Interfacial behavior of block copolymers in situ-formed in reactive blending of dissimilar polymers

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Abstract

Reactive melt blending of polyamide 6 (PA) and polysulfone (PSU) was carried out and the interfacial behavior of in situ-formed block copolymer was studied. A series of reactive PSUs with different functional groups at chain ends were prepared and used; PSU-epoxy, -triazine and -phthalic anhydride. The morphology development during melt blending was investigated by light scattering and transmission electron microscopy. The results suggested that when coupling reaction quickly proceeded and the in situ-formed copolymers were densely accumulated at the interface, they could be easily pulled out by external shear forces to form micelles in matrix. This micelle formation led to 10 nm order dispersion as a whole at late stages of mixing. By contrast, the pull out did not take place when the coupling reaction was slow and the copolymer chains were less accumulated at the interface. In this case, the in situ-formed block copolymer acted as a simple emulsifier to yield sub-μm level dispersion. The difference between the fast and slow reaction systems was discussed in terms of a balance between thermodynamic stability of copolymer chains at the interface and hydrodynamic effect for the pull-out. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Reactive blending; Light scattering; Polymer–polymer interface

1. Introduction

It has been known that blending of dissimilar polymers offers an attractive opportunity for the development of novel materials with useful combinations of properties [1]. However, the vast majority of these polymer pairs is 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 often called compatibilization. A compatibilization strategy frequently proposed is the addition of a pre-made block copolymer composed of the blocks, which are miscible with the component polymers or the component polymers themselves [2–6]. Another strategy is the reactive processing or the reactive blending, which involves an in situ coupling reaction of functionalized components to form a block or graft copolymer at the interface between the phases [7–14]. The latter approach is usually less expensive and more frequently used for industrial applications [15].

Recent studies [16,17] have shown that the pre-made block copolymer is less effective in stabilizing morphology than the in situ-formed copolymers. Furthermore, the in situ-formed copolymer in reactive processing leads to the finer dispersion and the narrower size distribution of particle size than the pre-made block copolymer, even when the amount of in situ-formed copolymer is significantly less than that of the pre-made block copolymer added. In most previous works, an effect of molecular architecture of potential compatibilizer (random, alternating, diblock and triblock copolymers) on interface reinforcement and on their compatibilizing performance has been studied mostly in pre-made copolymer sytsems [18–23]. For instance, in polystyrene (PS)/polyethylene (PE) system, a PS-*b*-PE diblock copolymer was shown to be more effective than graft, triblock, and star-shaped copolymers.

Theoretical works [24–29] have shown that the block copolymer should thermodynamically prefer to locate at the interface. By contrast, we recently found that the block copolymers formed in situ at the interface during melt mixing can be pulled-out from the interface to form micelles in bulk [30,31] However, the pull-out did not occur in the in situ-formed grafted copolymer system [31]. Then, the results led to the tube model for pull out mechanism, as

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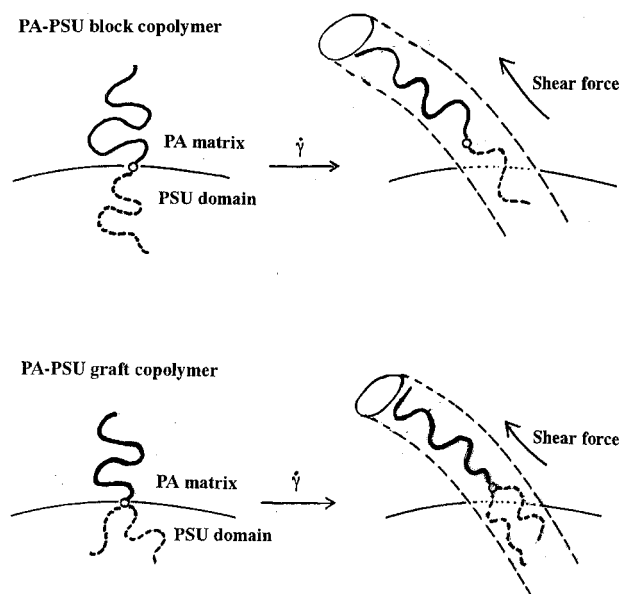**PA-PSU block copolymer**

