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Reactive blending of polysulfone with polyamide: a difference in interfacial behavior between in situ formed block and graft copolymers

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Abstract

Reactive blending of polysulfone (PSU) and polyamide 6 (PA) was carried out at 20/80 weight ratio using a gram-scale mixer at 260°C. Maleic anhydride-grafted PSU (PSU–MAH) and phthalic anhydride-terminated PSU (PSU–PhAH), having almost same molecular weight ($M_w \approx 20$ k) and functional group content (ca. 90 μmol/g) were prepared and used. The particle size reduction process was investigated by light scattering and transmission electron microscopy (TEM). Both reactive systems yielded finer particle size via faster particle size reduction process, compared with non-reactive system. Attainable particle size was in 10 nm-order in PSU–PhAH system, while in sub-μm scale in PSU–MAH system. TEM observation at early stage of reactive blending in PSU–PhAH system showed that the in situ formed PSU–PA block copolymers escaped from interface to form micelle in PA matrix. Such micelle formation was observed only in the melt-mixed blend but not in a quiescently annealed blend, suggesting that the block copolymer prefer to locate at the interface under static condition but they are easily pulled out when PA-brushes are subjected to external shear forces during melt-mixing. The micelle formation leads to the fine dispersion of 10 nm level in the final blend. By contrast, the micelles were never observed in the PSU–MAH blend, in situ graft copolymer forming system, even at the late stages of the reactive processing. It suggests that the graft copolymer is highly resistant to be pulled out by the external forces. Then the graft copolymer seems to act as a simple emulsifier to attain the size reduction to sub-μm level.

Keywords: Polymer blends; Reactive processing; Graft copolymer

1. Introduction

Blending of dissimilar polymers offers attractive opportunity for the development of novel materials with useful combination of properties [1]. However, the vast majorities of these polymer pairs are thermodynamically immiscible and, when blended, usually display poor properties, owing to their unstable morphology and poor adhesion between the phases. Such problems have been overcome by the introduction of a proper “compatibilizer” to modify the interfacial condition. The process is commonly called compatibilization. A compatibilization strategy frequently proposed is the addition of a premade block copolymer composed of blocks that are miscible with the homopolymers [2–6]. Another strategy is the reactive processing or reactive blending in which a graft or block copolymer can be formed by in situ coupling reaction of functionalized components [7–14]. This approach is more attractive for industrial applications [15]. The copolymer introduced by either ways is expected to play a dual role. One is to reduce interfacial tension and prevent coalescence, thus engendering finer dispersion. Another is to enhance adhesion between the phases in solid state, hence improving the mechanical properties.

Theoretical works [16–21] indicate that diblock copolymers prefer to locate at the interface and it should be very efficient in compatibilizing blends by lowering the interfacial tension and stabilizing the morphology against coalescence. Reduction of the interfacial tension by adding the premade block copolymers have been observed experimentally in several studies [22–27]. The compatibilizing effect of premade block copolymers on melt processing and static annealing was also confirmed [28,29]. However, the recent studies [28,30] have shown that the premade block copolymers are less effective in stabilizing morphology than the in situ formed copolymers. Further, it has been shown that the in situ formed copolymers in reactive processing lead to yield the finer dispersion and the narrower size distribution of particle size than the premade block copolymer, even

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Table 1
Characteristics of polymers used

Nomenclature	M_n[a]	M_w[a]	Viscosity no.[b]	Functionality[c]
PA	13 000	25 000		40
nf-PSU	5780	28 800	36.2	0
PSU–MAH	8000	21 300	28.9	93
PSU–PhAH	5300	20 660	29	85

[a] By GPC.

[b] Solution viscosity measured at 1 wt% polymer concentration in NMP, ml/g.

[c] Content of functional groups, μmol/g.

when the amount of in situ formed copolymer is significantly less than that of the premade block copolymer added.

Although the theory has shown that the block copolymer should thermodynamically prefer to lie at the interface, we recently found that the block copolymers formed in situ at the interface during reactive blending can escape the interface in the form of micelles [30,31]. These results are unexpected. Such behavior has never been observed for the in situ graft copolymer forming system. The aim of this study is to investigate a difference in compatibilization behavior between the in situ formed block and graft copolymers during melt blending. We carried out melt blending of functionalized polysulfones (PSU) with polyamide 6 (PA) at 20/80 weight ratio using a miniature mixer. Two types of functionalized PSUs were used; maleic anhydride grafted polysulfone (PSU–MAH) and phthalic anhydride terminated polysulfone (PSU–PhAH). The morphology developments were studied by light scattering and transmission electron microscopy (TEM). The stability of in situ formed copolymer at the interface was investigated at quiescent condition and the result was compared with that at dynamic condition. Kinetics of coupling reaction between functional groups ($-NH_2$/–MAH and $-NH_2$/–PhAH) was also investigated.

