

Morphology of compatibilized polymer blends in terms of particle size–asphericity map

P. Charoensirisomboon^a, T. Inoue^{a,*}, S.I. Solomko^b, G.M. Sigalov^b, M. Weber^c

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

^bInstitute of Problems of Chemical Physics, Russian Academy of Science, Chernogolovka 142432, Moscow region, Russian Federation

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

Received 14 September 1999; received in revised form 6 December 1999; accepted 17 January 2000

Abstract

Morphology of reactively compatibilized polymer blends was discussed in terms of particle asphericity (ζ)–size (a) map. Reactive melt blending of polysulfone (PSU) with polyamide 6 (PA) was carried out at 20/80 (PSU–PA) wt ratio by adding a few wt% of reactive PSUs; maleic anhydride-grafted PSU (PSU–MAH) or phthalic anhydride-terminated PSU (PSU–PhAH). Morphology development was investigated by light scattering, scanning electron microscopy (SEM) and transmission electron microscopy (TEM). SEM picture was analyzed by a new digital image analysis (DIA), based on the effective ellipse method. The new DIA allows us to analyze the particle size, the shape (asphericity) and their distributions, which are reminiscent of size reduction process and shape relaxation during melt blending. In in situ graft copolymer-forming (PSU–MAH) systems, the ζ – a map shifted rather vertically to higher asphericity and smaller particle sizes as the loading amount of reactive PSU increased, suggesting an emulsifying effect of the in situ-formed graft copolymer. By contrast, in in situ block copolymer-forming (PSU–PhAH) systems, the ζ – a map shifted rather horizontally to the smaller particle-size with an increase in the loading amount of reactive PSU. The difference in the ζ – a map between the in situ graft copolymer- and block copolymer-forming systems was interpreted by the “pull-out or not” of the in situ-formed copolymers from the interfacial region by shear forces during mixing. The pull-out of in situ-formed block copolymer was confirmed by TEM: tiny domains (20–40 nm in diameter) coexisted with the bigger particles (μm) with low ζ (probably, “naked particles”–not or less covered with the copolymers). © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Reactive blending; Emulsifier; Block copolymer

1. Introduction

Vast majorities of 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 alleviated by the introduction of a proper interfacial modifier. The process is often called compatibilization. A traditional compatibilization strategy is the addition of a pre-made block copolymer composed of the blocks, which are identical with or miscible with the component polymers [1,2]. Another strategy is the reactive processing or the reactive blending, in which the block or graft copolymer can be in situ-formed at the interface between phases by the coupling reaction of functionalized components [3–5]. The latter approach is generally more effective and less expensive for morphology

control, and thus more frequently used for industrial applications [6].

The presence of copolymers (either added or created in situ by coupling reaction) at the interfaces is believed to play dual roles in promoting mixing [7–10]. One is to reduce the interfacial tension and so promotes droplet breakup. The other is to provide the steric hindrance between dispersed particles and thus suppresses droplet coalescence. In other words, the copolymer is believed to play the role of an emulsifier.

The decrease in the interfacial tension by the presence of copolymer has been observed experimentally in several studies [11–13]. In general, it was found that by adding a small amount of the block copolymer the interfacial tension is dramatically reduced, while at the higher concentration it is not reduced further. Lately, several experimental and theoretical works [14–17], however, have suggested that the main contribution of the copolymers to finer particles and stable morphology, may be a suppression of particle coalescence under flow fields rather than a reduction of interfacial tension.

* 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 polymers used

Nomenclature	M_n^a	M_w^a	η^{*b}	Functionality ^c
PA	13,000	25,000	3400	1.00
PSU	14,500	41,000	85,000	0
PSU–MAH	7600	19,300	2400	1.05
PSU–PhAH	5,300	20,660	2300	0.88

^a By GPC, g/mol.

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

^c Reactive site per chain.

To be a good emulsifier and play either role, the copolymers are required to locate at the interfacial region. In other words, the emulsifying effect of the copolymers should be determined by the ability of copolymer chains to locate at the interface between the two phases.

Recent studies [18–20] have shown that the behavior of the copolymer in situ-formed during melt processing are more intricate and rather versatile. Their interfacial activities may depend on several factors such as molecular architecture of in situ-formed copolymer (graft or block), coupling reaction kinetics, and processing conditions. In a previous work [18], we have demonstrated experimentally a difference in interfacial behavior between in situ-formed block and graft copolymers under shear fields in reactive melt blending of polyamide 6 (PA) with reactive polysulfone (PSU). The in situ-formed graft copolymers prefer to stay at the interface and seem to play the role of an emulsifier to render finer dispersion (of sub- μm) than the non-reactive system. By contrast, the in situ-formed block copolymers are easily peeled or pulled out from the interface by external shear forces to form micelles in the PA matrix and eventually yields the 10 nm-level dispersion. Note that in the study, 100% reactive PSUs were used.

The difference in interfacial behavior between the in situ-formed graft and block copolymers may be expected even in diluted systems containing small amounts of the reactive component. In this study, we carried out a series of melt blending of reactive PSU, non-reactive PSU with PA at 20/80 weight ratio containing a few wt% of reactive PSU. Two types of reactive PSUs were used; maleic anhydride-grafted polysulfone (PSU–MAH) and phthalic anhydride-terminated polysulfone (PSU–PhAH). Thus, one can expect the in situ-formed graft and block copolymers, respectively. The morphology development was investigated by light scattering (LS), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). To analyze SEM picture, we applied a new digital image analysis (DIA) method [21]. This new method allowed us to analyze the particle size, the shape (asphericity ζ) and their distributions, which are reminiscent of the size reduction process and the shape relaxation during melt blending.