PA-PSU graft copolymer

Fig. 1. Tube model for the pull-out of in situ-formed copolymers; showing a difference in interfacial stability between in situ-formed block and graft copolymer under external shear force.

shown in Fig. 1. The tube model is to explain a difference in stability under shear fields between the in situ-formed block and graft copolymers; the graft copolymer (branched polymer with Y-shape) will be subjected to bigger spatial constraints by the pull-out than the block copolymer (linear chain) so that the former could be hardly pulled out under external shear forces.

As demonstrated in Fig. 1, the stability of copolymer at interface under shear fields may depend on molecular architecture. It would also depend on the amount of copolymer chains at interface. The theories have revealed that the interfacial free energy can be reduced by adding block copolymer chains [27]. However, if the copolymer chains are

Fig. 2. Chemical structures of synthesized polysulfones.

added too much, the chains should be forced to be elongated perpendicular to the interface. It will lead to an entropic penalty to increase the interfacial free energy. In other words, the excess accumulation of block copolymer chains will destabilize the interface. From the destabilized interface, the copolymer chains could be easily pulled out from the interface by external forces. Thus, the "pull-out or not" should depend also on the degree of accumulation of copolymer chains at the interface. In reactive blending, the faster coupling reaction may yield the higher amount of in situ-formed copolymer chains at the interface. Then, it is interesting to investigate the effect of coupling reaction on the interfacial behavior of in situ-formed copolymers.

In this paper, we prepared a series of end-functionalized polysulfone (PSU)s with different reactivity to amino chain-end of polyamide 6 (PA); PSU-phthalic anhydride; PSU-epoxy and PSU-triazine. All systems are expected to yield PSU-PA block copolymers; but the amount of in situ-formed copolymers in a limited time of melt blending should be different. Morphology development during reactive blending was investigated by light scattering and transmission electron microscopy.

2. Experimental section

2.1. Materials

PA used in this study was a commercial polyamide 6 (Ultramid B3, BASF; $M_n = 13,000$; $M_w = 25,000$). Three different types of functionalized PSUs were prepared following the synthesis procedure given in the literature [32–34]. As a control sample, PSU without functional group (nf-PSU) was also synthesized. Chemical structures of synthesized PSU are shown in Fig. 2.

2.1.1. nf-PSU

287.08 g (1 mol) dichlorodiphenylsulfone, 223.83 g Bisphenol-A (0.9805 mol) and 140.97 g K_2CO_3 were dissolved in 1600 ml dry *N*-methyl-2-pyrrolidinone (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 continuously removed. 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. Almost all (98 wt%) PSU chains had chlorine-end (by elemental analysis). The properties of this product are summarized in Table 1.

2.1.2. PSU-PhAH

287.08 g (1 mol) dichlorodiphenylsulfone, 228.28 g Bisphenol-A (1 mol) and 140.97 g K_2CO_3 were dissolved in 1600 ml dry NMP. The mixture was heated to190°C for 4 h in a nitrogen atmosphere. During this time, the
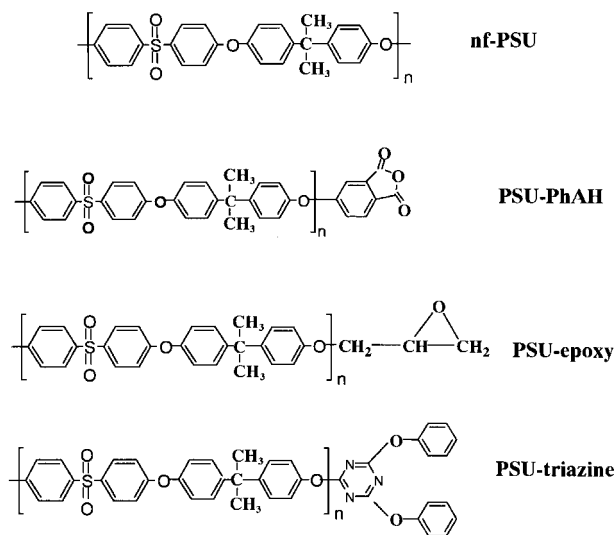
Table 1
Characteristics of synthesized polysulfones

