

Pull-out of copolymer in situ-formed during reactive blending: effect of the copolymer architecture

P. Charoensirisomboon^a, T. Inoue^{a,*}, M. Weber^b

^aDepartment of Organic and Polymeric Materials, Tokyo Institute of Technology, 2-2-12 Ookayama, Meguro-ku, Tokyo 152-8552, Japan

^bBASF Polymer Research Laboratory, D-67056, Ludwigshafen, Germany

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Abstract

Reactive melt blending of polyamide 6 (PA) and polysulfone (PSU) was carried out and the effect of the copolymer architecture on the pull-out of the copolymer in situ-formed during reactive blending was studied. To create various block and graft copolymers by reactive blending, three types of reactive PSU were prepared and used; maleic anhydride-grafted PSU, carboxylic-grafted PSU, and phthalic anhydride-terminated PSU. Polymer blend morphology was observed by transmission electron microscopy (TEM). The TEM results suggested that the block copolymers with linear chain structures are more easily pulled out to form micelles in the matrix than the graft copolymers having branch structure with trunk chains locating in the dispersed phase. Such graft copolymers stayed at the interface and played the role of emulsifiers. By contrast, the in situ-formed graft copolymers having trunk chains locating in the matrix were easily pulled out. The micelle formation via the pull-out of copolymers took place even in the rather symmetric block or graft copolymer system. Such interfacial behavior is against the current theories on polymer–polymer interface, which deal with the chain statistics under quiescent state; implying that the hydrodynamic contribution plays an important role of the pull-out. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Reactive blending; Polymer–polymer interface; Pull-out

1. Introduction

Compatibilization of polymer blends refers to the interfacial modification process, which would result in lower interfacial tension, restricted particle-coalescence and improved adhesion [1]. The process is somewhat similar to emulsifying an oil/water mixture by adding a surfactant. For two-phase polymer melt, graft or block copolymer is commonly used as a polymeric emulsifier. The block or graft copolymer can be incorporated by two ways. One is by an addition of pre-made copolymer and another is by an in situ-coupling reaction of functional polymers. The latter approach is called reactive compatibilization or reactive blending. The presence of the copolymer, either added or created in situ by the coupling reaction, at the interface is believed to play dual roles in promoting mixing [2–6]. One is to reduce the interfacial tension and so to promote droplet breakup. The other is to provide the steric hindrance between dispersed particles and thus to suppress droplet coalescence. To be a good emulsifier and play either role,

the copolymers are required to locate at the interfacial region. In other words, the prerequisite for the copolymers to be emulsifiers should be the ability to locate at the interface between the two phases.

The theory of block copolymers at the polymer–polymer interface [7] suggests that a symmetric AB block copolymer (A block length \approx B block length) prefers to stay at the interface, while a very asymmetric block copolymer (e.g. long A block/short B block) is unstable and tends to leave the interface as micelle in A homopolymer phase. This is the story at the quiescent state. The situation may be different when the copolymers are subjected to shear fields during melt processing.

Nakayama et al. [8,9] showed that in a reactive blend of polystyrene- ω -COOH with poly(methyl methacrylate)- ω -epoxy, the block copolymer formed at the interface during reactive blending, left the interface and dispersed in bulk as micelles. However, it was unclear at that time, whether the escape was caused by thermodynamic or by hydrodynamic contributions. We recently showed that the in situ-formed block copolymers unlikely escape from the interfacial region by themselves (due to thermodynamic reasons) but they are easily pulled out by external shear forces (hydrodynamic reasons) [10]. Note that the term

* Corresponding author. Tel.: + 81-3-5734-2439; fax: + 81-3-5734-2876.

E-mail address: tinoue@o.cc.titech.ac.jp (T. Inoue).

Table 1
Characteristics of reactive polysulfones

Description	M_n^a	M_w^a	Melt viscosity ^b	Functionality ^c
PSU–PhAH1	5400	21 000	2400	0.88
PSU–PhAH2	7200	20 400	2550	0.89
PSU–PhAH3	9100	26 000	13 000	1.38
PSU–MAH1	8000	21 300	2500	0.75
PSU–MAH2	9700	33 000	19 000	0.45
PSU–COOH1	3500	9800	450	1.35
PSU–COOH2	8700	40 000	20 000	0.85

^a By gel permeation chromatography, g/mol.