2. Experimental section

2.1. Materials

The PSU and PA used were commercial polymers of BASF AG, Ultrason S2010 and Ultramid B3, respectively. PSU is a condensation product of bisphenol-A and 4,4-dichlorodiphenylsulfone. PA is polyamide 6. Two different types of reactive PSUs, PSU–MAH and PSU–PhAH, were prepared by following synthesis procedures given in the literatures [22,23]. The detail of the synthesis method has been reported elsewhere [18,24]. Characteristics of the materials used are summarized in Table 1.

2.2. Melt mixing

To remove absorbed moisture, PA pellets were dried under vacuum (10^{-4} mmHg) at 80°C over night before blending. A mixture of non-reactive PSU and reactive PSU was melt blended with PA at 20/80 (PSU/PA) wt ratio using a miniature one gram-scale mixer (Mini–Max Molder, CS-183 MM, Custom Scientific Instruments Inc.) [25] at 260°C. Two different procedures for polymer blending were used. One was the one-step mixing, in which all component polymers (PA, PSU and reactive PSU) were simply put together in the mixer. The other was two-step mixing. In this case, PSU and reactive PSU were dissolved firstly and then blended in methylene chloride. Then, the solvent was evaporated at room temperature and at 40°C under vacuum for two days. The dried sample was melt-pressed and cut to pellet size. This pre-mixed PSU pellet was then melt-blended with PA.

During the mixing, a small amount of mixed melt (40 mg) was picked up by pincette at appropriate intervals and was quickly quenched in cool-water to freeze the two-phase structure in the melt. Thus, we prepared a series of mixed-and-quenched specimen with various mixing times. These specimens were analyzed by using LS and SEM.

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 profiles (angular dependence of scattered light intensity) with a time slice of 1/30 s started. The scattering apparatus consisted of a highly sensitive CCD camera with 576×382 pixels, a He–Ne laser of 632.8-nm wavelength and V_v (parallel polarization) optical alignment [26]. Since the two-phase structure in the melt is at a non-equilibrium state, it may coarsen with time after the re-melt. A scattering profile just after the re-melt provides information on the two-phase structure in the mixed-and-quenched blend.

The morphology was observed with a scanning electron microscope (model JSM-T220, JEOL Ltd) at the accelerating voltage of 15 kV. The quenched specimen was stained

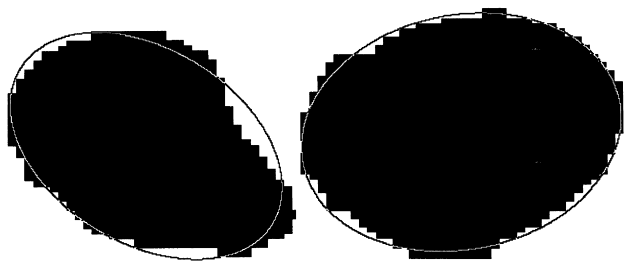


Fig. 1. Representation of real particle images by effective ellipses.

with RuO_4 at room temperature for 4 h to render better contrast between PSU and PA phases. A stained specimen was cryomicrotomed at -65°C to make a flat surface. After the deposition of a carbon layer, SEM observation was performed under backscattered electron mode. Note that the mentioned technique for SEM observation provides a nice contrast and reliable results on the two-phase morphology with the domain size of a few to sub- μm [27,28].

Original SEM pictures were manually transformed to black-and-white images. Then, the images were digitized using a scanner. These binarized SEM pictures were analyzed with the help of a custom-designed DIA computer program based on the method of effective ellipse (MEE) [21]. The main idea of MEE consists of the substitution of a real particle image by an effective ellipse. The effective ellipse is characterized by its semi-axis lengths, a (longer) and b (shorter). The effective ellipse parameters are chosen so that it represents the shape of the real particle in the best way (see Fig. 1). The details of the algorithms are given elsewhere [21]. Then, the particle shape can be discussed in terms of the particle asphericity parameter, $\zeta = a/b - 1$. Plotting the asphericity against the ellipse larger semi-axis length, one can discuss the size reduction and shape relaxation processes during melt blending. Note that the special procedure of the DIA program was worked out to distinguish partially overlapping particle projections.

For TEM observations, the quenched specimen was cryomicrotomed 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 RuO_4 vapor for 20 min. The two-phase morphology was observed by transmission electron microscope, JEM-100CX (JEOL), at an accelerating voltage of 100 kV.

2.4. Melt viscosity

The complex dynamic viscosity η^* was measured at 260°C by Rheometric Dynamic Spectrometer (Model RDS-7700) at parallel-plate mode (plate radius 12.5 mm, gap 1.0 mm) and 10% strain amplitude.

3. Results and discussion

For all the quenched-and-remelted blend specimens, the intensity of scattered light monotonically decreased with

