ELSEVIER

Polymer 42 (2001) 8825–8831

polymer

www.elsevier.com/locate/polymer

Reactive blending of polyamide with polyethylene: pull-out of in situ-formed graft copolymer

Lihua Pan[a], Tsuneo Chiba[a], Takashi Inoue[b,*]

[a]Department of Organic and Polymeric Materials, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152-8552, Japan
[b]Department of Polymer Science and Engineering, Yamagata University, Yonezawa 992-8510, Japan

Received 26 July 2000; received in revised form 7 May 2001; accepted 1 June 2001

Abstract

Reactive blending of polyamide 6 (PA) with polyethylene (PE) having reactive site, maleic anhydride (MAH), and PE having glycidyl methacrylate (GMA) units was carried out using a gram-scale mixer at 240°C. Morphology of reactive blend was studied by light scattering and transmission electron microscopy (TEM). TEM observation revealed that *Y-shape* PA–PE graft copolymers in situ-formed in PE-rich system, 30/70 PA/PE wt ratio, were easily pulled out from the interface and the copolymer micelles were dispersed in PE matrix when PA chain was short (lPA; $M_w = 29k$). It implies that the copolymers cannot act as an emulsifier for particle size reduction. Actually, light scattering analysis showed that the size reduction during melt mixing was a slow process. When PA chain was long (hPA; $M_w = 47k$), the pull-out of in situ-formed copolymers hardly occurred, and the average PA particle size quickly decreased during melt blending, implying a nice emulsifying effect of the copolymers. In PA-rich systems (65/35 PA/PE), the pull-out of *inverse Y-shape* graft copolymer took place only when PA chain was long. In a 40/60 lPA/PE-GMA blend, the pull-out of Y-shape graft copolymer took place to yield micelle formation in PE phase and phase inversion occurred to render a PA-matrix morphology when PE trunk chain was long. By contrast, neither the micelle formation nor the phase inversion took place in a short trunk PE chain system. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Reactive blending; Pull-out; Graft copolymer

1. Introduction

More and more attempts are being made to create a favorable morphology for enhancing blend performance of immiscible polymer pairs. It is well known that the block or graft copolymer consisting of component polymers can play a significant role in lowering interfacial tension and suppressing the coalescence of dispersed particles and hence resulting in a size reduction. Recent studies [1,2] have shown that the copolymer in situ-formed during melt mixing can facilitate a much better phase dispersion and thus render smaller droplets than premade copolymer. Moreover, the level to which the particle size reduction attains depends on the concentration of the coupling agent [3], suggesting the critical role played by the copolymer in situ-formed in reactive blending.

Recent studies on reactive blending of polyamide (PA) with polysulfone (PSU) [4–8] revealed a series of new aspects of interfacial behavior of the in situ-formed copolymers. One of the important findings was that the in situ-formed PA–PSU block copolymer could be pulled out from the interface under shear force to form micelles. It was also shown that the 'pull-out or not' highly depends on the molecular architecture of in situ-formed copolymers; the in situ-formed graft copolymers mostly stay at the interface to act as an emulsifier to yield sub-μm particle dispersion, while the block copolymers are easily pulled out from the interface by external force to form micelles in bulk [4].

The stable stay of in situ-formed graft copolymer at interface was for the 'inverse Y-shape' graft copolymer, having trunk chain anchoring in the dispersed phase side (Fig. 1a). The trunk chain of inverse Y-shape graft copolymer may be subjected to bigger spatial constraints by the pull-out than that of the block copolymer (linear chain, Fig. 1a) so that it could be hardly pulled out under external shear forces. If so, one may expect that 'Y-shape' graft copolymer (Fig. 1b) can be easily pulled out as in the case of block copolymer. However, when the anchored chain is very long, the Y-shape graft copolymer is expected to be hardly pulled out. These expectations initiated this study.

In this study, we replaced PSU by polyethylene (PE) since several PEs with reactive sites are commercially

---

* Corresponding author. Tel./fax: +81-238-26-3060.
E-mail address: tinoue@dip.yz.yamagata-u.ac.jp (T. Inoue).