2. Experimental section

2.1. Materials

The PA used was a commercial polyamide 6 (Ultramid B3, BASF). Two different types of functionalized PSUs, PSU–MAH and PSU–PhAH, were prepared following synthesis procedure given in the literature [32–34]. As a control sample; PSU without functional group (nf-PSU) was also synthesized. To analyze the kinetics of coupling reaction between the functional groups on PSU and the amino-chain end of PA, a polystyrene with an amino chain end ($PS-NH_2$) was also synthesized by anionic polymerization. The $PS-NH_2$ with sharp molecular weight distribution was useful to analyze the coupling reaction by gel permeation chromatography (GPC).

2.1.1. *nf-PSU*

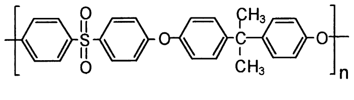
Dichlorodiphenylsulfone (287.08 g; 1 mol), Bisphenol-A (223.83 g; 0.9805 mol) and K_2CO_3 (140.97 g) were dissolved in 1600 ml dry *N*-methyl-2-pyrrolidone (NMP, dried with CaH_2 and distilled). The mixture was heated to 190°C for 6 h in a nitrogen atmosphere. During this time, the azeotropic mixture of NMP and water was removed continuously. The solution was cooled to room temperature, diluted with NMP (1600 ml) and filtered. Then, the polymer was isolated by precipitation in water. The polymer was extracted three times with hot water and dried for 12 h at 130°C. The amount of chlorine-end groups was 98 wt% (detected by elemental analysis). The characteristics of this product are summarized in Table 1.

2.1.2. *PSU–MAH*

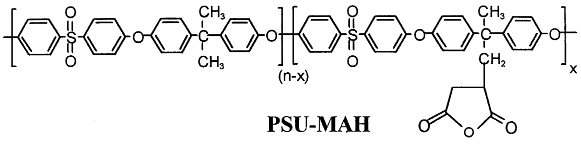
nf-PSU (50 g) was dissolved in chlorobenzene, the solution was heated to reflux. 11.3 g of maleic anhydride and 3.5 g dicumylperoxide were added over a period of 4 h. After refluxing for another 1 h, the solution was cooled to room temperature and the polymer was isolated by precipitation in ethyl alcohol. The polymer was filtered and redissolved in NMP and again precipitated in a mixture of NMP/H_2O (1/4). After filtration the polymer was extracted with hot water and dried. Finally, the product was dried at 130°C in vacuum for 12 h. The amount of anhydride groups was determined by potentiometric titration. The properties of the product are also given in Table 1.

2.1.3. *PSU–PhAH*

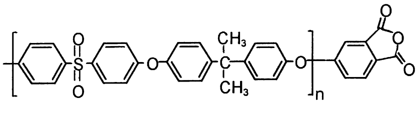
Dichlorodiphenylsulfone (287.08 g; 1 mol), Bisphenol-A (228.28 g; 1 mol) and K_2CO_3 (140.97 g) were dissolved in 1600 ml dried NMP. The mixture was heated to 190°C for 4 h in a nitrogen atmosphere. During this time, azeotropic mixture of NMP and water were continuously removed. Then, 26.58 g (0.16 mol) of 4 fluorophthalic anhydride and 9.3 g (0.16 mol) KF were added and the solutions were further stirred for 1 h. The solution was cooled to room temperature, diluted with NMP (1600 ml) and filtered. Then, the polymer was isolated by precipitation in water. The polymer was extracted three times with hot water and dried for 12 h at 150°C. The amount of phthalic anhydride end groups was determined by FT-IR. The characteristics of this product are summarized in Table 1.



nf-PSU



PSU-MAH



PSU-PhAH

2.1.4. PS–NH$_2$

Polymerization and reaction were carried out under high vacuum conditions (10^{-6} mmHg) in sealed glass reactors with break seals. Anionic polymerization of styrene, initiated by *sec*-butyllithium in heptane, was carried out in tetrahydrofuran (THF) at −78°C for 20 min. Then an excess (1.5 equivalent to initiator) of dried and purified 2,2,5,5-tetramethyl-1-(3-bromopropyl)-1-aza-disilacyclopentane in THF solution was added to the solution of the living polymer at −78°C, and the reaction mixture was allowed to stand for 30 min at −78°C. The polymer was then precipitated by the addition of an excess of methanol. It was purified twice by reprecipitation. The silyl protecting groups at the polymer ends were completely deprotected during the precipitation step. More details of synthesis method could be found elsewhere [35]. The obtained polymer had $M_n = 5310$ g/mol and $M_w/M_n = 1.07$.