Code	M_n[a]	M_w[a]	Functionality[b]	Viscosity no.[c]
nf-PSU	5700	28,800	0	36.2
PSU-PhAH	5310	20,660	85	29.0
PSU-epoxy	6960	20,010	57	27.0
PSU-triazine	6200	19,740	83	26.7

[a] By GPC.
[b] Content of functional group (μmol/g).
[c] Solution viscosity measured at 1 wt% polymer concentration in *N*-methylpyrolidinone.

azeotropic mixture of NMP and water was 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 solution was 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 anhydride end groups was determined by FT-IR. The properties of this product are also summarized in Table 1.

2.1.3. PSU-OH

287.08 g (1 mol) 4,4′-dichlorodiphenylsulfone 228.28 g Bisphenol-A (1 mol) and 140.97 g (1.02 mol) K_2CO_3 were dissolved in 1000 ml dry NMP. The mixture was heated to 190°C for 3 h in a nitrogen atmosphere. During this time the azeotropic mixture of NMP and water was continuously removed. The solution was cooled to room temperature, diluted with NMP (1600 ml) and filtered. After this procedure the polymer was isolated by precipitation in water. The polymer was extracted three times with hot water and dried. The amount of PSU chains with hydroxyl chain-end was 87 wt% (determined by potentiometric titration). This sample would be used to prepare PSU-epoxy and PSU-triazine.

2.1.4. PSU-epoxy

50 g of PSU-OH were dissolved in 250 ml NMP and 1.16 g (8.4 mmol) K_2CO_3 were added. The mixture was heated to 100°C. After the addition of 4.66 g (50.4 mmol) 1-chloro-2, 3-epoxypropane the mixture was further stirred for 5 h. Subsequently the mixture was cooled to room temperature and the product was isolated by precipitation in water. The polymer was extracted three times with water and dried. The amount of epoxy groups was analyzed by H-NMR. The properties of this product are summarized in Table 1.

2.1.5. PSU-triazine

50 g of PSU-OH and 4.37 g (14.6 mmol) 2-chloro-4, 6-diphenoxy-1,3,5-triazine were dissolved in 500 ml dichloromethane. The solution was cooled to 0°C and 0.58 g sodium hydroxide (NaOH) in 100 ml water were

added over a period of 1 h. The mixture was stirred for one more hour. After this time the organic phase was separated and subsequently washed with NaOH-solution and two times with water. The polymer was isolated by precipitation in ethanol. The white powder was vacuum dried at 100°C. The amount of diphenoxytriazine endgroups was determined by nitrogen analysis. The properties of this product are summarized in Table 1.

2.2. Melt mixing

PA pellets were dried under vacuum (10^{-4} mmHg) at 80°C for 12 h before mixing to remove moisture. Melt mixing was carried out in a miniature mixer of one gram-scale, Mini–Max Molder (CS-183 MMX, Custom Scientific Instruments Inc.) [35] at 260°C. Three rotational speeds were used: 50, 100, 150 rpm, corresponding to maximum shear rates 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 (ca. 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 specimens with various residence times in the mixer. These specimens were analyzed by light scattering (LS) and transmission electron microscopy (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. Immediately after a melt pressing, the time-resolved measurements of scattering profile (angular dependence of scattering light intensity) with a time slice of 1/30 s started. The scattering apparatus consisted of highly sensitive CCD camera with 384×576 pixels, a He–Ne laser of 632.8 nm wavelength and V_v (parallel polarization) optical alignment [36,37]. Since the two-phase structure in the melt is at a nonequilibrium state, it may coarsen with time after re-melt. A scattering profile just after the re-melt provides information on the two-phase structure in the mixed-and-quenched blend.