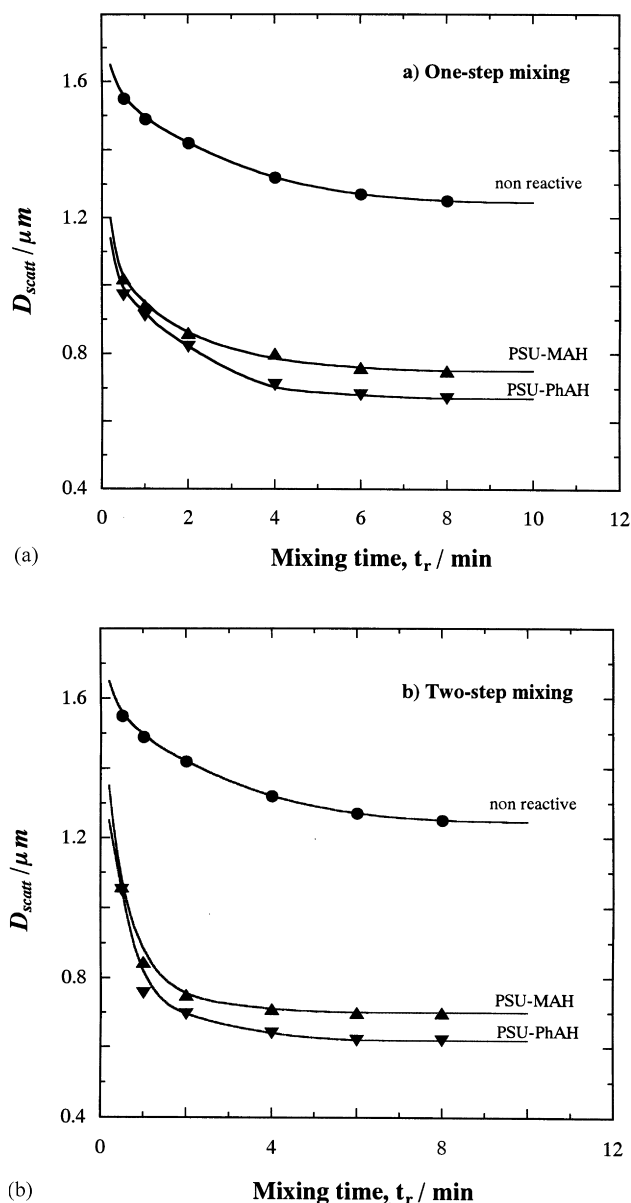
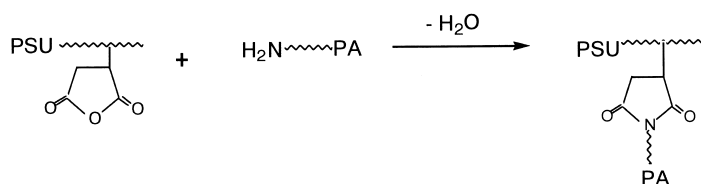


Fig. 2. Typical examples of time variation of PSU particle diameter D_{scatt} during melt mixing. Loading amount of reactive PSU in reactive system was 1 wt%: (a) one-step mixing and (b) two-step mixing.

the increase in scattering angle. The mean diameter of the dispersed PSU particle D_{scatt} was obtained by the Debye–Bueche plot [29,30]. More details on data analysis have been given elsewhere [3,5]. Fig. 2a and b shows representative plots of the mean PSU particle size as a function of mixing (reaction) time in one-step and two-step mixings, respectively. The loaded amount of reactive PSU was 1 wt%. One sees that the reactive systems, PSU–MAH and PSU–PhAH systems, yield finer particles via faster size reduction processes than the non-reactive system. The reactive systems may generate the PSU–PA graft and PSU–PA block copolymers as shown in Fig. 3. The copolymers are expected to play the role of an emulsifier to reduce the interfacial tension and to prevent particle coalescence.

(a) Graft copolymerization between PSU-MAH and PA



(b) Block copolymerization between PSU-PhAH and PA

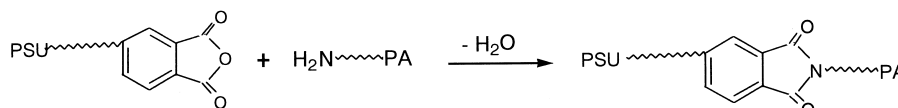


Fig. 3. In situ-coupling reactions between reactive PSU with PA to form graft and block copolymers.

In Fig. 2, there is no essential difference in the size reduction process between the one- and two-step mixings. However, there is a certain difference between PSU-MAH and PSU-PhAH systems: PSU-PhAH is more effective for the rapid size reduction to yield smaller particles than PSU-MAH, though the reactive site per chain of both reactive PSUs is quite comparable (see Table 1). The difference was observed for all blends of various loading amounts of reactive PSU (0.5, 1, and 3 wt%).

In Fig. 4, the particle size after 8 min mixing is plotted as a function of the loaded amount of reactive PSU. The open and close symbols represent D_{scatt} from the one- and two-step mixings, respectively; showing again no significant difference between the one- and two-step mixings. The higher amount of PSU-MAH leads to the smaller particle

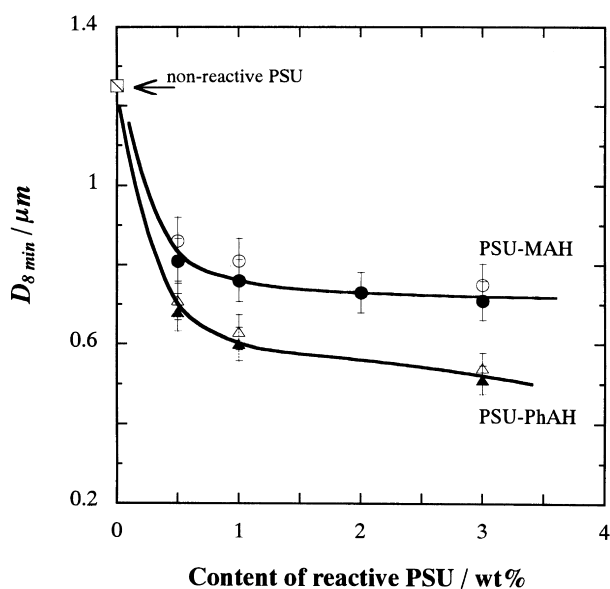


Fig. 4. Effect of the loading amount of reactive PSU on the mean PSU particle size; (○) one-step mixing, (●) two-step mixing.

size, clearly demonstrating the emulsifying effect of the in situ-formed graft copolymer. However, the emulsifying effect levels off at 2 wt%; i.e. there is no further decrease in D_{scatt} with more PSU-MAH loading. By contrast, the D_{scatt} of in situ-block copolymer forming system (PSU-PhAH) continuously decreases with the increase in the amount of PSU-PhAH. This may suggest a dissimilarity in size