^b Complex melt viscosity at 260°C, corresponding to the shear rate in mixer, P.

^c Reactive site per chain.

“pull out” is just for convenience but details of the mechanism are still unsolved.

In this paper, we extended our studies to focus on an effect of molecular architecture of in situ-formed copolymer on the pull out process. Melt blending of polyamide 6 (PA) with functionalized polysulfone (PSU) was carried out using a miniature mixer. Three types of reactive PSUs were prepared and used; maleic anhydride-grafted PSU (PSU–MAH), carboxylic-grafted PSU (PSU–COOH), and phthalic anhydride-terminated PSU (PSU–PhAH). By changing the blend composition and molecular weight of PSUs, one

can provide various molecular architectures of in situ-formed copolymers. Morphology developments were investigated by transmission electron microscopy (TEM).

2. Experimental

Polyamide 6 (PA) used was a commercial polyamide 6 (Ultramid B3, BASF AG; $M_n = 13\,000$; $M_w = 25\,000$; $\eta^* = 2400$ P). Three different types of reactive PSU; PSU–COOH, PSU–MAH, and PSU–PhAH were prepared following synthesis procedure given in the literature [11–14]. Characteristics of reactive PSUs used have been summarized in Table 1.

PA pellets were dried under vacuum (10^{-4} mm Hg) at 80°C for 12 h before mixing to remove moisture. Melt mixing was carried out in a one gram-scale mixer, Mini-Max Molder (CS-183 MM, Custom Scientific Instrument) at 260°C. Three rotational speeds were used; 50, 100, 150 rpm, corresponding to maximum shear rates of 7, 16, and 25 s^{-1} . The weight ratio of PSU/PA was either 20/80 or 80/20. During the mixing, a small amount of mixed melt (ca. 40 mg) was picked up by a pincette at appropriate intervals and was quickly quenched in ice-water to freeze the two-phase structure in the melt. These specimens were analyzed by TEM.

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 a 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 a nice contrast under TEM. The two-phase morphology was observed by a transmission electron microscope, JEM-100CX (JEOL), at an accelerating voltage of 100 kV.

The complex dynamic viscosity was measured at 260°C by a Rheometric Dynamic Spectrometer (Model RDS-7700) at a parallel-plate mode (plate diameter 25 mm, gap 1.0 mm) and 10% strain amplitude. The results have been summarized in Table 1.

3. Results and discussion

Fig. 1 shows TEM micrographs after 8 min mixing of 80/20 PA/PSU–MAH1 and PA/PSU–PhAH1 blends. The darker region is PSU phase stained by RuO_4 . One can see that there is an obvious difference in attainable particle size between the two reactive systems; 10 nm-level in PSU–PhAH (block copolymer-forming) and sub- μm in PSU–MAH (graft copolymer-forming) systems, suggesting a dissimilarity in size reduction process between two reactive systems. Such dissimilarity has shown to be caused by a difference in interfacial behavior of copolymer chains under shear fields. That is, the in situ-formed PSU–PA block copolymers at the interface were shown to be easily peeled or pulled out by shear forces to form micelles in PA

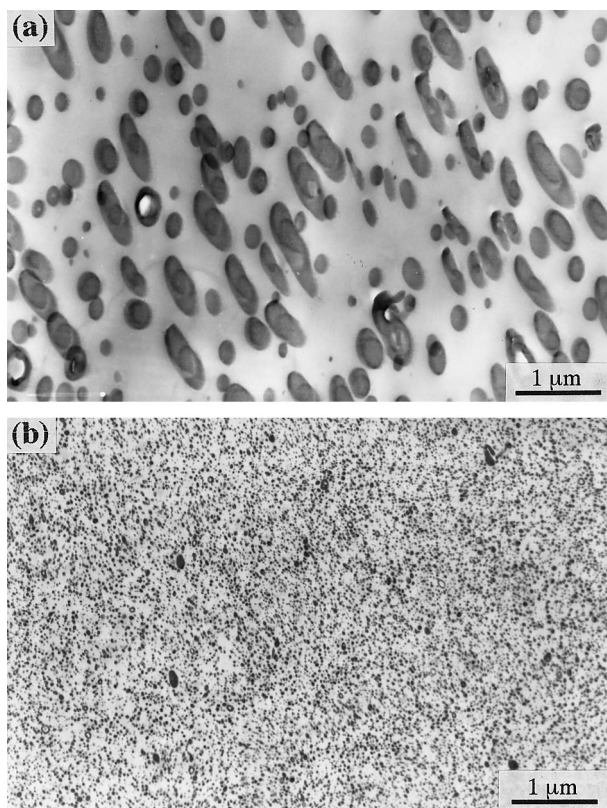


Fig. 1. TEM micrographs of 20/80 PSU/PA blends melt-mixed at 260°C with rotor speed 100 rpm for 8 min: (a) PSU–PhAH1/PA; and (b) PSU–MAH1/PA.