PII: S0032-3861(01)00441-4

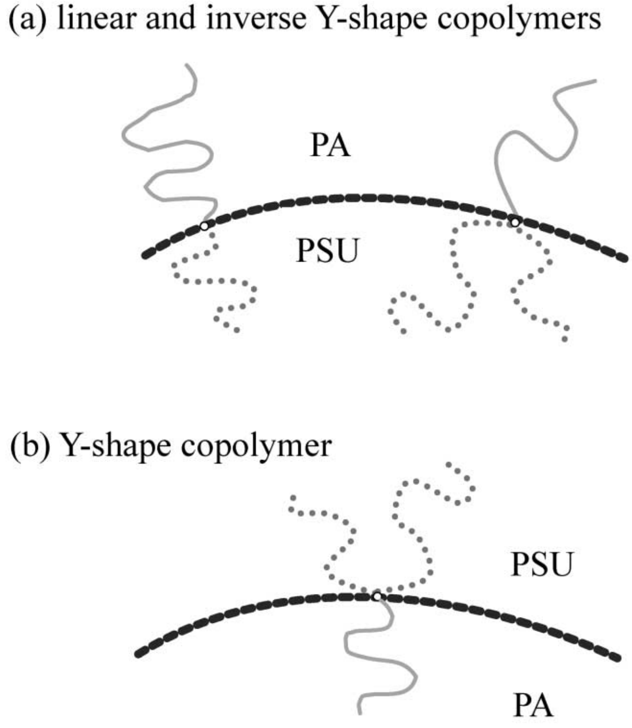

Fig. 1. Molecular architectures of in situ-formed copolymers at interface.

available. Melt blending of the reactive PE with PA was carried out using a miniature mixer. By changing blend composition and molecular weight of component polymers, one can provide various molecular architectures of in situ-formed graft copolymers. Morphology developed during reactive blending was studied by light scattering and transmission electron microscopy (TEM).

2. Experimental section

2.1. Materials

Two polyamide 6 (PA) samples, low molecular weight PA (lPA; $M_n = 15,300$, $M_w = 29,100$) and high molecular weight PA (hPA; $M_n = 22,500$, $M_w = 47,250$) were supplied from Ube Industry and Sumitomo Chem. Co., respectively. PE with maleic anhydride (MAH) units (PE-MAH) was supplied from Mitsui Chem. Co.: Admer NF505; $M_n = 21,400$, $M_w = 69,800$, MAH content = 0.1 wt%, melt flow index (MFI) = 0.8 g/10 min. As a PE with epoxide units (PE-GMA), two grades of molecular weight: Bondfast 20B (lPE-GMA); MFI = 20.0 g/10 min and Bondfast 2B (hPE-GMA); MFI = 3.0 g/10 min from Sumitomo Chem. Co. were used. It is a terpolymer of ethylene (83 wt%), glycidyl methacrylate (GMA) (12 wt%) and vinyl acetate (VA) (5 wt%). As a control sample, PE without functional group (nf-PE) supplied from Mitsubishi Chem. Co. (YUKARON ZF-50, MFI = 3.0 g/10 min) was also used.

The complex dynamic viscosity of the components was measured by a Rheometrics on dynamic mechanical spectrometer using 25 mm parallel plates under a fixed strain amplitude of 5% at 240°C. The gap between the two plates was set at 1.0 mm.

DSC measurement was conducted on a Seiko Exstar 6000 thermal analysis instrument with heating rate 10°C/min under N_2 flow rate 5 ml/min. Before measurement, each component polymer was weighed precisely around 7.00 mg and packed into the aluminium pan.

2.2. Melt mixing

PA pellets were dried under vacuum (10^{-4} mmHg) at 80°C for 24 h before mixing. PE samples were also dried at 70°C. Melt mixing was conducted in a miniature mixer of 1-g scale, Mini-Max Molder (CS-183MM, Custom Scientific Instruments Inc.) at 240°C. Rotational speed was set at 50 or 100 rpm, corresponding to a maximum shear rate of 7 and 14 s^{-1}, respectively. At appropriate time intervals, a small amount of mixed melt was picked up by a pincette and was immediately quenched in ice water to preserve the two-phase morphology formed at that mixing time. Morphology of these mixed-and-quenched specimens was analyzed by light scattering and TEM.

2.3. Morphology analysis

The mixed-and-quenched specimen was placed between two cover glasses and melt pressed at 240°C to obtain a thin film with thickness of ca. 15 μm on a hot stage attached on the light scattering equipment. After melt pressing, the time-resolved measurement of scattering profile (intensity of scattered light vs. scattering angle) was made at a time slice of 1/30 s. The scattering measurement was performed by 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. A scattering profile just after the remelt provides information on the morphology in the mixed-and-quenched blend. Details of data analysis is shown elsewhere [5].

For TEM observation, the quenched sample was exposed to ruthenium tetraoxide (RuO_4) vapor at room temperature for 2 h and then cryomicrotomed by an ultramicrotome (Reichert Ultracut-Nissei) at −60°C to obtain an ultrathin film of ca. 60 nm thickness. The ultrathin section was then mounted on 200 mesh copper grid and again exposed to the RuO4 vapor for another 1 h. Amorphous region of PE was preferentially stained by RuO4. Morphology was observed by a transmission electron microscope, JEM-100CX (JEOL), under an accelerating voltage of 100 kV. TEM pictures were digitized with a scanner. Assuming the shape of dispersed particles as circular, the diameter of the particle D_i was then calculated from the corresponding particle area A_i determined using a software of NIH Image Analysis System based on the digitized result. The mean particle size was thus calculated as follows:

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

where N was 100–200 in a TEM picture. The average D_{TEM} may be comparable to that by light scattering because the latter is based on the surface area per unit volume.