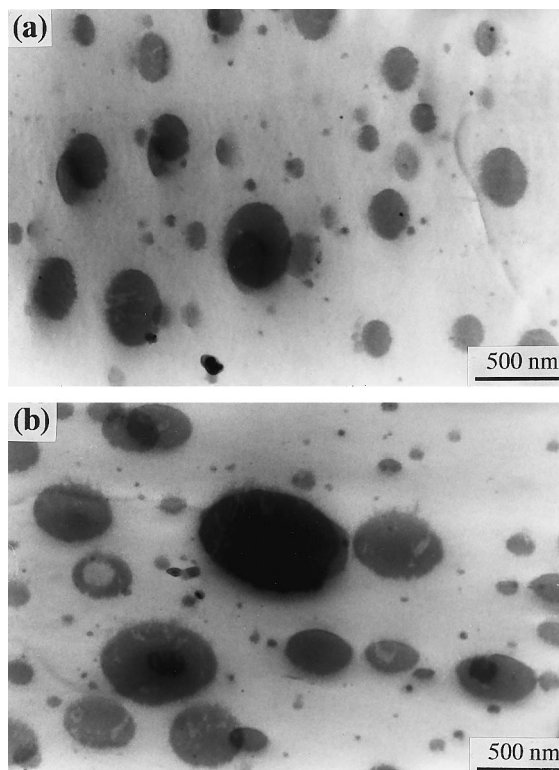
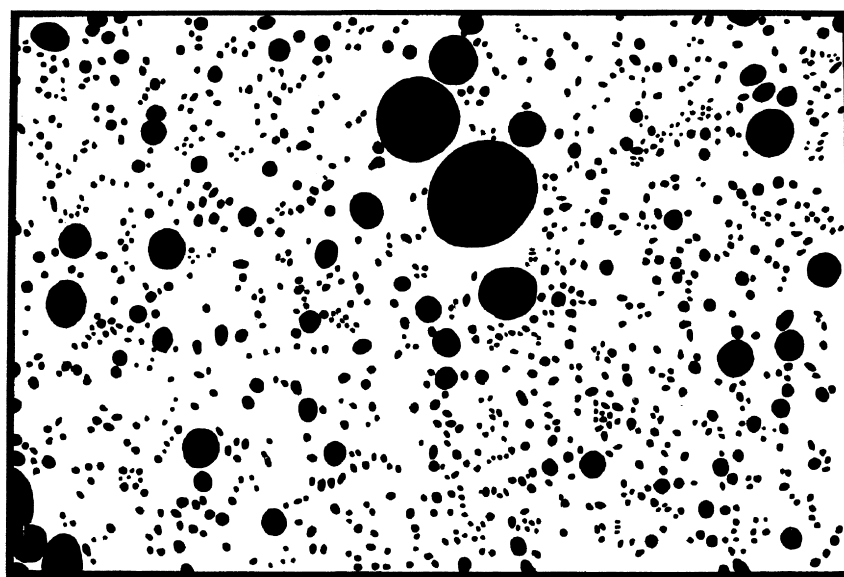
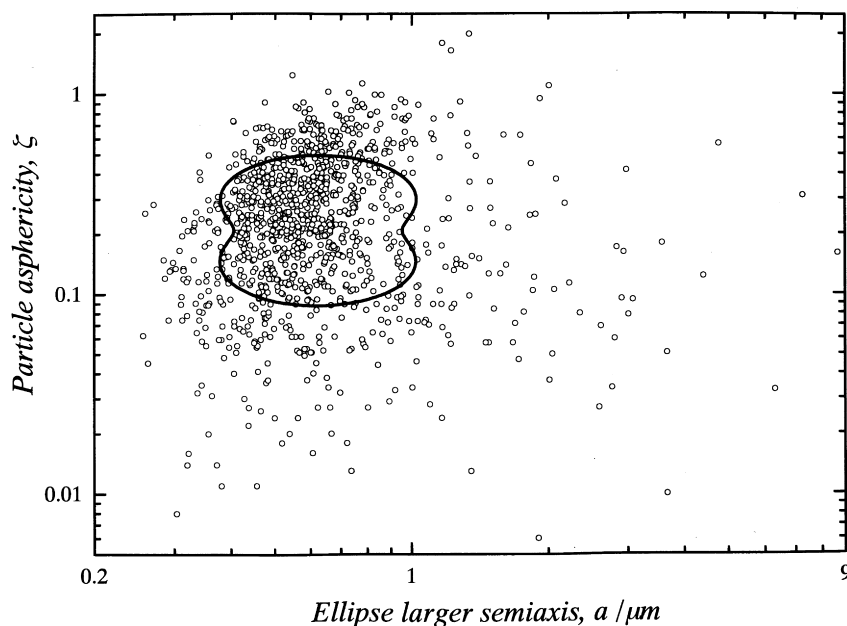


Fig. 5. TEM micrographs of PA/(PSU + PSU-PhAH) (= 80/20) blend after mixing at 260°C for 8 min. PSU-PhAH content: (a) 3 wt% and (b) 4 wt%.



(a)



(b)

Fig. 6. (a) Typical example of a binarized black-and-white SEM picture; two-step mixing of PA/(PSU + PSU-PhAH) = 80/(19 + 1) blend after mixing at 260°C for 8 min. The scale bar is for 10 μm . (b) Particle asphericity vs size plot obtained from (a) with the help of the DIA-MEE. The loop curve embraces the distribution core of 68% data points.

reduction processes between the graft copolymer- and block copolymer-forming systems.