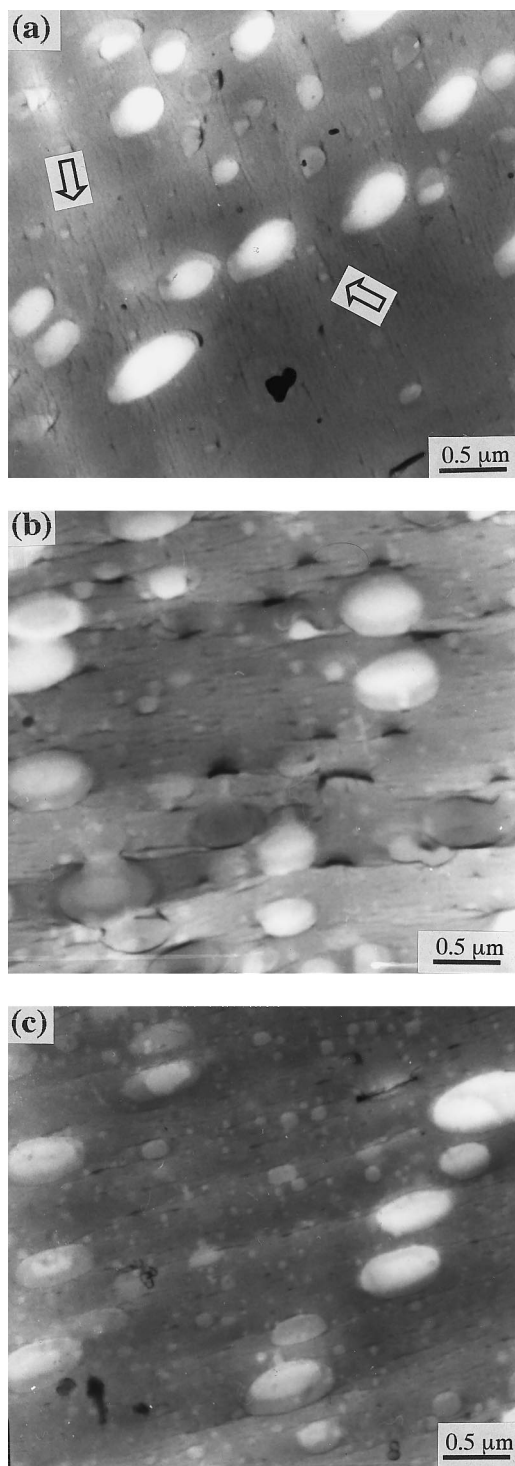


Fig. 2. TEM microraphs of 80/20 PSU–MAH2/PA blends melt-mixed at 260°C: (a) 3 min (rotor speed: 50 rpm); (b) 8 min (rotor speed: 50 rpm); and (c) 8 min (rotor speed: 150 rpm).

matrix and eventually yielded 10 nm-level dispersion with narrow particle-size distribution, while the in situ-formed graft copolymers were hardly pulled out and stayed at the interface to play the role of an emulsifier [10]. The results imply a clear difference in stability under shear fields

between the in situ-formed block and graft copolymers. The graft copolymer with trunk chain anchoring in the dispersed phase side (“inverse Y-shape”; see Fig. 4b and d) may be subjected to bigger spatial constraints by the pull-out than the block copolymer (linear chain, see Fig. 4a) so that it could be hardly pulled out under external shear forces.

Then, in the opposite case, i.e. when a long trunk chain resides in a matrix (Y-shape; see Fig. 4f), the graft copolymer is expected to be easily pulled out as in the case of the block copolymer. Such a graft copolymer may be created in a PSU–MAH-rich system; for e.g. in a 20/80 PA/PSU–MAH blend.