3. Results and discussion

Fig. 2 shows the mean particle size of the melt-mixed blends by light scattering as a function of mixing (reactive) time. PA/PE blend ratio is 65/35 (wt ratio). The morphology was proved to be PE particles dispersed in PA matrix by TEM (Fig. 3). In the non-reactive blend (lPA/nf-PE), the particle size decreases very slowly and levels off at 1.75 μm. By contrast, reactive systems yield much finer particles of sub-μm in a shorter time, i.e. via faster size reduction process. This is an expected result since the reactive system may generate the PA–PE graft copolymer that would play both roles of reducing the interfacial tension and preventing particle coalescence. Note that in such compositions of reactive blend, inverse Y-shape graft copolymer (Fig. 1a) should be formed in situ at the interface between dispersed PE phase and PA matrix via coupling reaction. The inverse Y-shape graft copolymer with longer graft PA chain (hPA) extending into matrix phase renders much finer dispersion.

Fig. 3 shows TEM micrographs of blend morphology evolved at late stage of blending (mixing for 15 min). The dark region is PE phase stained by RuO_4. As expected from the light scattering results, large PE particles of several μm are dispersed in PA matrix in non-reactive blend (Fig. 3a), while much finer morphology (Fig. 3b and c) has been established in reactive systems. In the reactive hPA system (Fig. 3c), one sees many tiny domains of ca. 30–50 nm in diameter coexisting with sub-μm PE particles. These tiny domains may be regarded as micelles of in situ-formed graft copolymers. However, when the PA chain is short (lPA system), such tiny particles are hardly found in both PA and PE phases (Fig. 3b). The results strongly suggest that in situ-formed inverse Y-shape graft copolymer with long graft PA chain (Fig. 10b) can be pulled out of interface to form micelle in the PA bulk during melt mixing, while that

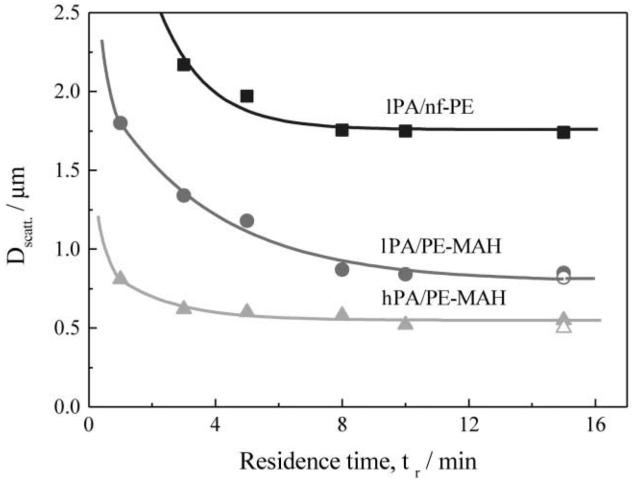

Fig. 2. Mean particle size variation with mixing time for 65/35 PA/PE blends at rotation speed of 100 rpm. Particle size measured by light scattering (filled symbol) and by TEM (open symbol).