2.2. Melt mixing

PA pellets were dried under vacuum (10^{-4} mmHg) at 80°C for 12 h before mixing to remove water completely. Melt mixing was carried out in a one gram-scale mixer, Mini–Max Molder (CS-183 MM, Custom Scientific Instruments Inc.) [36] at 260°C. Three rotational speeds were used: 50, 100 and 150 rpm, corresponding to maximum shear rate of 7,16 and 25 s^{-1}. Weight ratio of PSU/PA was fixed at 20/80. 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 residence times in the mixer. These specimens were analyzed by light scattering, TEM.

2.3. Morphology analysis

The quenched specimen was placed between two cover glasses and melt-pressed to a thin film (ca. 15 μm thick) at 260°C on a hot stage set on light scattering apparatus. After melt-pressing, the time-resolved measurement of scattering profile (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 [37,38]. As 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.

For TEM observation, the quenched specimen was cryomicrotomed at − 45°C by ultramicrotome (Reichert Ultracut-Nissei). The ultrathin section of ca. 60 nm thickness was mounted on 200 mesh copper grid and exposed to the vapor of ruthenium tetroxide (RuO_4) for 10 min. RuO_4 preferentially stains PSU phase to provide better contrast under TEM. The two-phase morphology was observed by TEM, JEM-100CX (JEOL), at an accelerating voltage of 100 kV. TEM picture was digitized using 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 the particle being circular. The average was obtained by

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

where N was 200–500 in a TEM picture. The average by Eq. (1) may be appropriate for the 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)).

2.4. Coupling reaction

Coupling reaction of PS–NH$_2$, a model polymer, with PSU–PhAH or PSU–MAH was carried out in chlorobenzene at 60°C. The reaction was performed at stoichiometric condition: [MAH]or [PhAH]/[NH$_2$] = 1. A small amount of reacted solution was picked up by microsyringe at appropriate intervals and the reaction was stopped by adding an excess amount of dimethylformamide (DMF) (to protect the amino groups). Then the powder product was collected by precipitation using hexane and methanol, vacuum dried at 25°C for 24 h and then was dissolved in THF. GPC instrument (HLC8020, Tosoh) equipped with the polystyrene gel column (TOSOH G 5000H$_{XL}$, G4000H$_{XL}$, and G3000H$_{XL}$) was used to observe the change in the molecular weight distribution with reaction. GPC chromatograms in THF were obtained by refractive index (RI) detection at 40°C.

Additionally, several experiments were performed. The experimental details are intentionally inserted in Section 3 for providing a better understanding.

3. Results and discussion

3.1. Size reduction process

For all the re-melted blend specimens, the intensity of scattered light monotonically decreased with increasing scattering angle. The mean diameter of the dispersed particles D_{scatt} was obtained by Debye–Bueche plot [39,40]. More details on data analysis have been given elsewhere [11,14]. Fig. 1 shows the PSU mean particle size as a function of mixing (reaction) time of the blends made at 260°C (100 rpm). A very rapid decrease in the particle size is observed. The size decreases in three decades, from mm scale (pellet size) to μm level, in a short time. The

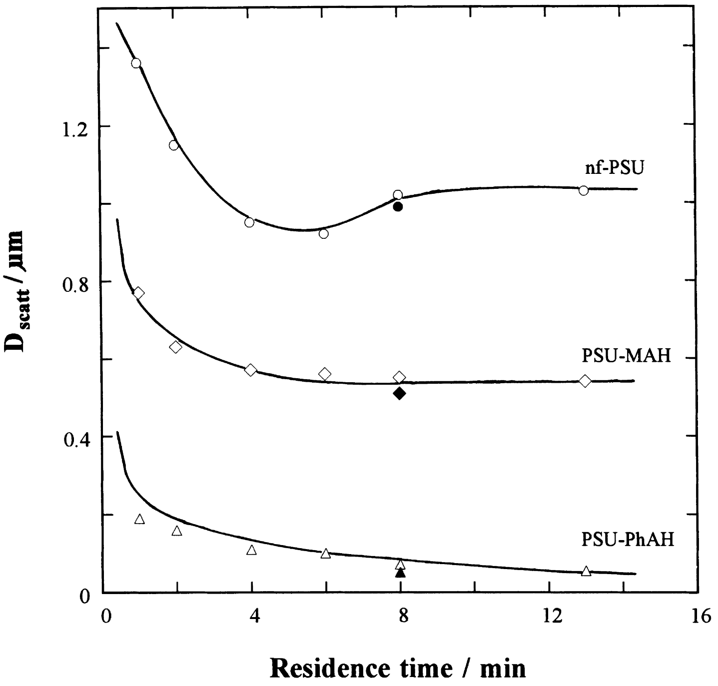


Fig. 1. Time variation of PSU average particle diameter D_{scatt} during melt mixing at 260°C at a rotor speed of 100 rpm.