All blend specimens in this study exhibited a light scattering profile of monotonously decreasing function, i.e. the intensity of scattered light I decreased monotonously with increasing scattering angle θ. From such scattering profile, a series of morphology parameters are obtained by the Debye–Bueche plot; i.e. by the plot of $I(q)^{-1/2}$ vs. q^2, where q is the magnitude of scattering vector, given by $q = (4\pi/\lambda') \sin(\theta/2)$; λ' being the wavelength of light in specimen [38,39]. One can obtain the correlation length ξ from the slope and the intercept of the $I(q)^{-1/2}$ axis by

$$I(q)^{-1/2} = (8\pi\langle\eta^2\rangle\xi^3)^{-1/2}(1 + \xi^2 q^2) \qquad (1)$$

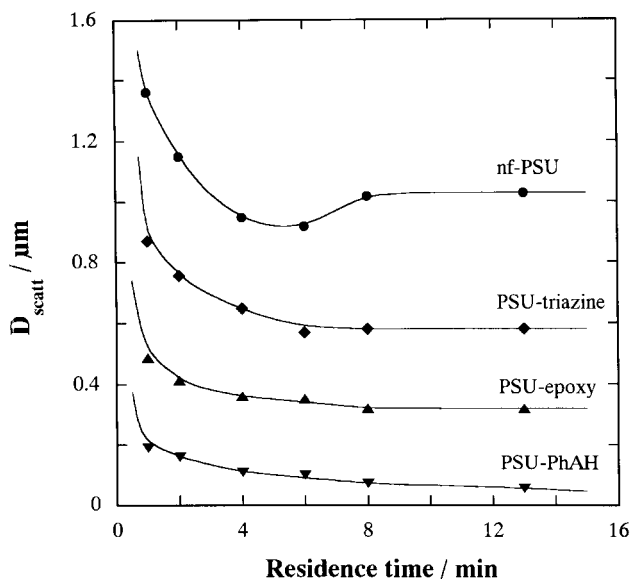where $\langle\eta^2\rangle$ is the mean-square fluctuation of the refractive

Fig. 3. Time variation of PSU average particle diameter D_{scatt} during melt mixing at 260°C at a rotor speed of 100 rpm.

index. Once the value of ξ is given, other morphology parameters, such as the specific interfacial area S_{sp} and the mean diameter of the dispersed particles D_{scatt} can be calculated:

$$S_{sp} = 4\phi(1 - \phi)/\xi \tag{2}$$

$$D_{scatt} = 6\phi/S_{sp} \tag{3}$$

where ϕ is the volume fraction of the dispersed PSU phase.

For TEM observation, the quenched specimen was cryo-microtomed 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 20 min. RuO_4 preferentially stains PSU phase to provide nice contrast under TEM. 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 being circular. The average was obtained by

$$D_{TEM} = \sum_{i=1}^{N} D_i^3 / \sum_{i=1}^{N} D_i^2 \tag{4}$$

where N was 200–500 in a TEM picture. The average by Eq. (4) 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. (4)) and surface-average diameter (denominator in Eq. (4)).
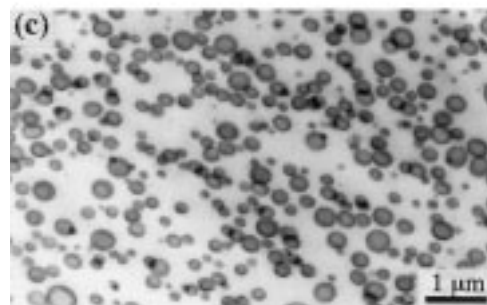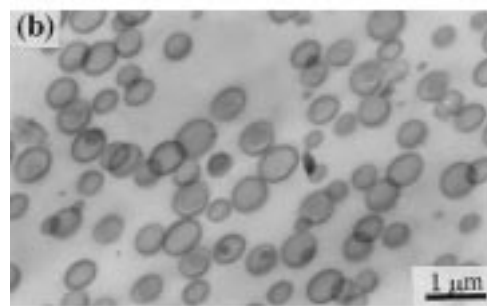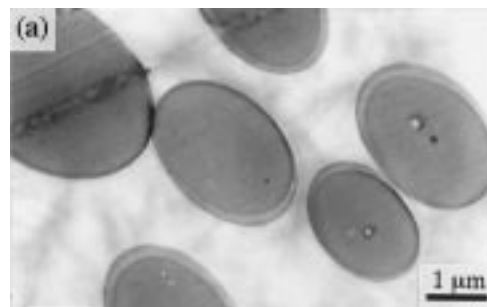