In the previous study using 100% reactive PSU, we have found obvious differences in size reduction process and attainable particle size between the two reactive systems; 10 nm-level particles in PSU-PhAH (block copolymer-forming system) and sub- μm in PSU-MAH (graft copolymer-forming system) [18]. The block copolymers in situ-formed by the coupling reaction at the interface were

easily pulled out by shear forces to form micelles in PA matrix and eventually yielded 10 nm-level dispersion with narrow particle size distribution. By contrast, the in situ-formed graft copolymers appeared to be hardly pulled out; they stayed at the interface to play the role of an emulsifier. Such difference, pull-out or not, may be expected also in the present systems (with much lower amount of reactive PSU).

Fig. 5a is a TEM micrograph of PA/(PSU + PSU-PhAH) = 80/(17 + 3) blend after mixing for 8 min. In this

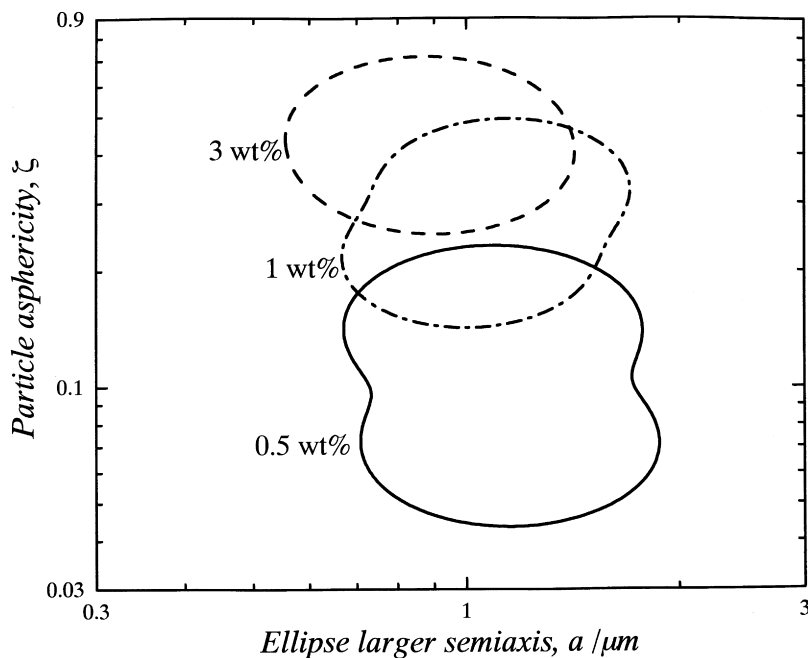


Fig. 7. Particle asphericity vs size correlation for the two-step mixing 80/20 PA/(PSU + PSU-MAH) blends after 8 min mixing. Numbers indicate content of PSU-MAH.

block copolymer-forming system, one sees clearly tiny domains of PSU (20–40 nm in diameter). The tiny domain may correspond to the micelles of in situ-formed PA-PSU block copolymers. When the higher amount of PSU-PhAH was loaded, the higher was the population of the tiny domains (Fig. 5b). Such tiny domains were never observed in the graft copolymer-forming (PSU-MAH) systems. Thus, the pull-out of in situ-formed copolymer took place also in the diluted block copolymer-forming systems, while it did not in the graft copolymer-forming systems. The presence of tiny domains should significantly affect the decrease in average particle size. The higher loading amount of PSU-PhAH leads to the higher population of tiny domains and then to the smaller average particle size (D_{scatt} in Fig. 4).

The results in Figs. 4 and 5 imply that the in situ-formed block copolymers are pulled out from the interface and the bigger particles (of more than sub- μm ; much bigger than the tiny domains) should be “naked” (not or less covered with the copolymers). The in situ-formed copolymers should stay at the interface for a while and help the size reduction; however, later they could be pulled out to render “naked” particles. If so, the naked particles of sub- μm to μm should have high interfacial tension so that they have a small asphericity ζ . Consequently, the asphericity–particle size (ζ – a) map of the block copolymer-forming system should be different from those of the non-reactive and graft copolymer-forming systems, as will be discussed below.

During melt mixing of immiscible polymers, in general, the dispersed particles are alternatively subjected to shear stress and left to relax (see Appendix). The larger the particle, the more it is deformed during shearing and the less it recovers to the spherical shape during “rest” time. The relaxation to the spherical shape is driven by the interfacial tension

(Γ) and hindered by the viscosity of the particle and the matrix (η_{d} , η_{m}). The relaxation time τ for the drop shape is given by

$$\tau \sim f(k) \frac{D\eta_{\text{m}}}{\Gamma} \quad (1)$$

where k is the viscosity ratio $k = \eta_{\text{d}}/\eta_{\text{m}}$, $f(k)$ a function of k , and D the particle diameter [31].

Interfacial effects dominate over bulk effects when the particle size is small enough, and vice versa. Then, once the blend is quenched, the shape relaxation process is virtually frozen, and all particles remain more or less aspherical. This leads to a correlation between particle size and asphericity, both parameters having a rather wide distribution. To study the effect of compatibilizer type, content, and way of mixing on the blend morphology, the ζ – a maps obtained for corresponding SEM pictures should be compared. Every picture has hundreds to more than a thousand particles on it (Fig. 6a), every particle yielding a point at the ζ – a map (see Fig. 6b that includes 1107 points). To make the trends in the map changes visible and tractable, we plotted a loop curve that embraced the distribution core. In essence, this curve is a 68% line for two-dimensional distribution.¹ Then, the 68% curves for the ζ – a maps may be easily compared.

¹ To obtain the above 68% line, we considered the ($\ln a$, $\ln \zeta$) distribution and found the distribution center. Then we plotted a straight line through the distribution center at a certain angle α and found the projections of all the points on this line. This yielded a one-dimensional distribution. The angle α was varied from 1 to 180° at 1° interval. The points corresponding to ± 1 standard deviations were kept for every angle α thus giving the above loop curve. Note that “ ± 1 standard deviations” mathematically correspond to “68%”.