morphology of the blend after 8 min mixing was shown in TEM micrographs Fig. 2. The darker region is PSU phase stained by RuO_4. The average particle sizes by TEM are shown by closed symbols in Fig. 1, showing a better agreement between the values by light scattering and by TEM. From Figs. 1 and 2, one can see the effect of functional components on the size reduction process. Both reactive systems yield finer particles via faster size reduction processes, compared with non-reactive system. These are expected results, as the reactive system may generate the PSU–PA graft or PSU–PA block copolymer[1], which would play a role of emulsifier to prevent particle coalescence and to reduce the interfacial tension.

There is a difference in attainable particle size between the two reactive systems; sub-µm in PSU–MAH system and 10 nm level in PSU PhAH system. Further, in Fig. 1, the size reduction in PSU–PhAH system still continues even after 8 min mixing, whereas the particle size levels off at around 4 min in PSU MAH system. The results imply that there must be dissimilarity in size reduction process between the two reactive systems.

Fig. 3 shows TEM micrographs of PA/PSU–PhAH blend at very early stage (1 min) of mixing. In low magnification (Fig. 3(a)), one can see large PSU sheets and fine PSU domains nearby. At higher magnification (Fig. 3(b)) the fine domains of 16–20 nm diameter are clearly seen near the PSU sheets. Similar result was obtained at 2 min mixing. The results imply that many PSU–PA block copolymers are in situ formed even at the early stages and they are escaping from the interface region as micelles or being pulled out by external shear forces into PA matrix. Note that, the estimated size from TEM micrograph Fig. 3(b) (ca. 16–20 nm) is very close to domain size of pre-made PSU–PA block copolymer prepared by solution method (A premade block copolymer prepared by coupling amorphous polyamide ($M_n = 9400$) with PSU–PhAH ($M_n = 5500$, 2.8 wt% PhAH end group (Ref [31]). Much bigger particles are also seen in Fig. 3. They are probably the solubilized micelles; i.e. PSU domains swollen by un-reacted PSU domains. Successive micelle formation at later stages of melt mixing could yield the fine and uniform dispersion of PSU domains in Fig. 1(c). By contrast, such micelles are never seen in PSU–MAH system (Fig. 1(b)), implying that the pull out or the escape of copolymers does not occur in the PSU–MAH system, which may yield graft copolymers.

According to the theory of polymer–polymer interface by Leibler [18], symmetric block copolymer prefers to locate at the interface, whereas asymmetric copolymer tends to go to the bulk as micelles. The in situ formed copolymer in this study should have a rather better symmetry (see Table 1) so that they are expected to stay at the interface. However, a slight deviation from the symmetry and/or the difference in molecular architecture (block or graft) might cause a destabilization of the copolymers at the interface and force them to leave the surface as micelles. Such thermodynamic stability or instability of the in situ formed copolymers was investigated as follows.

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[1] Primary amine on PA chain and cyclic anhydride on PSU chain reacts to yield amic acid. The amic acid is converted to imide at high temperature [7]. Then, PA and PSU chains are combined by imide linkage to form block or graft copolymer.