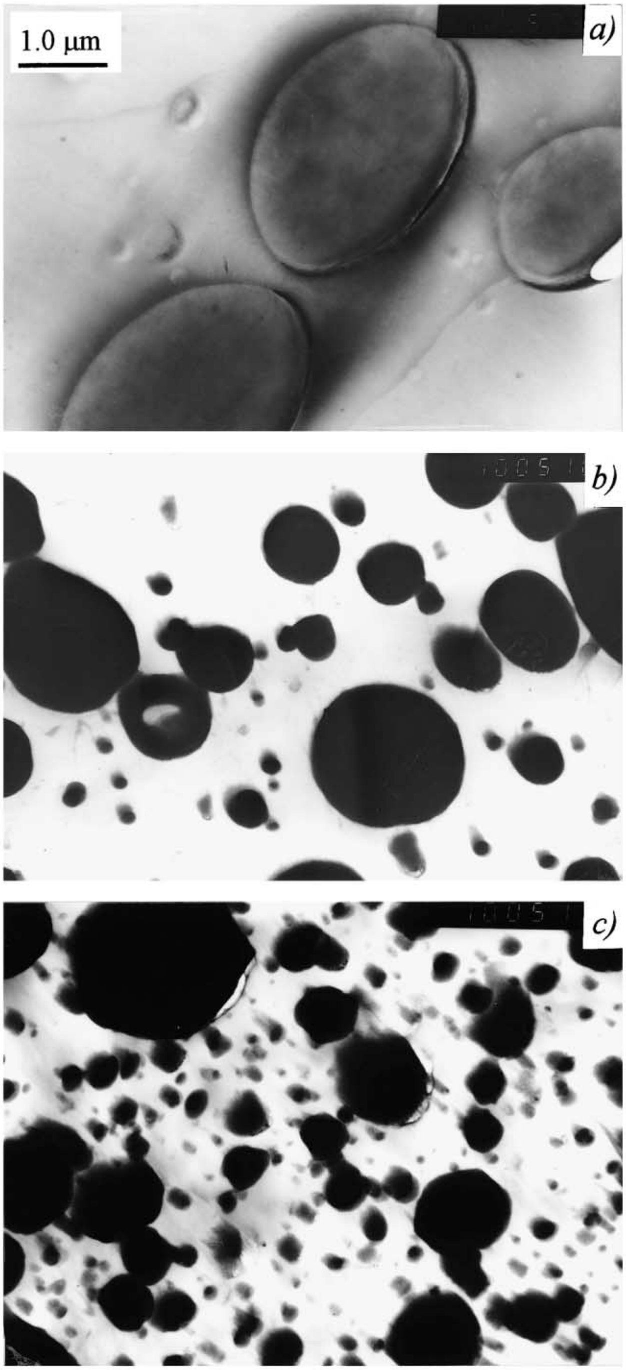

Fig. 3. TEM micrographs of 65/35 PA/PE blends after mixing for 15 min: (a) lPA/nf-PE; (b) lPA/PE-MAH; (c) hPA/PE-MAH.

with short graft PA chain would mostly stay at the interface as an emulsifier (Fig. 10a). That is, there is a clear difference in interfacial stability between the two inverse Y-shape graft copolymers at the interface under shear field.

From TEM observation under lower magnification (Fig. 4b), one sees an asphericity of PE particles, especially for big particles in the bimodal size distribution: the asphericity is higher in hPA blend than in lPA one, implying lower interfacial tension caused by nice emulsifying effect of in situ-formed graft copolymer staying at the interface [9]. The result may imply that the presence of inverse Y-shape graft copolymer with long graft chain residing in the matrix favors emulsifying effect more efficiently than that with short chain. It may be consistent with the theoretic prediction by Leibler [10]. Anyhow, the big particles seem to be covered with the in situ-formed copolymers, even after the pull-out in the limited mixing time. In other words, a part of in situ-formed copolymers accumulated at the interface is pulled out of interface, while other copolymers may remain at the interface. Then, the nice emulsifying effect caused by the copolymer with longer graft PA chain in hPA system may be responsible to yield the finer particles. Of course, the micelle formation by pull-out also contributes significantly to the size reduction.

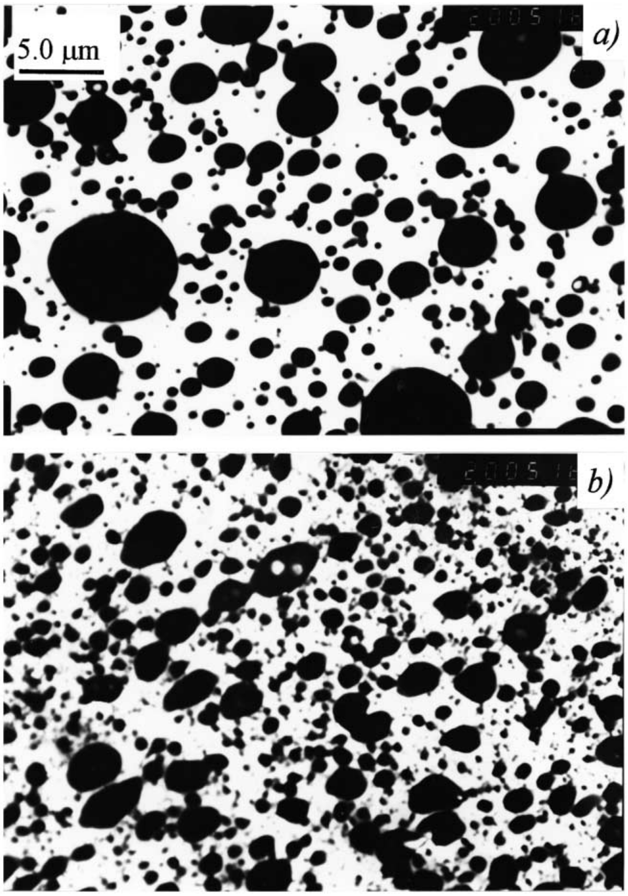

Fig. 4. TEM micrographs of 65/35 reactive blends at lower magnification: (a) lPA/PE-MAH; (b) hPA/PE-MAH.

In order to obtain in situ-formed Y-shape graft copolymer having trunk chain locating in matrix as shown in Fig. 1b, PE-rich blends with composition of 30/70 PA/PE-MAH were prepared. Fig. 5a and b shows TEM micrographs for the blends of lPA /PE-MAH and hPA/PE-MAH after mixing for 15 min at the rotation speed of 50 rpm. The attainable particle size in the lPA system (Fig. 5a) is much finer than that in the hPA system (Fig. 5b). The tiny domain with 10-nm level is densely distributed in the lPA system, implying that pull-out of in situ-formed copolymer took place.