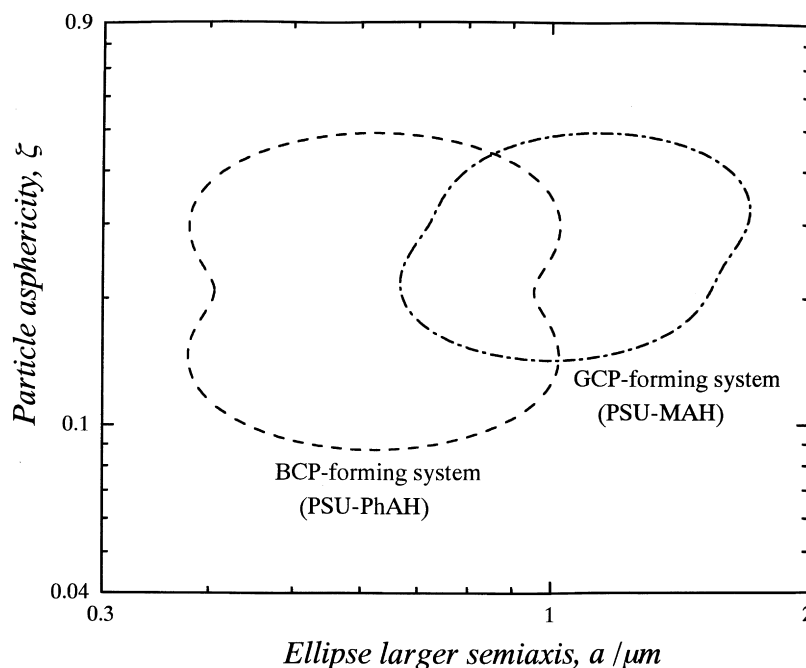


Fig. 8. Particle asphericity vs size in PA/(PSU + reactive PSU) = 80/(19 + 1) blends, comparing in situ-graft copolymer (GCP) forming and in situ-block copolymer (BCP) forming systems.

In a reactive system, the in situ-formed graft copolymer would reduce the interfacial tension [32] and lead to more aspherical shape of particles. Then the distribution core would be shifted upwards, compared with the non-reactive system. This has been shown to be actually realized in a PA/PSU-MAH system [21].

Such a trend is also expected for the present (diluted)

systems. The results of the DIA-MEE analysis of PSU-MAH systems are shown in Fig. 7. One sees that the larger amount of reactive component rendered somewhat finer and considerably more aspherical particles, as expected. Moreover, the ζ - a distribution becomes more narrow and uniform in line with increase in the PSU-MAH content.

In Fig. 8, the 68% lines for PSU-PhAH and PSU-MAH

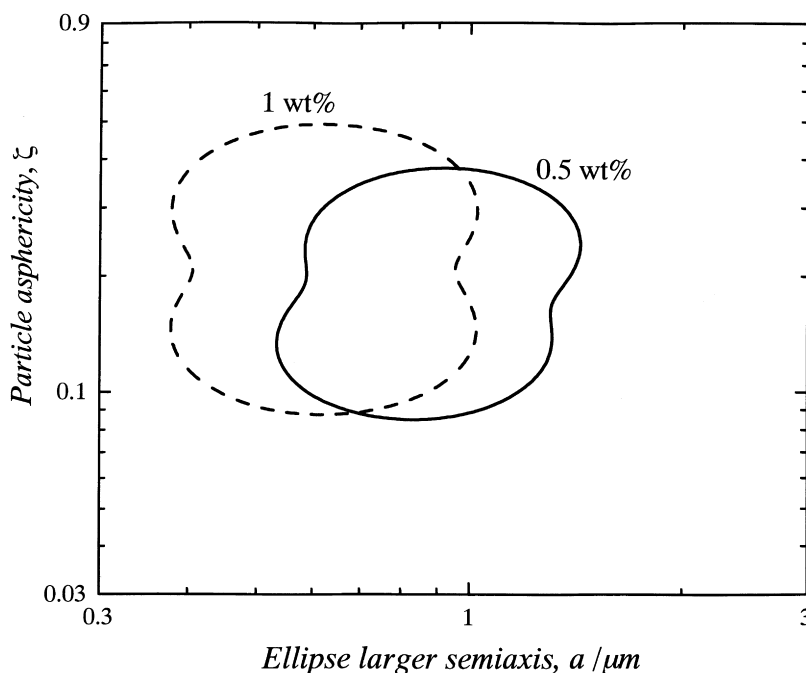


Fig. 9. Particle asphericity vs size for the two-step mixing of 80/20 PA/(PSU + PSU-PhAH) blends after 8 min mixing, showing a horizontal shift of the distribution core to the direction of smaller particle side as the loading amount of PSU-PhAH increases. Numbers indicate content of PSU-PhAH.