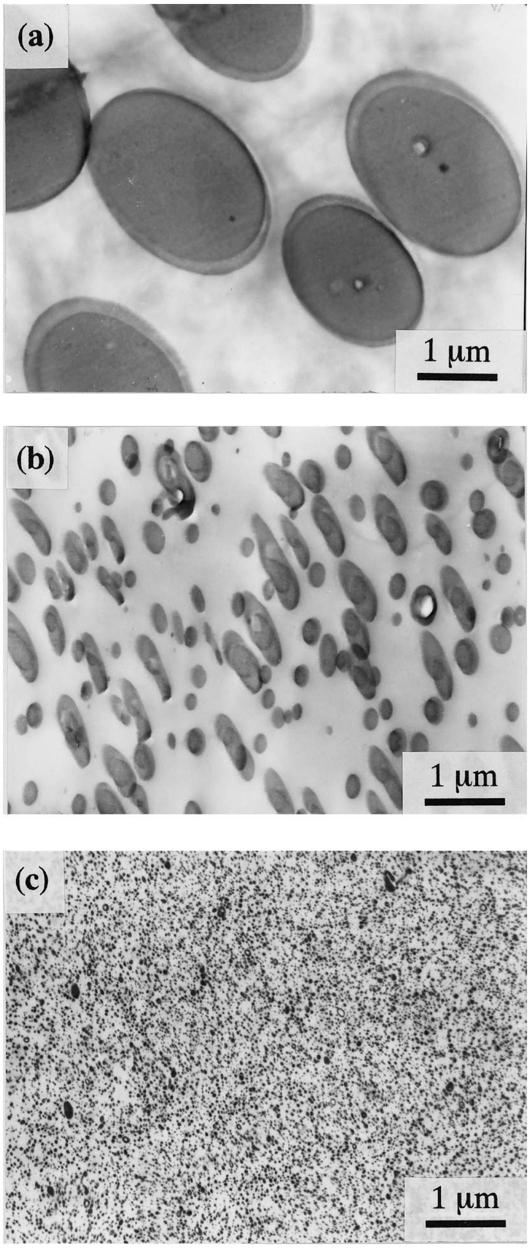

Fig. 2. TEM micrographs of 20/80 PSU/PA blends melt-mixed at 260°C for 8 min (rotor speed: 100 rpm): (a) nf-PSU/PA; (b) PSU–MAH/PA; and (c) PSU–PhAH/PA.

3.2. Self-assembly or pulled out

If the in situ formed copolymers are thermodynamically unstable at the interface, they tend to go to the bulk by themselves (without the aid of external force) as micelle. Such self-assembling could be tested by TEM observation of a reactive specimen after static annealing. The reactive specimen before annealing was prepared as follows.

PA and nf-PSU were melt blended at 30/70 (PA/nf-PSU) weight ratio at 260°C for 3 min. The blend was immersed in a large amount of THF, a good solvent for PSU but non-solvent for PA, and precipitated PA particles were collected and dried. This was repeated three times. PA particles thus prepared (2–5 μm in diameter) were added to a THF solution of PSU–PhAH. By evaporating THF, a solution cast film of 80/20 PSU–PhAH/PA was prepared. After vacuum drying at room temperature, the film specimen was subjected to a static annealing at 260°C (same temperature as for the reactive blending).

Figs. 4(a) and (b) show TEM micrographs of the PA/PSU–PhAH blends before and after annealing (for 10 min), respectively. Note that the dark region in TEM is PSU phase stained by RuO_4. It is clearly shown that there is not any micelle in the annealed blend. That is, the self-assembling or micelle formation does not occur during the quiescent annealing: the in situ formed block copolymers may stay at the interface. Then, one may conclude that, in reactive blending, the copolymers seem to be mechanically pulled out by the external forces to form micelle in PA matrix. Similar result were obtained for the static annealing of PA/PSU–MAH system; i.e. the micelle formation was not observed, as expected.

In Fig. 4, the interface before annealing is rather smooth, while annealed specimen shows a small undulation with an amplitude of ca. 8 nm at the interface. The undulation may result from a large amount of the block copolymers at the interface. When the in situ formed block copolymer chains are accumulated too much at the interface, the copolymer chains are forced to elongate perpendicular to the interface and destabilize the interface. In other words, the excess accumulation may lead to a negative interfacial tension [41], so that the interfacial area will tend to increase by undulation.

For the morphology development in the melt blending of immiscible polymers, Wu [42] proposed a semi-empirical relationship between the particle diameter D, interfacial tension Γ, viscosity of the dispersed phase η_d and the matrix phase η_m, and the shear rate $\dot{\gamma}$:

$$D = 4(\eta_d/\eta_m)^{0.84}\Gamma/(\dot{\gamma}\eta_m) \qquad \text{for } \eta_d > \eta_m. \tag{2}$$

This is based on the break-up model by Taylor [43,44]; i.e. when the shear force ($\eta_m\dot{\gamma}$) overcomes the interfacial force of particle (Γ/D), the particle will break, otherwise it cannot. Wu showed that both non-reactive PA/ethylene–propylene rubber (EPR) system and the corresponding reactive system (PA/EPR–MAH) follow Eq. (2). The PA/EPR–MAH system may generate PA–EPR graft copolymer. Then, the PA/PSU–MAH blend, the graft copolymer forming system, is expected to follow Eq. (2). By contrast, morphology development mechanism in PA/PSU–PhAH system is very different from the break-up model so that the PA/PSU–PhAH system will not follow Eq. (2).

