Reactive compatibilization of nylon 6/styrene–acrylonitrile copolymer blends. Part 2. Dispersed phase particle size

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Abstract

The relation between the dispersed phase particle size and blend composition has been examined for blends of nylon 6 and styrene/acrylonitrile copolymer (SAN) over a wide range of compositions that traverse the phase inversion points for simple binary blends and those reactively compatibilized by the addition of imidized acrylic polymer (IA) or styrene/acrylonitrile/maleic anhydride terpolymer (SANMA). Nylon 6/SAN blends can be considered as a simpler version of industrially important polyamide (PA)/ABS blends; therefore, this study is useful for the better understanding of diminishing dispersed phase particles for PA/ABS blends with compatibilizers.

For uncompatibilized blends, the relationship between particle size and composition is symmetric about the phase inversion composition; whereas, blends compatibilized with IA show an intense asymmetric behavior, i.e. SAN dispersed particles in a nylon 6 matrix are quite small, while nylon 6 particles in a SAN matrix are much larger and are elongated. On the other hand, the blends compatibilized with SANMA show a weak asymmetry. This asymmetry is seen for three nylon 6 materials of differing molecular weight.

Possible causes for the asymmetric behavior have been considered. Concerning the conformation of graft polymer molecules at the interface, a crowding problem caused by the side chains of a graft polymer, when a nylon 6 phase disperses in a SAN matrix phase, may contribute to this asymmetric effect. The shift of the phase inversion composition to higher or lower nylon 6 volume fraction away from the 50/50 composition, may also directly contribute to the asymmetric trend, since generally the average domain size grows as the volume fraction of the minor phase increases due to the greater possibility of coalescence. Using Wu's equation, predicting the dispersed phase particle size, it is suggested that the viscosity increase of a nylon 6 phase due to the formation of graft polymers may affect the asymmetric behavior. However, the predicted asymmetry was less pronounced than the experimentally observed asymmetry. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Nylon 6; Styrene/acrylonitrile; Imidized acrylic polymer

1. Introduction

Part 1 of this series explored the effect of reactive compatibilization on the phase inversion behavior of nylon 6 blends with a styrene/acrylonitrile copolymer, SAN; studies on this simple blend system provide a basis for a better understanding of morphology development in commercially important but more complex blends of polyamides with ABS materials [1–7]. The ranges of compositions were co-continuous morphologies and where each component forms dispersed particles, with and without an imidized acrylic polymer (IA) or a styrene/acrylonitrile/maleic anhydride terpolymer (SANMA) compatibilizer.

The purpose of this paper is to explore the relationship between the dispersed phase particle size and the blend composition, especially near the phase inversion. To our knowledge, the relation between domain size and blend composition over a wider range of the compositions has not been reported for nylon 6/SAN blends; whereas, several studies have focused on compositions where the polyamide forms the matrix [8,9]. It is of particular interest to compare the effect of addition of the compatibilizers, IA or SANMA, on the morphology of nylon 6/SAN blends. The domain size of the blends without compatibilizers increases as the minor phase concentration increases, and the relation between domain size and composition shows a symmetric trend at the phase inversion composition. Near the point of phase inversion, however, it has been observed that the compatibilizers effectively diminish the size of SAN dispersed particles in a nylon 6 matrix; whereas, beyond the point of phase inversion the domains of nylon 6 form large particles in the

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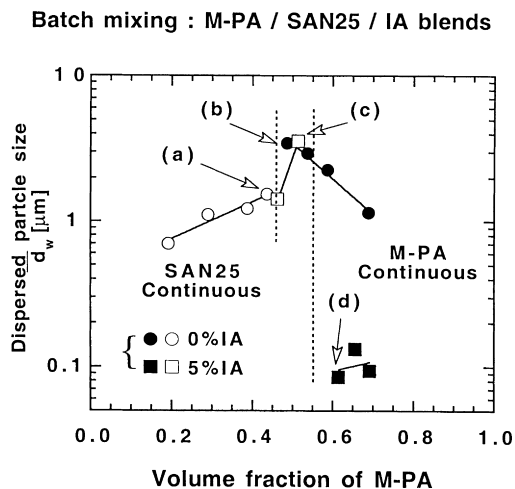
Batch mixing : M-PA / SAN25 / IA blends

Fig. 1. Effect of the addition of IA on the relation between the dispersed phase particle size of M-PA/SAN25 blends and the composition prepared in a Brabender batch mixer.

examines the effects of batch mixing versus extrusion and the acrylonitrile (AN) content of the SAN copolymer on domain size. All materials and experimental procedures were identical to those used in the first paper in this series [10].