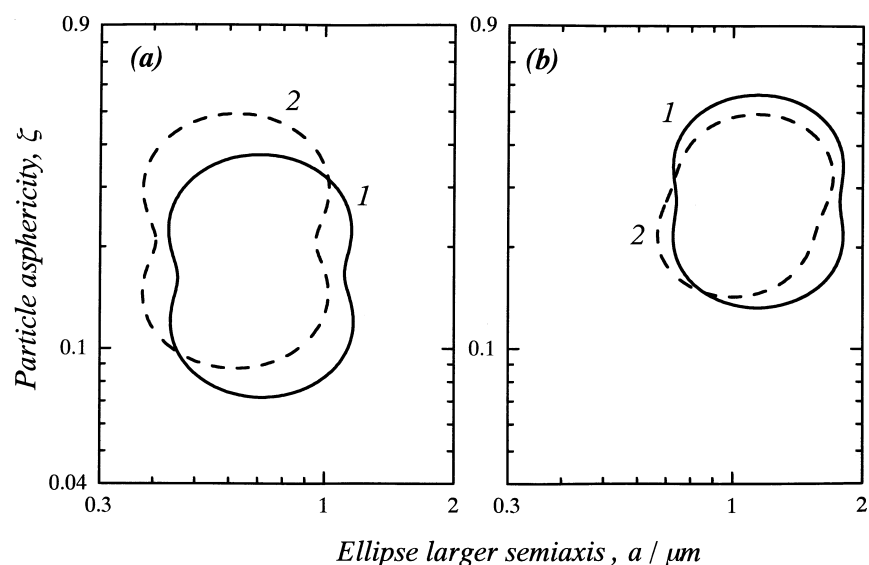


Fig. 10. Particle asphericity vs size of PA/(PSU + reactive PSU) = 80/(19 + 1) blends after mixing for 8 min; comparing the one-step mixing (1) and the two-step mixing (2): (a) PSU-PhAH and (b) PSU-MAH systems.

systems, containing the same amount of reactive component (1 wt%), are shown to compare the asphericity–particle size maps of the block copolymer- and graft copolymer-forming systems. The block copolymer-forming system has smaller particle size and wider distribution over ζ than the graft copolymer-forming system. Note that the map was created on the basis of SEM observation and then, in the block copolymer-forming systems, the tiny domains in Fig. 5 (by TEM) are missing. If such data points were added by TEM observation, the 68% line would move somewhat leftward. The difference in the ζ – a map between the block copolymer- and graft copolymer-forming systems may be interpreted by the “pull-out or not” of the in situ-formed copolymers, as has been discussed above. That is, the in situ-formed block copolymers will be pulled out from the interface to render the naked particles with high interfacial tension that could relax much faster to more spherical shape than the particles covered with the stable (non-pull out) graft copolymers.

In Fig. 9, the data for PSU-PhAH systems with different loading amounts of reactive component (0.5 and 1 wt%) are shown. By loading more PSU-PhAH, the distribution core shifts rather horizontally toward smaller particle dimensions. It may suggest that higher amount of in situ-formed copolymers yields more effective size reduction; however, the pull-out causes the presence of the naked particles with small asphericity.

As can be seen in Figs. 7 and 9, there is a difference in the effect of the loading amount of reactive component between the in situ graft copolymer- and block copolymer-forming systems. The map shifts rather vertically to higher asphericity and smaller particle as the loading amount of PSU-MAH increases, while it shifts rather horizontally to the smaller particle-side in the case of PSU-PhAH. Such a difference may be caused by “pull-out or not” as has been discussed.

All data discussed so far (Figs. 7–9) are for the two-step mixing. In Fig. 10, the data points for the one-step and two-step mixings after mixing for 8 min, containing the same amount of reactive component (1 wt%), are compared. It can be seen that there is no significant difference in the average particle size between blends prepared by the one-step and two-step mixings, as expected from the LS results (Fig. 3). However, one can see a slight difference in the location of the 68% line between the two-step and one-step mixings. The difference between the one-step and two-step mixings is bigger in the block copolymer-forming system (Fig. 10a) than in the graft copolymer-forming system (Fig. 10b). The 68% line of the in situ block copolymer-forming system appears at the higher ζ region in the blends by the one-step mixing than by the two-step mixing. The higher population of the high ζ particles may imply more uniform surface coverage of individual particles with the in situ-formed copolymers. The uniform coverage may be rarely achieved for the one-step mixing, compared with the two-step mixing. Because when the three components are put together in the one-step mixing, the reactive PSU chains will touch directly and react with the PA chains at an early stage of mixing to render a limited supply (and/or shortage) of reactive chains for non-reactive PSU particles in the later stages. Therefore, some non-reactive PSU particles may not be covered by the copolymer and these particles should have high interfacial tension and thus low ζ . Such an effect should appear clearer in the faster coupling reaction (PSU-PhAH) system than the slower reaction (PSU-MAH) system [18]. By contrast, in the two-step mixing, in which reactive PSU and non-reactive PSU are premixed, the individual particles may have rather equal probabilities to be covered with the in situ-formed copolymer.

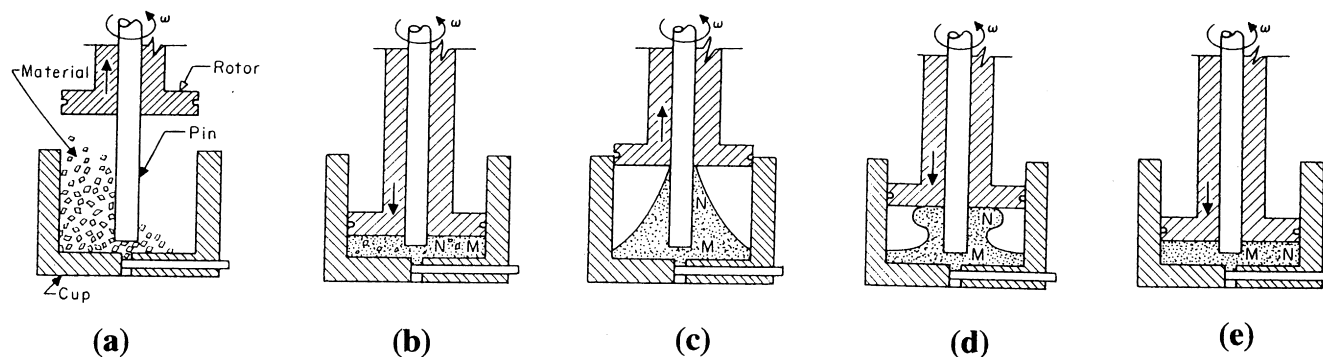


Fig. 11. Schematic representation of mixing mechanism in the one-gram scale mixer, Mini-Max molder.