Fig. 2a is a TEM micrograph of the 20/80 PA/PSU–MAH2 blend after mixing for 3 min. In this graft copolymer-forming system, one sees clearly tiny domains (30–50 nm in diameter) coexisting with sub- μm PA particles. The tiny domains may correspond to the micelles of in situ-formed PA–PSU graft copolymers, suggesting that the pull-out of the in situ-formed copolymer took place in the Y-shape graft copolymer-forming systems. Note that such tiny domains are never seen in Fig. 1a. The longer the mixing time (8 min), the higher was the population of the tiny domains as can be seen in Fig. 2b. Further, the population increased when the mixing was carried out at higher shear rate as can be seen in Fig. 2c.

Fig. 3 shows TEM micrographs of 20/80 PA/PSU–COOH blends after mixing for 8 min at a rotation speed 100 rpm. It can be seen in Fig. 3b (PSU–COOH2/PA) that the tiny domains in 10 nm-level particle size also appeared as in Fig. 2. This result suggests that the micelle formation can take place also even in a less reactive system of carboxylic-amine (compared with the anhydride–amine system). This is another example of Fig. 4f. However, when the molecular weight of PSU–COOH was quite low (short trunk chain), the micelle formation did not take place and only big particles of PSU (sub- μm \sim μm) were observed as shown in Fig. 3a. It corresponds to a situation of Fig. 4e.

In Fig. 4 are schematically summarized the results of “pull-out or not” for various copolymers in situ-formed in reactive blending of PSU and PA. “Yes/No” means “pull-out/no pull-out” Numbers in and out of parenthesis are the weight and number average molecular weights (M_w and M_n) of component polymers, respectively. Cartoon (a) is by Fig. 1b, (b) by Fig. 1a, (e) by Fig. 3a, and (f) by Figs. 2 and 3b, respectively. Cartoons (c) and (d) are from our previous studies [15]. Note that the formation of block and graft copolymers by reactive blending was confirmed by GPC analysis as in a previous article [16].

As has been discussed in the introduction, the theory of the block copolymer at the polymer–polymer interface [7] suggests that the symmetric AB block copolymer (A block length \approx B block length) prefers to stay at the interface, whereas the asymmetric block copolymer (e.g. long A block/short B block) is unstable to locate at the interface

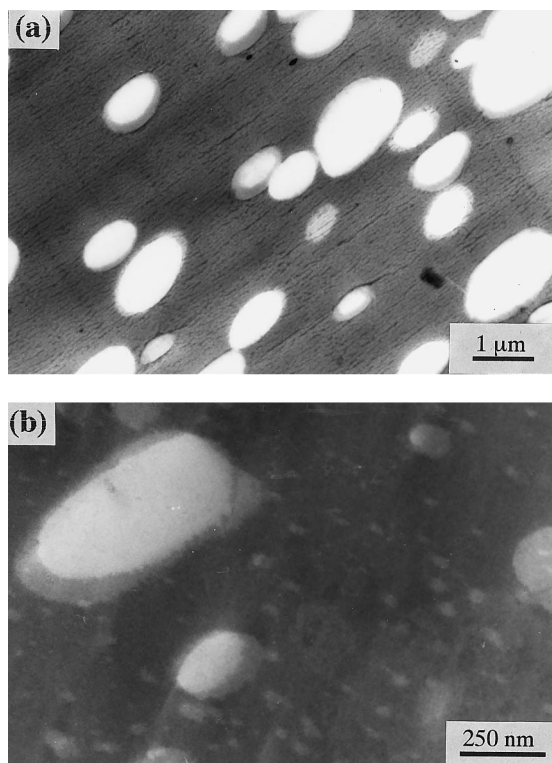


Fig. 3. TEM micrographs of 80/20 PSU-COOH/PA blends melt-mixed at 260°C with rotor speed 100 rpm for 8 min: (a) PSU-COOH1/PA; and (b) PSU-COOH2/PA.

and tends to leave the interface as micelle into the A homopolymer phase. Following the theory, the rather symmetric block copolymer (Fig. 3a) should stay at the interface. However, the experimental result (Fig. 1b) was against the theoretical prediction. The theory mostly deals with the chain conformations in restricted space so that there should not exist any significant difference between the block and graft copolymer systems and the results could be applied also for the graft copolymer systems. If so, the asymmetric in situ-formed graft copolymer (Fig. 4e) should leave the interface and form micelles in the PA phase. However, the experimental result (Fig. 3a) was against it and the micelles were not found. Further, the theory asks that the symmetric copolymer in Fig. 4f (corresponding to Figs. 2 and 3b) should stay at the interface, while the experimental results showed the micelle formation in the PSU phase. These experimental results strongly suggest that the theory is developed just for static condition and it may not be enough to discuss the stability/instability of the copolymers under shear flow, where hydrodynamic forces are applied for the copolymers.