Fig. 5 shows the mean diameter of PSU particles by TEM analysis on the blends after 8 min mixing as a function of shear rate in the mixer. The particle size in the PSU–MAH system highly depends on the shear rate as expected

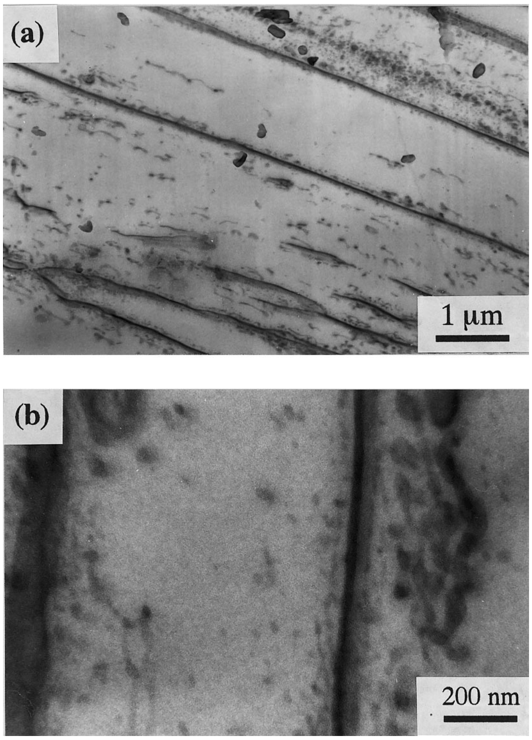

Fig. 3. TEM micrographs of 20/80 PSU–PhAH/PA blend at an early stage of melt mixing (1 min mixing) at 260°C (rotor speed: 50 rpm): (a) low magnification; and (b) high magnification.

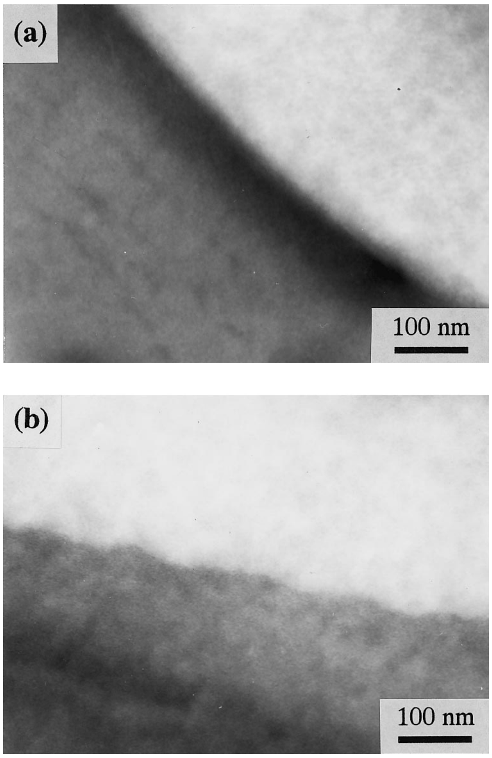

Fig. 4. Static study TEM micrographs of 80/20 PSU–PhAH/PA blend: (a) as cast (non annealed); and (b) annealed at 260°C for 10 min.

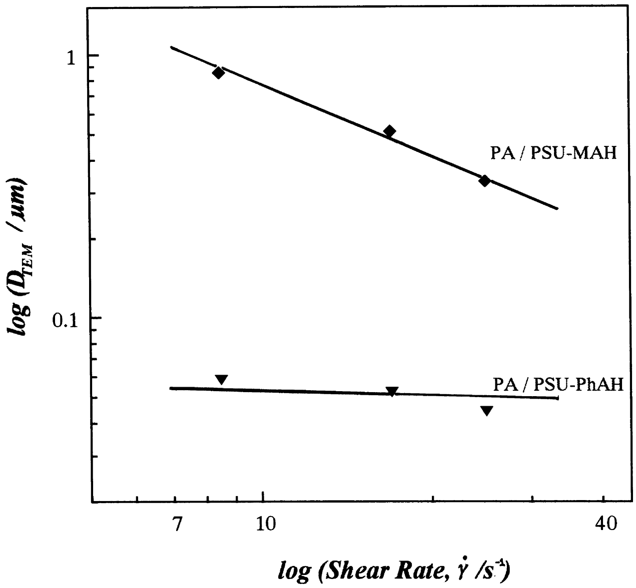

Fig. 5. Effect of applied shear rate on the average PSU particle diameter.

from Eq. (2). By contrast, the less dependence is seen in the PSU–PhAH system. Note that the melt viscosities of component polymers (PA, PSU–MAH or PSU–PhAH) were shown to be almost constant for more than 20 min at 260°C in the frequency range of 10–100 rad/s, which covered the range of shear rate in Fig. 5, by Rheometric measurements [31], suggesting no chain degradation. The results in Fig. 5 may be supplemental evidences for the particle size reduction mechanism via micelle formation in the PSU–PhAH system and for the break-up mechanism in the PSU–MAH system.