2. Results

2.1. Domain size versus composition for nylon 6/SAN25/IA blends

Fig. 1 shows the relation between the weight average dispersed particle diameter, $\bar{d}_w$, and composition for M-PA/SAN25 blends including the effect of adding 5 wt% of imidized acrylic polymer, IA, as a compatibilizer. The dotted lines show the phase inversion composition for the compatibilized and uncompatibilized blends. The relation between $\bar{d}_w$ and composition for blends without IA (circular points) is almost symmetric about the phase inversion composition; whereas, blends compatibilized with IA (rectangular points) show a strongly asymmetric trend, i.e. SAN25 dispersed particles in the nylon 6 matrix are much smaller than the nylon 6 dispersed particles in the SAN25

SAN matrix and it seems that the compatibilizer is not as effective in reducing the domain size. That is, the relation between domain size and composition for the compatibilized blends shows an asymmetric trend. This work also
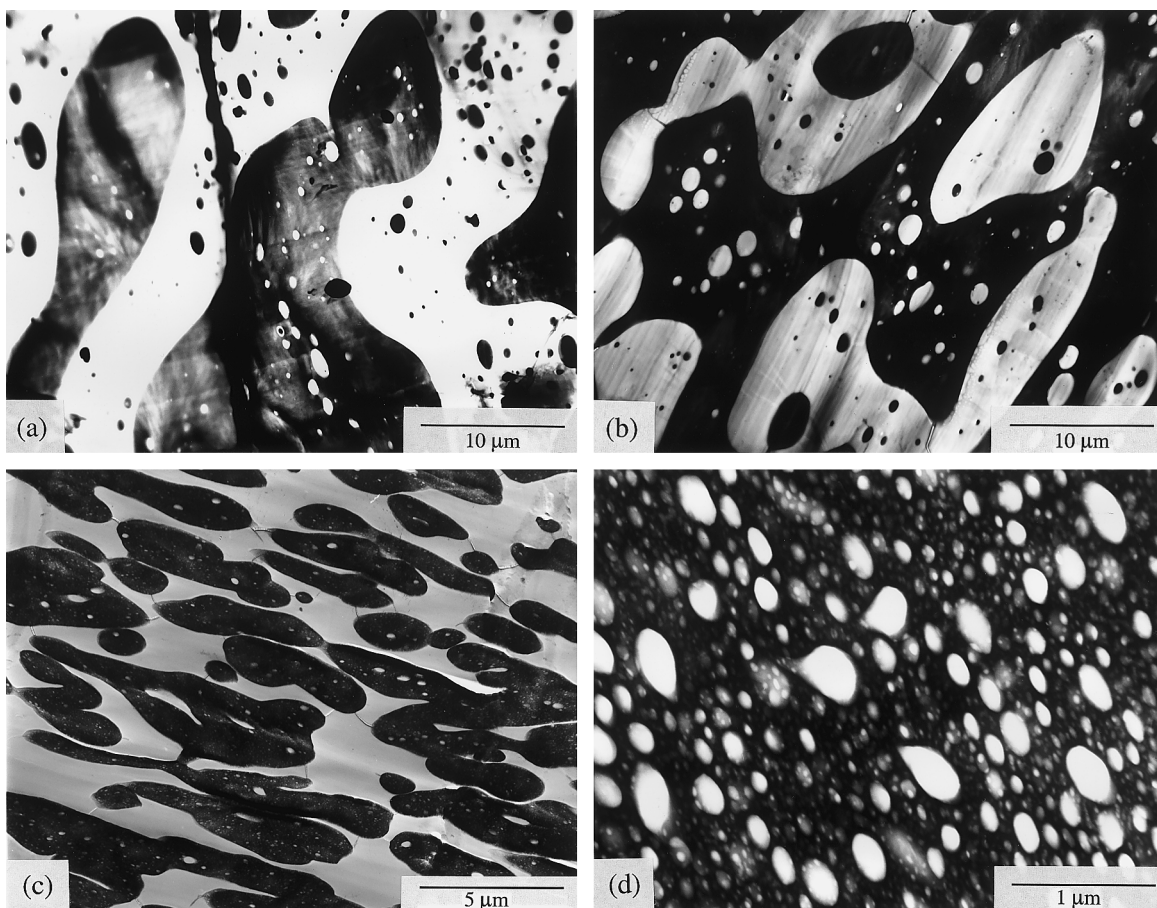