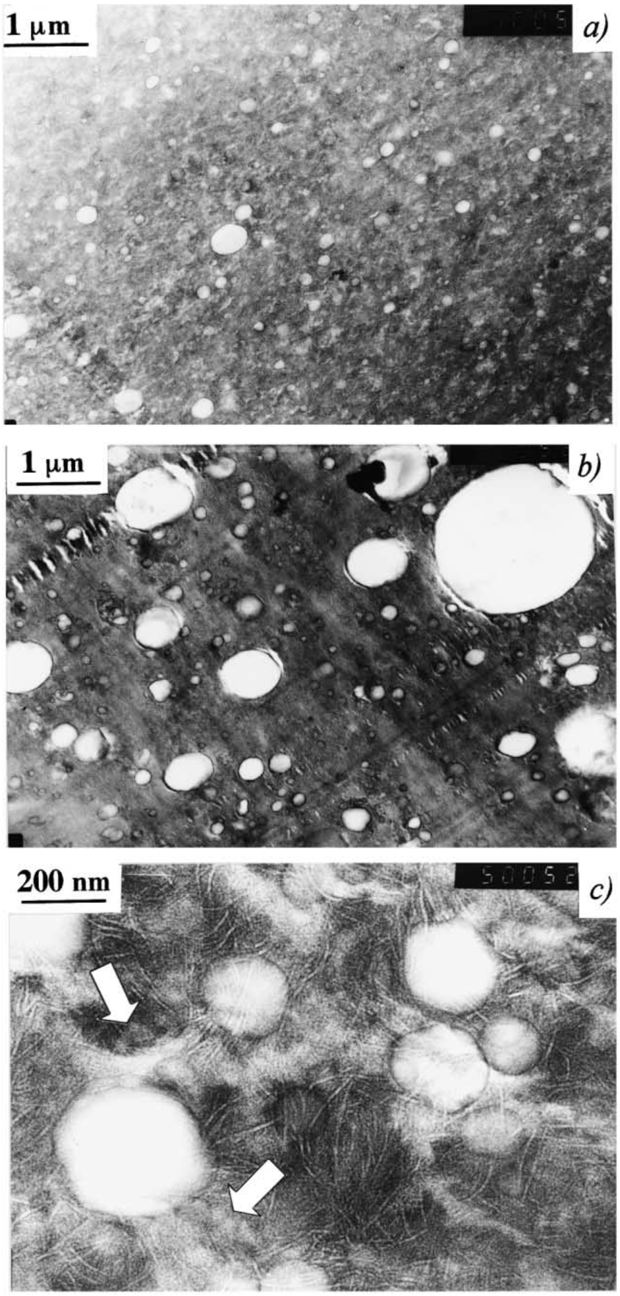

Fig. 5. TEM micrographs of 30/70 PA/PE-MAH blends after melt mixing at 50 rpm: (a) lPA/PE-MAH (15 min); (b) hPA/PE-MAH (15 min); (c) lPA/PE-MAH (8 min).

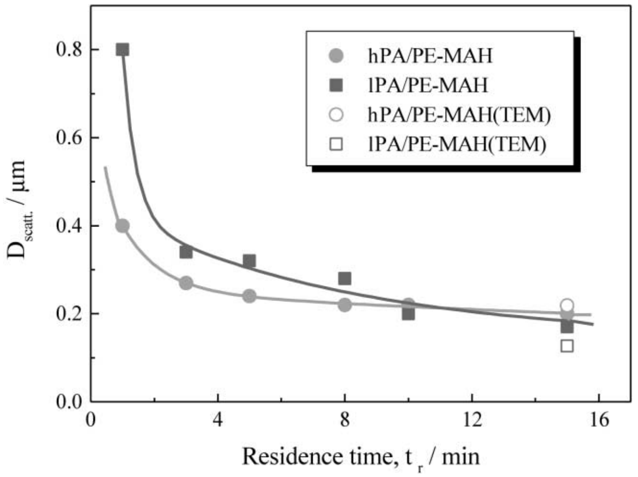

Fig. 6. Mean particle size in 30/70 PA/PE-MAH blends as a function of mixing time during melt mixing at rotation speed of 50 rpm (open and filled symbols: see Fig. 2).

However, in the hPA blend, micelle is hardly found. TEM micrograph at high magnification for the lPA blend after mixing for 8 min (Fig. 5c) shows less populated tiny domain in shorter time mixing. By mixing further, such micelle becomes more populated and is uniformly distributed in the matrix (Fig. 5a), suggesting the pull-out of in situ-formed copolymer is a rather slow process.

Actually, light scattering analysis (Fig. 6) indicates that the size reduction in lPA system (mixing at rotation speed 50 rpm) is a slow process; however, the size can be reduced to smaller than that of the hPA system at late stages, i.e. one sees a crossover in size reduction curves in Fig. 6.