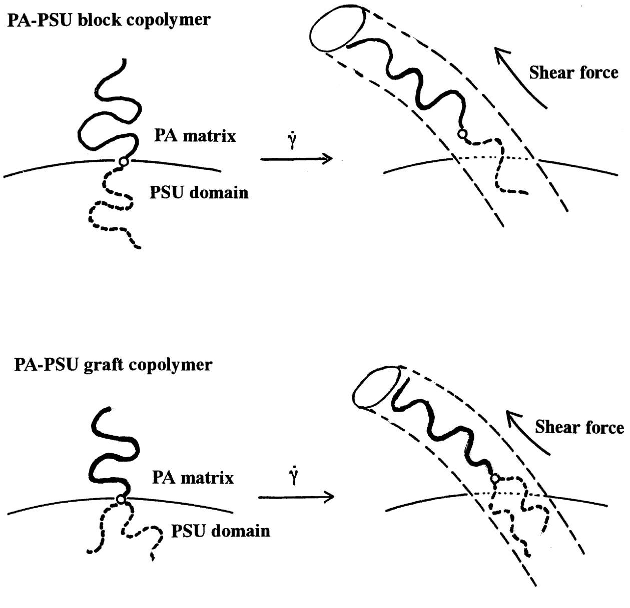

Fig. 6. Tube model for the pull-out in situ formed copolymers; showing that graft copolymer will be subjected to greater spatial constraints by the pull-out than block copolymer.

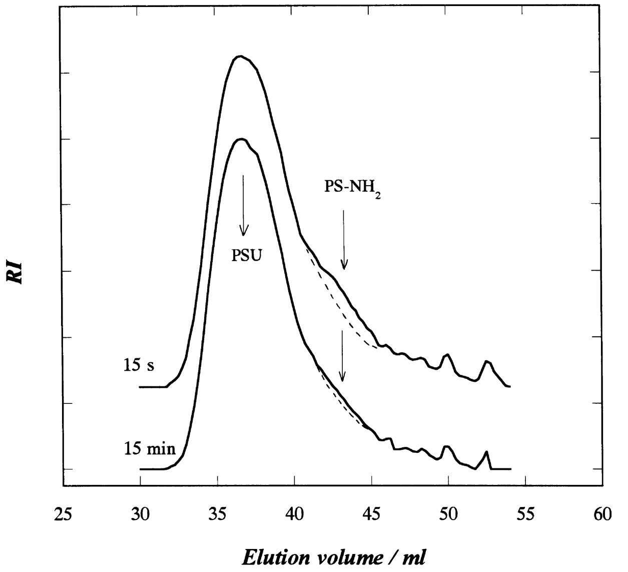

Fig. 7. GPC chromatograms of PS–NH$_2$/PSU–PhAH system after 15 s and 15 min reaction times.

Then, one may conclude that the fine dispersion of 10 nm level in the PSU–PhAH system can be achieved via micelle formation by the pull-out of the in situ formed block copolymers, whereas the in situ formed graft copolymers in PSU–MAH system are not mechanically pulled out but they prefer to stay at the interface to render the sub-μm dispersion. It means a significant difference in the hydrodynamic stability between the block and graft copolymers under external shear fields. It is conceivable if one employs the tube model for the pull-out process as shown in Fig. 6. The graft copolymer is a branched polymer with Y-shape, while the block copolymer a linear polymer. Then, the graft copolymer will be subjected to higher spatial constraints (higher entropy penalty) for the pull out than the block copolymer so that the graft copolymer could be hardly pulled out under external shear forces. Thus, the pull-out mechanism seems to be plausible.

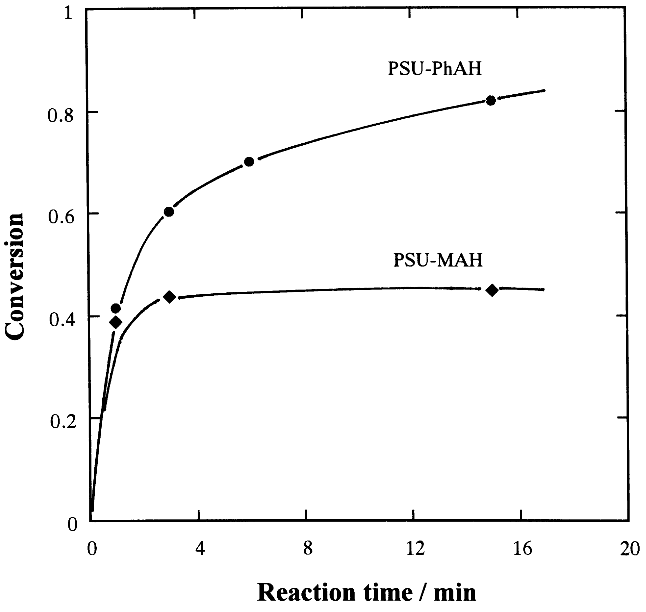

Fig. 8. Conversion vs. time in PS–NH$_2$/PSU–MAH and PS–NH$_2$/PSU–PhAH systems at 60°C.