Fig. 4. TEM micrographs of 20/80 PSU/PA blends melt-mixed at 260°C for 8 min (rotor speed; 100 rpm): (a) nf-PSU/PA, (b) PSU-triazine/PA, (c) PSU-epoxy/PA, and (d) PSU-PhAH/PA.

2.4. Melt viscosity

The dynamic viscosity was measured at 260°C by Dynamic-Stress-Rheometer (DSR) at parallel-plate mode (plate diameter 25 mm, gap 1.0 mm).

3. Results and discussion

Fig. 3 shows the mean PSU diameter by light scattering

Table 2
Morphological parameters of blends mixed at 260°C for 8 min (ξ, correlation length; S_{sp}, specific interfacial area; D_{scatt}, mean diameter of PSU particles by light scattering; D_{TEM}, mean diameter by TEM)

Code	ξ (μm)	S_{sp} (μm^{-1})	D_{scatt} (μm)	D_{TEM} (μm)
PA/nf-PSU	0.55	1.10	1.02	1.10
PA/PSU-PhAH	0.038	15.9	0.07	0.079
PA/PSU-epoxy	0.176	3.43	0.32	0.38
PA/PSU-triazine	0.250	2.42	0.46	0.62

D_{scatt} as a function of residence (reaction) time. One can see a rapid decrease in the particle size. The size decreases in three decades, from mm scale (pellet size) to μm scale, in short time (2 min). TEM micrographs of the blends after 8 min mixing are shown in Fig. 4. The dark region is PSU phase stained by RuO$_4$. The morphological parameters by light scattering and TEM are summarized in Table 2, showing a nice agreement between the values by two analyses.

Figs. 3 and 4 show that the reactive systems yield finer particles via faster size reduction processes, compared with non-reactive system. These are expected results since the reactive system may generate the PSU-PA block copolymer, which would play a role of emulsifier to prevent particle coalescence during blending and to reduce the interfacial tension.

There is an obvious difference in attainable particle size between the two reactive systems; 10 nm level in PSU-PhAH and sub-μm in other systems; PSU-epoxy and PSU-triazine. Furthermore, in Fig. 3, the size reduction process in PSU-PhAH system still continues even after 8 min mixing, whereas, the particle size levels off at around 6 min in other systems. The results imply that there must be a dissimilarity in size reduction process between the PSU-PhAH system and the other two reactive systems. TEM micrographs of PA/PSU-PhAH blend showed that at very early stage (1 min) of mixing, fine PSU domains existed
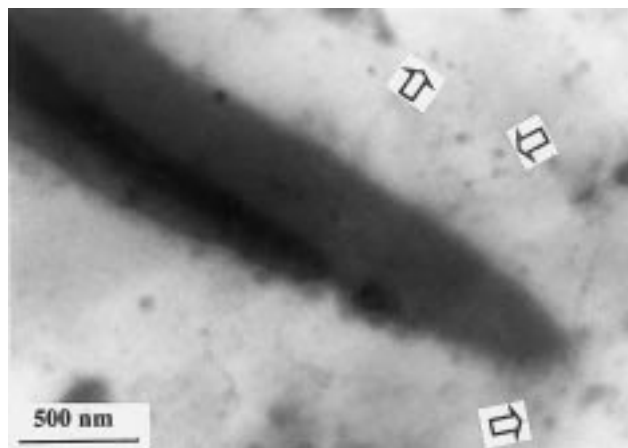

Fig. 5. High magnification TEM micrograph of 20/80 diluted PSU-PhAH/PA blend at a early stage of melt mixing (1 min mixing) at 260°C. [PhAH] = 55 μmol/g.

