inversion can be interpreted in terms of the increase in viscosity of PSU phase by the pull-out of the in situ formed block copolymers and the consequent micelle formation.[1]

The phase inversion from PA particles/PSU matrix to PSU particles/PA matrix was also found in other blends containing higher amount of *l*PSU–PhAH (RL3 and RL4). TEM micrographs similar to Fig. 7 were also observed.

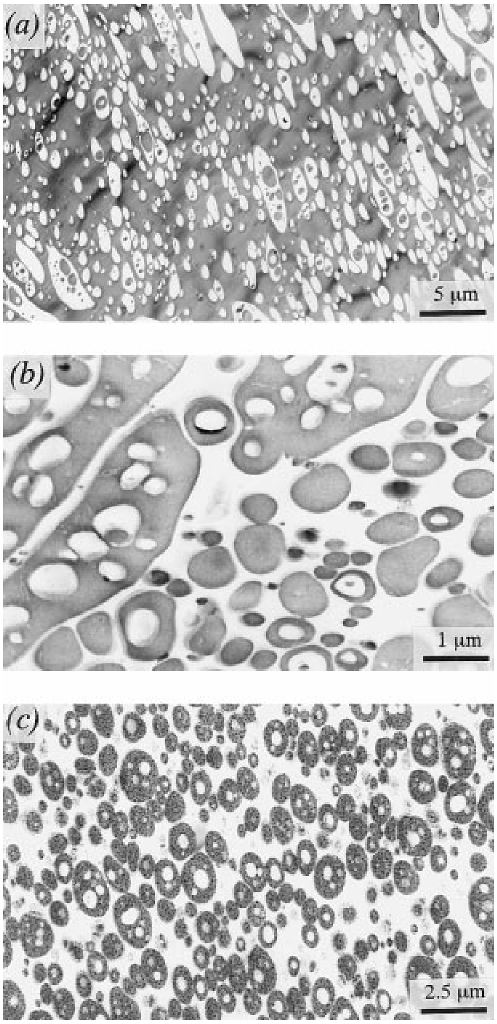

Fig. 7. TEM micrographs of 4/61/35 *l*PSU–PhAH/PSU/PA (RL2) blend melt-mixed at 310°C for (a) 1 min; (b) 3 min and (c) 8 min showing phase inversion.

Another point to be discussed is why phase inversion could take place when *l*PSU–PhAH was employed but not in the case of *h*PSU–PhAH system. In other words, why the pull-out of in situ formed PA–PSU block copolymers did not take place in RH1, RH2 and even RH3 systems.

The theory of block copolymer suggests that a symmetric AB block copolymer (A block length ≈ B block length) prefers to locate at interface but a very asymmetric block copolymer (of long A block and short B block) is unstable at interface and tends to stay in A homopolymer phase as micelles [13]. However, in *l*PSU–PhAH/PA system which would generate a rather asymmetric block copolymer, the micelles were formed in PSU phase (in B phase, not in A). Then we need another explanation.

In the previous study [19], we have shown that the dense accumulation of in situ formed copolymer chains at the interface appears to be a prerequisite for the pull-out process

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[1] The cross-over at $t_r = 3$ min agrees very well with the experimental result. However, it would be just a coincidence. The calculated cross-over point could slightly deviate from the observed one, if one could use the real $\eta_1(t_r)$ and take account of a slight change in composition (ϕ_1/ϕ_2) with the micelle formation.

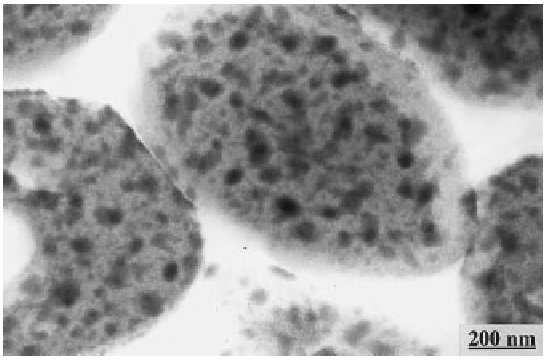

Fig. 8. High magnification TEM micrograph of RL2 blend (after 8 min mixed at 310°C), showing the occluded PSU–PA micelles in PSU particles.

by external shear forces. It implies that when the amount of in situ formed block copolymers is relatively high, they are subjected to a spatial entropy penalty caused by chain stretching perpendicular to the interface. By contrast, in the case of low accumulation, the copolymers are free from the penalty so that they can stay at the interface with stability and they are hardly pulled out. The population of the in situ formed copolymer during reactive blending depends on the kinetics of coupling reaction. Recent theoretical studies [31,32] of polymer–polymer reaction kinetics at an interface separating two immiscible polymers have shown that the reaction kinetics in entangled melt system is diffusion-controlled and the rate constant k can be written as:

$$k \sim \frac{1}{N \ln N} \tag{3}$$

where N is the degree of polymerization. Thus, one may expect much smaller k in *h*PSU–PhAH system than in *l*PSU–PhAH system. Hence, the in situ formed block copolymers in *h*PSU–PhAH system may prefer to stay at the interface and play a typical role of emulsifier.

4. Conclusion

Thus, two examples of different interfacial behavior of in situ formed block copolymers were demonstrated. When the in situ formed block copolymers stay at the interface, they act as a typical emulsifier to render faster size reduction process, finer particle size and better morphology stability, compared with non-reactive system. However, when the in situ formed block copolymers are pulled out from the interface to form micelle in bulk, they behave as a phase-inversion-aid.