However, one has to discuss again the thermodynamic stability of the copolymers at the interface. The less stable copolymers would be pulled out more easily. As has been discussed earlier, the excess accumulation of copolymer chain at interface causes the conformational entropy penalty to destabilize the chains themselves. The population of in situ formed copolymers during reactive blending depends on the kinetics of coupling reaction and the diffusivity of reactive components [45,46]. One cannot expect a significant difference in the chain diffusivity nor in the amount of reactive sites between PSU–MAH and PSU–PhAH. A difference is conceivable in coupling reaction rate between [MAH] and [PhAH] with amino-end of PA.

3.3. Coupling reaction kinetics vs. molecular architecture

The amount of reactive sites in PSU–MAH, PSU–PhAH and PA is very low so that it is quite difficult to follow the reaction kinetics by spectroscopic methods such as nuclear magnetic resonance (NMR) and infrared spectroscopy (IR). GPC analysis of the reaction product basically works better [11,47,48]. However, a problem is the choice of a solvent for GPC analysis which should be a common solvent for both PA and PSU. 1,1,1,3,3,3-hexafluoroisopropanol (HFIP) was the only common solvent we found. However, HFIP is highly toxic and very expensive. This is why we prepared the model polymer, PS–NH$_2$, by anionic polymerization. Using this model polymer with sharp molecular distribution, the GPC analysis can be performed more easily than in the case of PA with broad distribution. Chlorobenzene was found to be a common solvent for PSU and PS–NH$_2$. The ternary solution of 2 wt% total polymer content was transparent. In this single-phase solution, one can escape from an effect of difference in thermodynamic interaction between PS vs. PSU on the reaction kinetics.

Fig. 7 shows two examples of GPC chromatograms of reaction products. PS–NH$_2$ peak decreased with reaction time as shown in Fig. 7. By the area under PS–NH$_2$ peak, amount of remaining PS–NH$_2$ was estimated and then the conversion was calculated. Time-conversion curves are shown in Fig. 8. The coupling reaction between PSU–PhAH and PS–NH$_2$ proceeds faster than in PSU–MAH/PS–NH$_2$ system.

From the results in Fig. 8, one may expect the faster supply of copolymers at the interface in PSU–PhAH system than in PSU–MAH system. Then, the higher population of copolymers is expected at the interface of PSU–PhAH system than that of the PSU–MAH system in the reactive blending. However, the difference is not so large. For instance, after 1 min of reaction, in PSU–PhAH system a certain amount of copolymers would be accumulated at the interface to destabilize the copolymers. Same amount of copolymers could be accumulated even in the slowly reacting system (PSU–MAH system), e.g. after ca. 2 min reaction, to attain the same stability to be mechanically pulled out. Such pulling out has never occurred as shown in Fig. 1, even after 13 min reaction. Consequently, one may conclude that the thermodynamic instability of the in situ formed copolymers at the interface is not a key factor for the pull-out and hence for the micelle formation. The key appears to be the difference in molecular architecture between block and graft copolymers, as schematically shown in Fig. 6.

4. Conclusions

Thus, a difference was focused in the interfacial behavior between in situ formed block and graft copolymers in reactive blending of PA–PSU systems. As has been perceived, the in situ formed PA–PSU graft copolymer seems to play a role of emulsifier (so called compatibilizer) to reduce the interfacial tension and to prevent particle coalescence; consequently, the PA/PSU–MAH system yields much finer dispersion (of sub-μm) than the non-reactive system. By contrast, the in situ formed PA–PSU block copolymers are easily pulled out by external shear forces to form micelles in PA matrix during melt mixing; then the reactive processing of PSU–PhAH system eventually yields the 10 nm-level dispersion. This is essentially the solvent free synthesis of the block copolymer [32]. It should be noted that the in situ formed block copolymer could be the emulsifier at quiescent state but not at dynamic condition under external forces. On the basis of such understanding of the interfacial behavior of the in situ formed copolymers, it seems to be quite reasonable that the in situ formation of graft copolymers has been utilized to the commercially important polymer blends, e.g. “super tough nylon” (PA/EPR–MAH) and “Noryl GTX” (PA/polyphenylene-ether–MAH) [15], in which the optimum dispersion for the material performance is usually in the range of sub-μm, but the in situ formation of block copolymers has never applied successfully for such materials.

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