near large PSU sheets [31]. Diameter of the fine domains was $16 \sim 20$ nm (see also Fig. 5). Those results imply that a lot of PSU-PA block copolymers are in situ-formed even at the early stages and they are pulled out from the interface region by external shear forces and they are dispersed in PA matrix as micelles. Note that the estimated size ca. $16 \sim 20$ nm is very close to domain size of pre-made PSU-PA block copolymer prepared by solution polymerization method [30]. Bigger particles seen in Fig. 4d 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. 4d. By contrast, such micelles are never seen in PSU-epoxy and -triazine systems, even at the late stages (Fig. 4b and c), implying that the pull out of copolymers did not occur.

The difference (pull-out or not) may be caused by the kinetics of coupling reaction. As discussed in Section 1, in the fast reactive system, the in situ-formed block copolymer chains should be accumulated in excess to destabilize the interface, therefore, the copolymer chains should be easily pulled out by external shear forces. This should be the case of PSU-PhAH system. On the contrary, in the case of slow coupling reaction system, the population of block copolymer may not be enough to destabilize the interface and the copolymer chains act just as the emulsifiers.

One can find the kinetic data in the literature. Orr and Macosko prepared a series of monodisperse polystyrene (PS)s with reactive chain ends; PS-NH$_2$, -epoxy and -anhydride (AH), and measured the reaction rate of coupling reaction in PS-NH$_2$/PS-epoxy and PS-NH$_2$/PS-AH systems at 180°C [40]. They found that the rate of a coupling reaction between the amine and the anhydride (PS-NH$_2$/PS-AH) was extremely fast, e.g. 99% conversion in less than 1 min [41]. Rates of generation of block copolymer was roughly estimated by 99%/60 s = 1.7×10^{-4} mol/l s. Coupling reaction between the amine and the epoxy (PS-NH$_2$/PS-epoxy) was much slower (1.1% conversion after 2 min ($\approx 9.2 \times 10^{-6}$ mol/l s). That is, there is a big difference (two orders of magnitude) in coupling reaction rate between two coupling pairs. Then, one can expect a big difference in the population of in situ-formed copolymer chains at interface between the PSU-PhAH and the PSU-epoxy systems. PSU-triazine may be less reactive than epoxy so that it would yield less amount of in situ-formed copolymer in a limited time of mixing.[1]

PSU-epoxy and PSU-PhAH have almost same molecular

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[1] Probably, the reactivity of triazine sites is low so that only one site may react with PA to yield diblock copolymer (but not Y-shape block copolymer by reaction of two sites). The situation may be similar to the PSU-epoxy system; i.e. only the ring opening of epoxide takes place and the succeeding reaction of hydroxyl group with amine or carboxylic end-group does not occur without catalyst. Therefore, the linear block copolymer will be formed. Actually, a GPC chromatogram of reaction product of PSU-epoxy with PS-NH$_2$ showed only a new peak corresponding to a linear block copolymer (Polym Prepr Jpn, 47 (1998) 2718).

Table 3
Effect of content of PhAH and shear rate on micelle formation

Content of PhAH (μmol/g)	$\dot{\gamma}_{max}$ (s^{-1})[a]	Micelle formation[b]	Σ/Σ_0 [c]
17	17	No	0.03
17	25	No	0.04
34	8.5	No	0.13
34	17	Yes	0.20
34	25	Yes	0.25
55	8.5	Yes	0.32
55	17	Yes	0.41
55	25	Yes	0.53
84	8.5	Yes	1.30
84	17	Yes	1.96
84	25	Yes	2.50

[a] Calculated from the gap between rotor and heater cup and the rotation speed of mixer.

[b] Micelles were observed or not by TEM after 2 min mixing.