In the present reactive systems lPA/PE-MAH and hPA/PE-MAH, in situ-formed graft copolymers could be classified as symmetric ones (PA chain length ≈ PE chain length), especially for hPA/PE-MAH. Assuming that the theory [11] for block copolymer can be applied for the graft copolymer-forming system, in situ-formed graft copolymers should stay stable at the interface. However, the experimental results are against the theory. The theory is for the quiescent state. The situation may be different when the copolymers are subjected to shear fields during melt processing.

Thus, the pull-out or not seems to depend not only on the molecular architecture but also on the strength of shear fields. A good example is shown in Fig. 7. The Y-shape graft copolymer with long anchoring graft chain can be pulled out to form the micelles at a high shear field (100 rpm; Fig. 7), while it rather stably stays at interface at the low shear field (50 rpm; Fig. 5b).

Henderson [12] 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 imposed on the copolymer chain extending into matrix phase. The withdrawal force for the copolymer chain to be pulled out should be larger or equal to the sum of frictional and interface thermodynamic contributions. The longer the anchoring block, the higher are the applied forces required for pull-out. This may explain why in the PE-rich systems, pull-out was easy even at the low shear force (50 rpm) in the lPA blend in situ-forming Y-shape graft copolymer with short linear chain locating in the dispersed phase (Fig. 10c), while the pull-out of copolymer with long PA chain in situ-formed in the hPA system took place only at high shear force (100 rpm) as shown in Fig. 10d. When the applied forces are not enough for overcoming the thermodynamic interfacial barrier, pull-out may not happen as in the cases of Fig. 10a and d (50 rpm) and Fig. 10e.

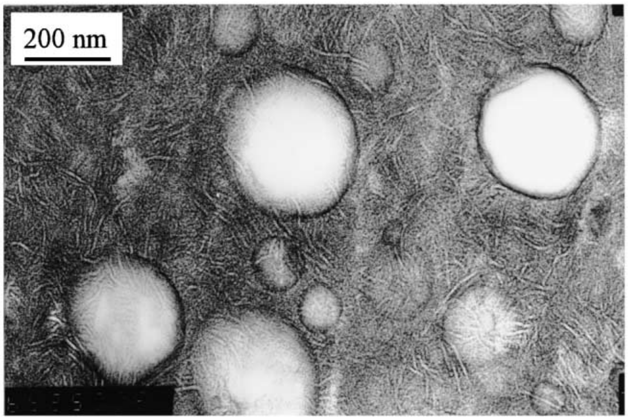

Fig. 7. TEM micrograph of 30/70 hPA/PE-MAH blend after mixing for 15 min at 100 rpm.

As to the PA-rich reactive blends, the in situ-formed graft copolymer generated in the hPA system should be subjected to greater shear force owing to the higher matrix melt viscosity than in the lPA system. If the imposed shear force on the copolymer chains is lower than that required for their pull-out, the copolymers would stay stable at the interface as in the case of Fig. 10a. Otherwise, they should be pulled out of interface to form micelle as the situation in Fig. 10b. Then, the difference in interfacial behavior of inverse Y-shape graft copolymer between hPA/ PE-MAH and lPA/PE-MAH blends could be mainly caused by the difference in hydrodynamic withdrawing forces.

When epoxide-graft PE, PE-GMA, was melt-mixed with PA at 40/60 lPA/PE-GMA, phase inversion occurred in a high molecular weight PE-GMA (hPE-GMA) system, while not in a low molecular weight (lPE-GMA) system as shown in Fig. 8. Fig. 8 shows the TEM micrographs of the two blends after mixing for 15 min. Note that the two PE-GMAs have almost the same melt viscosity at mixing conditions, melting point and functionality (Table 1), but different molecular weights (MFI). The lPE-GMA system has a PA particles-in-PE matrix morphology, whereas the hPE-GMA system has a PE particles-in-PA matrix morphology. The former morphology is quite natural for the 40/60 blend; i.e. the major component PE is the matrix and the minor PA, the dispersed phase, as expected. By contrast, the latter system