Fig. 2. TEM photomicrographs of binary M-PA/SAN25 blends: (a) 45/55, (b) 50/50, and ternary M-PA/SAN25/IA blends: (c) 52.5/42.5/5, (d) 62.5/32.5/5. The nylon 6 phase has been stained dark with phosphotungstic acid (PTA).

Cumulative distribution plots of blends of M-PA/SAN25 without IA (a&b) and with IA (c&d) : prepared in Brabender
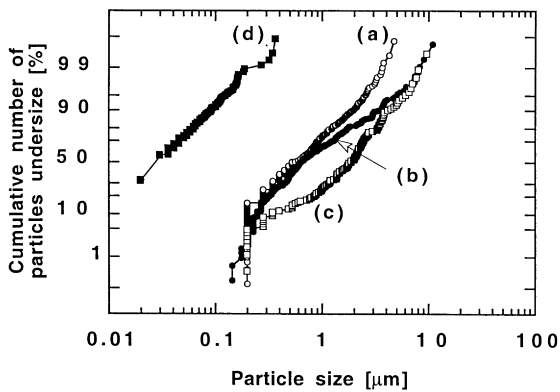

Fig. 3. Cumulative distribution plots of the dispersed phase particle size of binary M-PA/SAN25 blends: (a) 45/55, (b) 50/50, and ternary M-PA/SAN25/IA blends: (c) 52.5/42.5/5, (d) 62.5/32.5/5.

matrix. These trends are illustrated by a series of TEM photomicrographs (Fig. 2) and the cumulative size distribution shown on the fraction of the dispersed particles that are below a certain size, i.e. undersize (Fig. 3). The letters in parenthesis in Fig. 1 correspond to those in Figs. 2 and 3. Fig. 2a and b shows for the uncompatibilized blends that the morphology in (a) is similar to that in (b) with regard to the domain size and the shape; however, the role of the continuous phase is reversed, i.e. the SAN25 is continuous in (a), while the nylon 6 is continuous in (b). Fig. 2c and d shows for the IA compatibilized blends that the morphology in (c) is significantly different from that in (d). The large elongated nylon 6 domains in the SAN25 matrix are seen (c); whereas, the SAN25 dispersed phase forms uniformly diminished particles in the nylon 6 matrix (d). Fig. 3 shows that the particles of uncompatibilized blends (a) and (b) have a similar size distribution regardless of

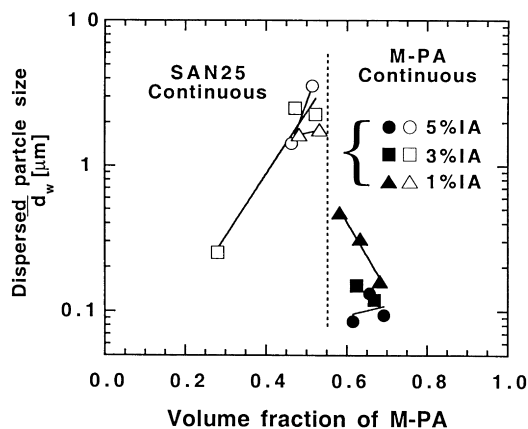**Batch mixing : M-PA / SAN25 / IA blends**

Fig. 4. Effect of IA content on the relation between the dispersed phase particle size of ternary M-PA/SAN25/IA blends prepared in a Brabender batch mixer.

which material forms the dispersed phase; whereas, for blends compatibilized with IA, SAN25 particles in a nylon 6 matrix (d) have a much smaller size range compared to nylon 6 particles in a SAN25 matrix (c).