To be discussed further is an effect of shear on the stability of copolymer chains at the interface. Henderson's work [17] pointed out that the ABA triblock copolymer chains in a melt blend of A and B homopolymers would be gradually pulled out by frictional forces acting during the flow on the chain extending into matrix phase. The total withdrawal

force required the chain to be pulled out and is the sum of frictional and interface thermodynamic contributions. The frictional force is a function of a static friction coefficient per monomer, the degree of polymerization of the block subjected to the pull out, and the area chain density (chains/area). That is, if the block length is long, it will need more force and thus more difficult to be pulled out, compared with a short block. Thus, if the applied shear forces are not high enough to overcome the thermodynamically interfacial contribution, the pull out of chain will not happen and the copolymer should stay at the interface. This may be the case of Fig. 4c.

In Newtonian fluids, the shear stress τ is proportional to matrix viscosity (η_m) and shear rate ($\dot{\gamma}$); $\tau = \eta_m \dot{\gamma}$. The larger η_m and $\dot{\gamma}$ would yield the larger shear stress. That is, at a given shear rate, a higher matrix-melt viscosity will lead to a larger shear stress. Then, if the generated shear stress is lower than the shear stress required causing chain pull out, the copolymer chain should stay at the interface to play a role of emulsifier. This may partly be a reason why the pull out did not take place in PA/PSU-COOH1 = 20/80 (Figs. 3a and 4e), where the PSU-COOH1 matrix melt viscosity is relatively low (see Table 1).

Another point to be discussed is the difference in morphology between the block copolymer- and the graft copolymer-forming systems. In both systems, the pull-out took place; however, the block copolymer-forming resulted in a 10 nm-level dispersion with narrow particle-size distribution (Fig. 1a), whereas the graft copolymer-forming system yielded the bimodal distribution consisting of sub- μm particles and tiny domains of 10 nm-level (Figs. 2 and 3b). A plausible interpretation could be given in terms of the coupling reactivity and the thermodynamic stability of copolymer chains at the interface as follows.

One cannot expect a significant difference in coupling reaction rate between amine-phthalic anhydride (PhAH) and amine-maleic anhydride (MAH) pairs. However, there is a difference in the location of the reactive site on the PSU chain: PhAH is at the chain end and MAH is at the mid-segment. According to the theory of polymer-polymer interface [18], chain ends prefer to locate at interface. They have higher probability to be at the interface than the mid-segments. Then, the reactive end-group, PhAH, would have a higher population at the interface than MAH, so that the faster coupling reaction can be expected for the PSU-PhAH (block copolymer-forming system). The fast reaction would result in a high population of block copolymers at the interface in a limited time of melt mixing.

When the block copolymer chains are incorporated too much at the interface, the chains should be forced to be elongated perpendicular to the interface. It will lead to an entropic penalty to increase the interfacial energy. Such unstable copolymer chains accumulated in excess could be easily pulled out from the interface by external forces. By the pull-out, the tiny domains are formed. Simultaneously,