[c] Note that the values of Σ were calculated using the kinetics data at 180°C [40,41]. Then, a correction should be required for the Σ values at 260°C. However, the revision may be small (~17%-up), since the reaction rate is determined by the chain diffusivity D in entangled polymer-melt systems which is proportional to the absolute temperature T [45]. [Σ(260°C)/Σ(180°C) $\sim D$(260°C)/D(180°C) $\sim$ (273 + 260)/(273 + 180) = 1.17]. One can find the literature data supporting such weak temperature dependence of reaction rate in an entangled system [43].

weight. Then, one cannot expect a significant difference in diffusivity of reactive PSUs and in molecular architecture of block copolymers to be in situ-formed.[1] However, the functionality of PSU-PhAH (85 μmol/g) is higher than PSU-epoxy (55 μmol/g) (see Table 1). For comparison, a diluted PSU-PhAH system having functionality 55 μmol/g was also prepared by adding non-reactive PSU.[2] Then melt blending of PA/diluted PSU-PhAH was carried out. Fig. 5 shows TEM micrograph of the blend after 1 min. One can observe the fine PSU domains of ca. 16–20 nm diameter near the PSU sheet, suggesting the pull-out of in situ-formed copolymer as in the case of 85 μmol/g PSU-PhAH system [31]. Thus, the difference (pull-out or not) between PSU-PhAH and PSU-epoxy was confirmed at the same functionality level.

Then, if PSU-PhAH system is diluted further with non-reactive PSU and the functionality is reduced further, the rate of block copolymer generation would be reduced to reach the same rate as the PSU-epoxy system in which the in situ-formed copolymers are not pulled out. That is, in a highly diluted PSU-PhAH system, the micelle formation by pull-out could not take place. Actually, the micelles were not observed when PhAH was diluted below 34 μmol/g (see Table 3).

In Table 3 also summarized is the effect of applied shear

[2] Diluted PSU-PhAH was prepared as follows. Firstly, PSU-PhAH and non-reactive PSU (having M_n comparable with PSU-PhAH) were dissolved and blended in THF. Then, the solvent was evaporated at room temperature and then under vacuum at 40°C for 2 days. Finally, the dried sample was melt-pressed at 200°C and cut to proper size for melt-blending experiment.

on the micelle formation. At [PhAH] = 34 μmol/g, the highest shear rate induced the micelle formation but lower rate did not. At higher PhAH contents, the micelle formation took place under all shear rates. At lower contents ([PhAH] < 34 μmol/g), the micelles did not appear at all shear rates. The results clearly suggest that the in situ-formed copolymers are easily pulled out, when the copolymer chains are densely accumulated at the interface; while, in the case of less accumulation, the copolymer chains are pulled out only at high shear rate (or by strong shear forces).

Then, to be further discussed is the excess accumulation of in situ-formed copolymer chains. An interface consisting of a dense monolayer of block copolymer chains may be a good approximation for the saturated interface. Area density of copolymer chains at the saturated interface (Σ_0) should be nearly equal to that in the microdomain of the block copolymer in bulk. A symmetric diblock copolymer is known to form the lamellar domain, in which Σ_0 is given by [42,43]

Σ_0 = (half of lamellar spacing)/(volume of a copolymer chain)

$$= (\Lambda/2)/(M_n/\rho N_A) \qquad (5)$$

where M_n is the number average molecular weight, ρ the density, and N_A is Avogadro's number. For a pre-made PSU-PA block copolymer with M_n = 15,000, Λ was estimated to be 36 nm [44]. Assuming ρ = 1.0 g/cm^3, Σ_0 is given to be 0.59 chain/nm^2. The area density of copolymer chains at the interface Σ may be estimated by the aforementioned kinetics data and morphology parameter (S_{sp}). Then one can describe the degree of the surface coverage of PSU particles by the in situ-formed block copolymer chains by Σ/Σ_0. The calculated results for Σ/Σ_0 after 2 min mixing are summarized in Table 3.