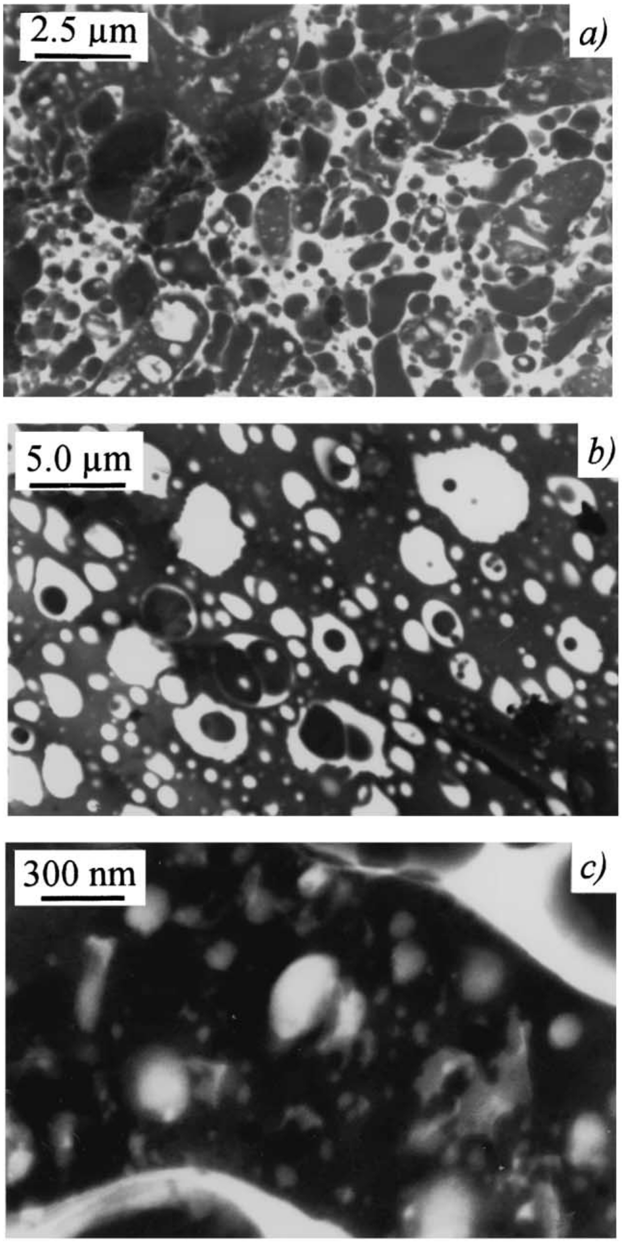

Fig. 8. TEM micrographs of 40/60 lPA/PE-GMA blends after melt mixing for 15 min: (a) lPA/hPE-GMA; (b) lPA/lPE-GMA; (c) lPA/hPE-GMA (higher magnification).

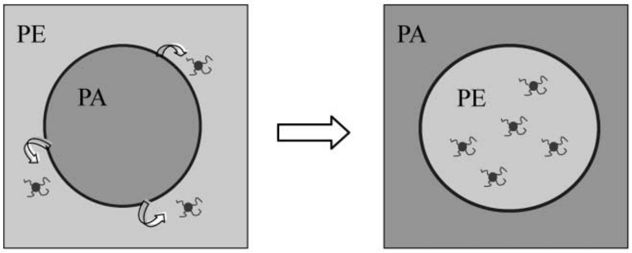

Fig. 9. Schematic representation of phase inversion as a result of micelle formation via pull-out.

shows the inversed morphology, in which a lot of PA micelles are occluded in PE particles (Fig. 8c).

It has been well recognized that in binary polymer blend, the relative transition temperature, e.g. softening temperature for amorphous component polymers or melting temperature for semi-crystalline ones, and melt viscosity ratio of the component polymers are the important parameters for morphology evolution. At very early stage of melt mixing, the component with lower transition temperature forms the continuous phase encapsulating unmolten particles of the other component [13–18] even when the former is a minor component. In our cases, owing to the large difference in melting points between lPA and PE-GMA (Table 1), we also found the similar phenomenon: the PE component as matrix and PA as dispersed particles for both current systems at very early stages of melt mixing. In the lPE-GMA system, the PE matrix morphology was maintained at the later stages of mixing (Fig. 8b), as expected from the PE-rich composition (60/40). However, in the hPE-GMA system, the phase inversion took place to yield the PA matrix morphology (Fig. 8a).

For the early stages of mixing, one can expect an in situ-formation of the Y-shape copolymers. When the trunk chain is short, the copolymer could be hardly pulled out (Fig. 10e), whereas the graft copolymers with long trunk chain would be easily pulled out (Fig. 10f) to form micelles. Actually, TEM observation showed that in the hPE-GMA system, a lot of micelles were seen in the PE phase, while in the lPE-GMA system, such micelles were never found. By the micelle formation in PE matrix, the matrix melt viscosity is expected to increase, and then, the phase inversion could

Table 1
Characteristics of component polymers

Component	lPA	hPA	PE-MAH	lPE-GMA[a]	hPE-GMA[b]	nf-PE
Melt viscosity[c]	2700	14,120	15,600	11,000	11,140	13,700
T_m[d]	221.0	221.9	120.0	90.8	94.6	118.0

[a] MFI = 20 g/10 min at 125°C.

[b] MFI = 3.0 g/10 min at 125°C.

[c] Complex melt viscosity under frequency of 14 rad s^{-1} at 240°C (poise).

[d] Melting point measured by DSC at heating rate 10°C/min (°C).