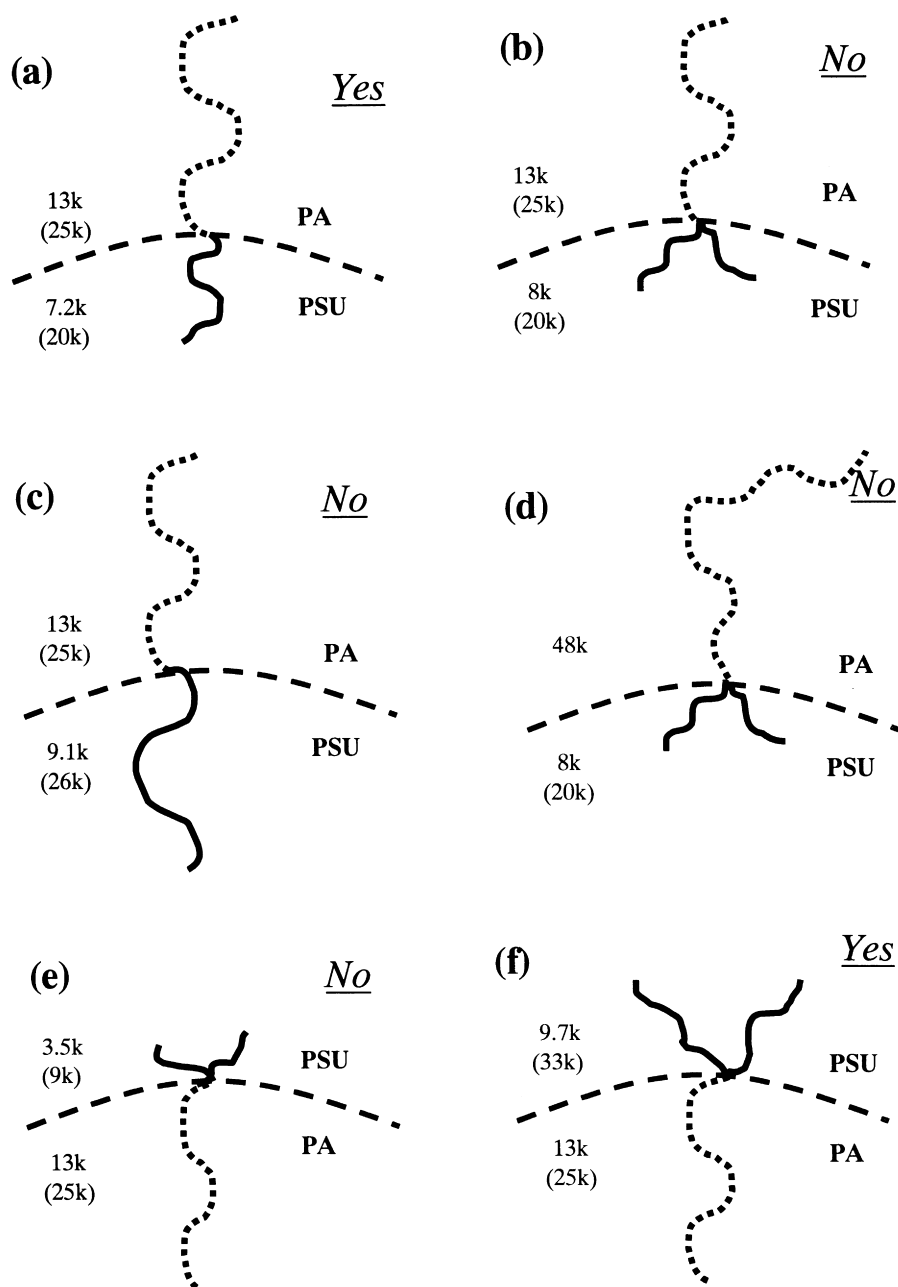


Fig. 4. Schematic representation of pull-out or not for various copolymers in situ-formed in reactive PSU/PA blends. Numbers in and out of parenthesis are M_w and M_n of component polymers.

the big particles get slim and eventually their size could be reduced to 10 nm-level. Then, the narrow particle-size distribution could be achieved as a whole. By contrast, in the PSU–MAH (graft copolymer-forming) system, the supplying rate of graft copolymer chains may not be high enough to destabilize the interface so that the pull-out may proceed slowly. Then, the big particle could remain unnaked in a limited time of mixing. Consequently, tiny domains could coexist with sub- μm particles to provide the bimodal distribution.

4. Conclusion

In this study, the effect of in situ-formed copolymer architecture on the micelle formation in the reactive blending of PA with PSU was investigated. The micelle formation in reactive blending appears to be induced by the external shear forces; i.e. via the pull-out of copolymer chains from the interfacial region. The pull-out or not of in situ formed-copolymers was found to be highly dependent on the copolymer architecture. The block copolymers with

linear chain structure are more easily pulled out than the graft copolymers with branch structure. While the in situ-formed graft copolymer having trunk chains locating in the dispersed phase (inverse Y-shape) is hardly pulled out and plays the role of a emulsifier, the graft copolymer having trunk chains in the matrix (Y-shape) can be pulled out easily. The pull-out and micelle formation took place even in the rather symmetric in situ graft copolymer-forming system in which the copolymer is thermodynamically expected to be stable at the interface.

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