Fig. 4 shows this asymmetric trend for a broader range of IA contents. The higher the IA content, the greater the asymmetry. The asymmetry has been examined as a function of the polyamide molecular weight and the trends are similar for all three polyamides. Fig. 5 shows diagrams for blends based on L-PA (Fig. 5a) and H-PA (Fig. 5b). In all cases, IA effectively diminishes the size of SAN25 particles dispersed in a nylon 6 matrix; whereas, IA is not effective in reducing the nylon 6 domain size in a SAN25 matrix, especially near the phase inversion composition.

2.2. Effect of compatibilizer type

Fig. 6 shows corresponding results for M-PA/SAN25/SANMA blends. The data show that the degree of asymmetry is less for blends compatibilized with SANMA compared to those compatibilized with IA; however, the asymmetry still exists. It is important to note that the SANMA terpolymer contains 33 wt% of AN; whereas, SAN25 contains 25 wt% AN. According to the literature, SAN materials are generally immiscible with one another when their AN contents differ by more than about 5 wt% [11,12]; thus, this SANMA is not expected to be fully miscible with SAN25. On the other hand, prior work has established that IA is fully miscible with SAN25 [8]. A question arises as to whether the miscibility between the SAN phase and the compatibilizer may affect the relation between dispersed particle size and composition. This issue is addressed here by using an SAN material that contains 32.5 wt% of AN, see Table 1 in Part 1 [10], which should be miscible with the SANMA compatibilizer. Table 1 summarizes the miscibility of the two compatibilizers with two SAN materials used in this work, see Table 1 in Part 1 [10]. The pairs of SAN25/IA, and SAN32.5/SANMA are considered as miscible. The miscibility of SAN32.5 with IA was examined here. A 50/50 blend of SAN32.5/IA was prepared in the Brabender batch mixer, at 240°C for 10 min at 60 rpm; a small sample was quenched into liquid nitrogen, and optically observed. From the opaque appearance of the sample, it was judged that SAN32.5 and IA blend are immiscible.

In Figs. 7 and 8, the relation between the average size of the dispersed particles and composition for nylon 6 blends with SAN32.5, instead of SAN25, is shown. In these blends, the IA compatibilizer is immiscible with the SAN phase, while SANMA now miscible with the SAN phase. Comparison of the results with SAN32.5 with those for SAN25 gives a definitive test of compatibilizer miscibility with SAN. Figs. 7 and 8 show the dispersed phase particle size for M-PA/SAN32.5 blends compatibilized with IA and SANMA, respectively. Without compatibilization, M-PA/SAN32.5 blends show a symmetric trend similar to M-PA/

Batch mixing : L-PA / SAN25 / IA blends

(a)

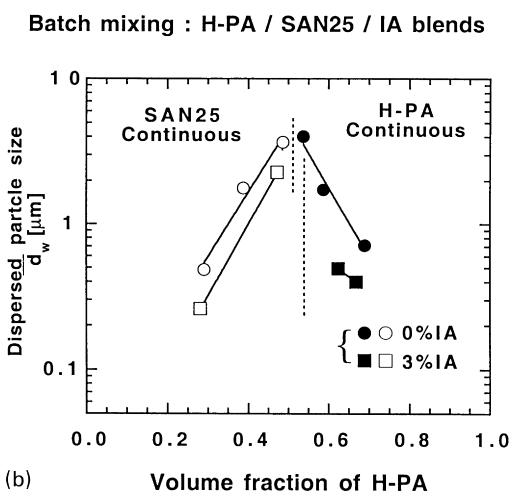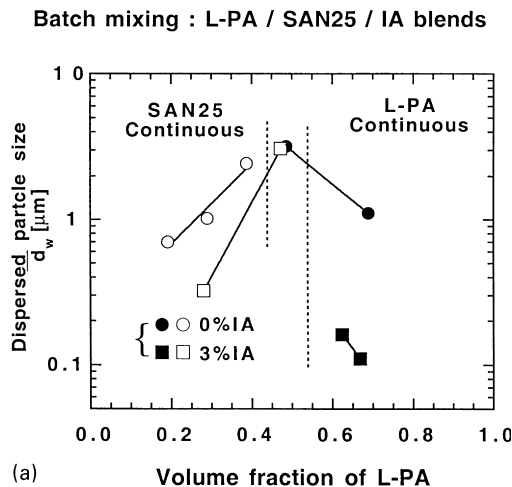**Batch mixing : H-PA / SAN25 / IA blends**

(b)

Fig. 5. Effect of nylon 6 molecular weight on the relation between the dispersed phase particle size of blends compatibilized with and without IA. Nylon 6 has low molecular weight (L-PA) in part (a) and high molecular weight (H-PA) in part (b).