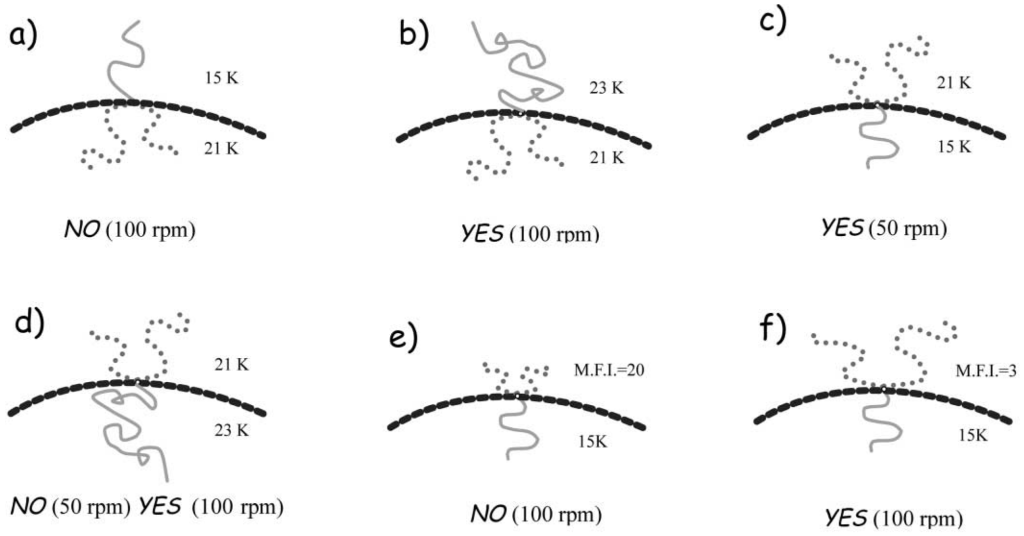

Fig. 10. Illustration of pull-out or not for various graft copolymers in situ-formed in reactive blending.

occur to yield the PA-matrix morphology. The situation is schematically shown in Fig. 9.

Fig. 10 is a schematic summary for the pull-out or not of various copolymers with different molecular architectures investigated in this paper. Numbers in each cartoon are number average molecular weight of component polymers. For PE-GMA, MFI is shown instead of molecular weight. The value following 'Yes' or 'No' is the rotor speed used, representing a relative magnitude of shear force applied.

4. Conclusion

As an interesting interfacial behavior, pull-out or not of in situ-formed graft copolymers from the interface between two phases during melt-mixing process was investigated in reactive blending of PE with PA. Y-shape in situ-formed PA–PE graft copolymers could be easily pulled out of the interface and the copolymer micelles were dispersed in PE phase in the case of short PA chain anchoring in dispersed phase and/or long trunk PE chain buoying in matrix. Such copolymer could not act as an emulsifier for size reduction. However, when PA chain was long or trunk PE chain was short, the pull-out of in situ-formed copolymers hardly occurred and the copolymers preferred to stay at the interface to work as good emulsifiers. Then, the copolymers could render a fast size reduction. For the inverse Y-shape graft copolymer in situ-formed in PA-rich systems, the pull-out took place only when PA chain was long. For a 40/60 PA/PE reactive blend, phase inversion occurred to yield a PE particle-in-PA matrix morphology, when the in situ-formed graft copolymer was pulled out to form micelles. The pull-out or not of in situ-formed graft copolymer was found to be dependent also on the magnitude of external shear force applied.

References

[1] Sundararaj U, Macosko C. Macromolecules 1995;28:2647.
[2] Nakayama A, Guegan P, Hirao A, Inoue T, Macosko CW. ACS Polym Prepr 1993;34:840.
[3] Okamoto M, Inoue T. Polym Engng Sci 1993;33:175.
[4] Charoensirisomboon P, Chiba T, Solomko SI, Inoue T, Weber M. Polymer 1999;40:6803.
[5] Ibuki J, Charoensirisomboon P, Ougizawa T, Inoue T, Koch E, Weber M. Polymer 1999;40:647.
[6] Charoensirisomboon P, Inoue T, Weber M. Polymer 2000;41:4483.
[7] Charoensirisomboon P, Chiba T, Inoue T, Weber M. Polymer 2000;41:5977.
[8] Charoensirisomboon P, Inoue T, Weber M. Polymer 2000;41:6907.
[9] Sigalov GM, Ibuki J, Chiba T, Inoue T. Macromolecules 1997;30:7759.
[10] Leibler L. Physica A 1991;172:258.
[11] Leibler L. Makromol Chem Macromol Symp 1988;16:1.
[12] Henderson CP, Williams MC. J Polym Sci, Polym Lett 1979;17:257.
[13] Shih C-K, Tynan DG, Denelsbeck DA. Polym Engng Sci 1991;31:1670.
[14] Sundararaj U, Macosco CW, Rolando RJ, Chan HT. Polym Engng Sci 1992;32:1814.
[15] Shih C-K. Adv Polym Tech 1992;11:222.
[16] Shih C-K. Polym Engng Sci 1995;35:1688.
[17] Sundararaj U, Macosco CW, Shih C-K. Polym Engng Sci 1996;36:1769.
[18] Scott CE, Joung SK. Polym Engng Sci 1996;36:1666.