In Table 3, the excess accumulation of in situ-formed copolymer chains corresponds to $\Sigma/\Sigma_0 > 1$. For the undiluted system ([PhAH] = 84 μmol/g), Σ/Σ_0 is higher than 1 and the micelle formation actually takes places. It is interesting that, even when Σ/Σ_0 is much smaller than 1 (but bigger than 0.2) in the diluted systems, the micelle formation takes place. The results imply that the copolymer chains are not necessarily being in the excess to be pulled out as micelles. Actual excess under shear fields seems to start with the less accumulation (Σ/Σ_0 = 0.2). The results of non-micelle-forming systems suggest that the copolymer chains stably stay at the interface when their accumulation is less than a critical value ($\Sigma/\Sigma_0 \leq 0.2$). It may imply that the hydrodynamic force cannot overcome the thermodynamic stability provided for the copolymer chains at interface.

In the non-micelle-forming system, the size reduction process is expected to follow the empirical equation proposed for the break-up model by Wu [46]

$$D = 4(\eta_d/\eta_m)^{0.84} \Gamma/(\dot{\gamma}\eta_m) \qquad for\ \eta_d > \eta_m \qquad (6)$$
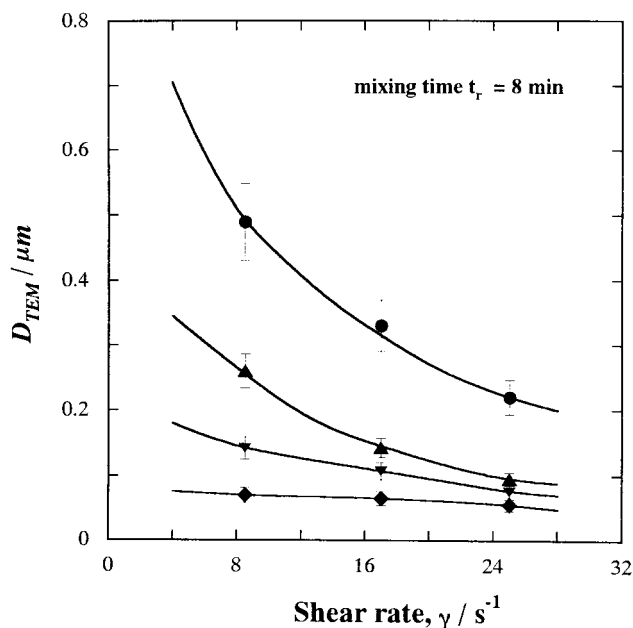
Fig. 6. Effects of applied shear rate and PhAH content on the average PSU particle diameter after 8 min mixing at 260°C: (●) 17 μmol/g, (▲) 34 μmol/g, (▼) 55 μmol/g, and (◆) 85 μmol/g.

where Γ is the interfacial tension between the phases, η_d is the melt viscosity of dispersed phase, η_m and is that of matrix. Eq. (6) was established for PA/maleic anhydride-grafted poly(ethlyene-*co*-propylene), in which graft copolymers were formed and the micelle formation was not expected. As shown in Fig. 6, the particle size in the highly diluted system ([PhAH] = 0.17 μmol/g; non-micelle-forming system) depends very much on the shear rate. Actually a straight line could be processed for D vs. $\dot{\gamma}^{-1}$ plot. Note that the melt viscosities of component polymers were shown to be almost constant at 260°C in the frequency range of 10–100 rad/s, so that the effect of viscosity ratio in Eq. (6) can be neglected in the present systems. The higher [PhAH] content system shows the less shear rate dependence. It is reasonable since the micelle formation should be incorporated in size reduction process of such highly reactive systems.

4. Conclusion

The pull out of in situ-formed block copolymer in reactive blending of PA/PSU systems was focused in this study. The pull out of in situ-formed block copolymer from the interface regions was found in the highly reactive system PA/PSU-PhAH. The pull-out appears to be controlled by not only the hydrodynamic instability under shear but also by the thermodynamic instability caused by the amount of accumulated block copolymers. When the amount of block copolymer are less, they are more stable at the interface and play a role of emulsifier to prevent particle coalescence to yield sub-μm dispersion, following the break-up

mechanism for the size reduction process. This situation was found in the slow coupling reaction systems, PA/PSU-epoxy and PA/PSU-triazine, as well as in fast coupling reaction system PA/PSU-PhAH when the amount of functional group was very low.

Acknowledgements

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