4. Conclusion

Thus, the morphology of compatibilized polymer blends has been discussed in terms of particle size–asphericity map. The in situ-formed graft copolymer seems to stay at the interface and play the role of an emulsifier and thus leads to the finer and more aspherical particles, compared to the non-reactive system. Larger amount of PSU–MAH gave somewhat finer and essentially more aspherical particles. On the other hand, the in situ-formed block copolymer is more effective for the size reduction; however, it could be pulled out by shear forces from the interfacial region to form micelles in the matrix and then to render the “naked” particles with high interfacial tension. Consequently, the higher loading amount of PSU–PhAH leads to smaller average particle size but has little effect on particle shape. The difference between the one-step and two-step mixings is negligible for the in situ graft-copolymer forming systems. For the block copolymer-forming systems, the distribution slightly shifts to smaller and more elongated particles as we changed from the one-step to two-step mixing.

Acknowledgements

The authors gratefully acknowledge the German Government, BMBF for providing them a research fund (Project 03 N30283). We also thank to Tsuneo Chiba, TIT, for helping SEM experiments.

Appendix. Mixing mechanism in mini-max molder

During melt-mixing of immiscible polymers in extruder, for example, the polymer melt alternatively experiences high shear fields (at the narrow gap between the barrel surface and the top of screw flight) and low shear fields (especially at the bottom of screw channel). A similar situation is provided in our miniature mixer, mini-max molder [25]. As shown in Fig. 11, (a) materials are fed, (b) the rotor is lowered and the rotation is continued for a while (e.g. 15 s), (c) the rotor is raised for a short time (1 s), (d) the

rotor is lowered again, (e) the rotation is continued (15 s), and then the cycle (b)–(c) is repeated at an appropriate intervals (e.g. 6 s). During the rotation (b,e) the high shear rate is produced near the periphery of the rotor. It decreases to essentially zero at the center. When the rotor is raised (c), the melt climbs up the rotating pin as a result of the Weissenberg effect. When the rotor moves downwards, the position *N* is scraped off the pin and moved radially outwards from the axis of rotation (d). Consequently, the “back folding” process is accomplished, as shown by the moved position of *M* and *N* in Fig. 11e. Thus, an extensive and homogenous mixing is achieved by both the smearing out of the melt along circular paths (b,c) and by the “back folding” (c–e). In this mixing procedure, the polymer melt is alternatively thrust into both the high shear fields and the low shear fields.

References

- [1] Fayt R, Jerome R, Teyssie P. *Makromol Chem* 1986;187:837.
- [2] Favis BD, Willis JM. *J Polym Sci: Polym Phys* 1990;28:2259.
- [3] Okamoto M, Inoue T. *Polym Engng Sci* 1993;33:175.
- [4] Scott EC, Macosko CW. *Polymer* 1995;36:461.
- [5] Li H, Chiba T, Higashida N, Yang Y, Inoue T. *Polymer* 1997;38:3921.
- [6] Utracki LA. *Commercial polymer blends*. London: Chapman & Hall, 1998.
- [7] Leibler L. *Macromolecules* 1982;15:1283.
- [8] Noolandi J, Hong KM. *Macromolecules* 1982;15:482.
- [9] Leibler L. *Makromol Chem Macromol Symp* 1988;16:1.
- [10] Wu S. *Polym Engng Sci* 1987;27:335.
- [11] Anastasiadis SH, Gancarz I, Koberstein JT. *Macromolecules* 1989;22:1449.
- [12] Wagner M, Wolf BA. *Polymer* 1993;34:1460.
- [13] Liang H, Favis BD, Yu YS, Eisenberg A. *Macromolecules* 1999;32:1637.
- [14] Sundararaj U, Macosko CW. *Macromolecules* 1995;28:2647.
- [15] Sondergaard K, Lyngaae-Jorgensen J. *Polymer* 1996;37:509.
- [16] Beck Tan NC, Tai SK, Briber RM. *Polymer* 1996;37:3509.
- [17] Milner ST, Xi H. *J Rheol* 1996;40:663.
- [18] Charoensirisomboon P, Chiba T, Solomko SI, Inoue T, Weber M. *Polymer* 1999;40:6803.
- [19] Charoensirisomboon P, Inoue T, Weber M. *Polymer* 2000;41:4483.
- [20] Charoensirisomboon P, Inoue T, Weber M. *Polymer* 2000;41 (in press).

- [21] Sigalov GM, Ibuki J, Chiba T, Inoue T. *Macromolecules* 1997;30:7759.
- [22] EP 513 488, 30.03.1991, BASF AG.
- [23] WO 97/04018, 20.07.1996, BASF AG.
- [24] Weber M, Heckmann W. *Polym Bull* 1998;40:227.
- [25] Maxwell B. *SPE Journal* 1972;28:24.
- [26] Charoensirisomboon P, Saito H, Inoue T, Weber M, Koch E. *Macromolecules* 1998;31:4963.
- [27] Goizueta G, Chiba T, Inoue T. *Polymer* 1992;33:886.
- [28] Goizueta G, Chiba T, Inoue T. *Polymer* 1993;34:253.
- [29] Debye P, Bueche AM. *J Appl Phys* 1949;20:518.
- [30] Moritani M, Inoue T, Motegi M, Kawai H. *Macromolecules* 1970;3:433.
- [31] Scholz P, Froelich D, Muller R. *J Rheol* 1989;33:481.
- [32] Asthana H, Jayaraman K. *Macromolecules* 1999;32:3412.