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Appendix A

From the high magnification TEM micrograph in Fig. 8, one can clearly see the dark spots, which should be assigned to PA cores of PSU–PA micelles. If it is so, why were the PA cores stained more deeply by RuO_4 than PSU? It has

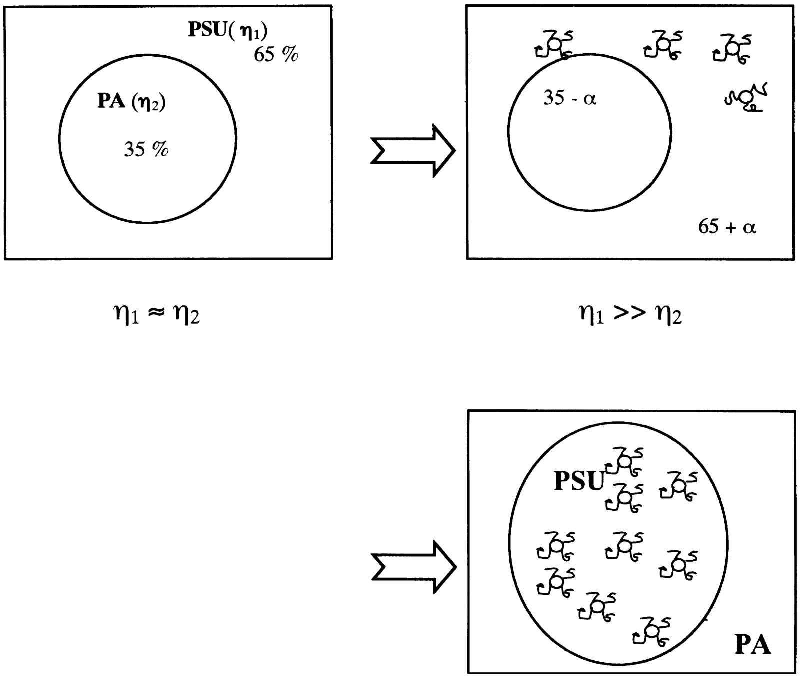

Fig. 9. Schematic representation of the phase inversion induced by the pull-out of in situ formed block copolymers.

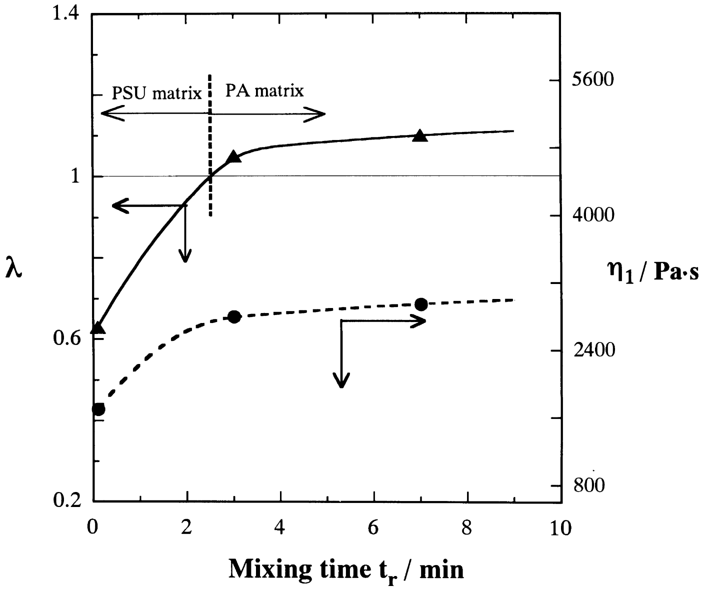

Fig. 10. λ and η_1 vs. mixing time plot, indicating the phase inversion point.

been shown that amorphous regions of semi-crystalline polymers, such as PA, polyethylene, polypropylene, and poly(butylene terephthalate) can preferentially be stained by RuO_4 [33,34]. Then one can expect that the crystallization in PA cores was suppressed (probably due to the spatial constraint) and the cores are highly amorphous. Actually the degree of crystallization by DSC results in *l*PSU–PhAH system was much lower ($X_c \approx 15\%$) than that in *h*PSU–PhAH system. ($X_c \approx 21\%$). Consequently, the core part could be stained more deeply than PSU. To confirm it, we prepared a 80/20 *l*PSU–PhAH/PA blend, in which a lot of micelles of in situ formed block copolymers should be generated and consequently highly amorphous PA cores are expected to be formed in a quenched specimen. Note that melt processing and TEM sample preparation conditions were similar as to other blends, given in Section 2. Fig. 11 shows TEM micrograph of the 80/20 *l*PSU–PhAH/PA blend after 7 min of mixing. As expected, one can see dark spots of PA cores with diameter of around 30 nm dispersed in a gray PSU matrix. Thus, PA phase can be stained by RuO_4 more deeply than PSU when PA crystallization is suppressed.

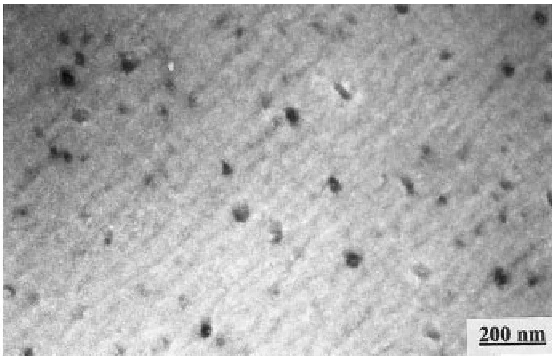

Fig. 11. TEM micrograph of a 80/20 *l*PSU–PhAH/PA blend melt-mixed at 310°C for 7 min.

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