Table 1
Miscibility of materials

SAN material	Campatibilizer	Miscibility
SAN25	IA	Miscible[a]
SAN32.5	SANMA	Immiscible[b]
SAN32.5	IA	Immiscible
SAN32.5	SANMA	Miscible

[a] See Ref. [8].
[b] Based on information in Refs. [11,12] and assuming the small amount of maleic anhydride in SANMA does not significantly alter the miscibility between SAN copolymers of different AN contents.

SAN25 blends. The AN content of the SAN copolymer does not seem to be a key factor affecting the asymmetric trend. The blends compatibilized with IA show an intense asymmetry; whereas, the blends compatibilized with SANMA show a more symmetric trend. It is interesting to see that IA effectively diminishes the size of SAN32.5 particles dispersed in the nylon 6 matrix although IA is not fully miscible with SAN32.5; likewise, SANMA diminishes the size of SAN25 particles dispersed in the nylon 6 matrix.

To quantify the asymmetry effect, an "asymmetry index", may be defined as

$$\text{asymmetry index} = (\bar{d}_{\mathrm{w}})_{\mathrm{PA}}/(\bar{d}_{\mathrm{w}})_{\mathrm{SAN}} \qquad (1)$$

where $(\bar{d}_{\mathrm{w}})_{\mathrm{PA}}$ and $(\bar{d}_{\mathrm{w}})_{\mathrm{SAN}}$ are the average nylon 6 and SAN dispersed particle sizes for the blends whose compositions are just on either side of the phase inversion point. Since the asymmetry index represents the ratio of nylon 6 dispersed particle size to SAN dispersed particle size, its value grows as the difference in particle sizes increases. Table 2 summarizes the asymmetry index, obtained experimentally, for all combinations of the components studied here. The two uncompatibilized blends and the M-PA/SAN32.5 blend compatibilized with SANMA show the fairly symmetric
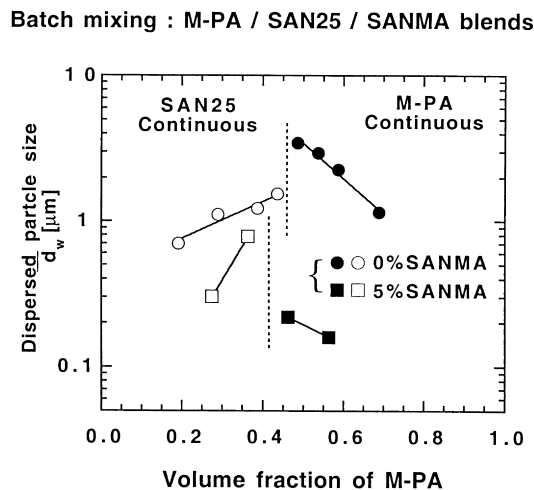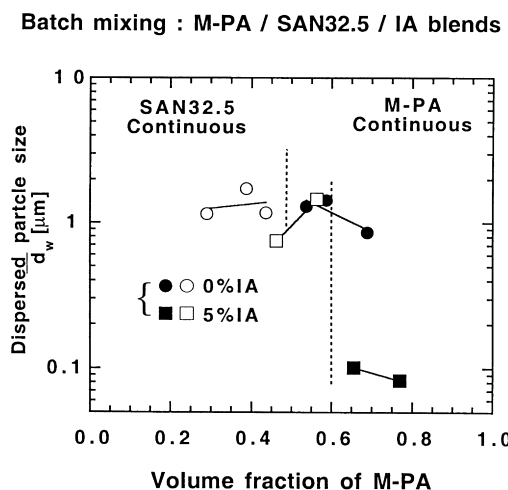
Batch mixing : M-PA / SAN25 / SANMA blends

Fig. 6. Effect of the addition of SANMA on the relation between the dispersed phase particle size of M-PA/SAN25 blends and the composition prepared in a Brabender batch mixer.

Batch mixing : M-PA / SAN32.5 / IA blends

Fig. 7. Effect of the addition of IA on the relation between the dispersed phase particle size of M-PA/SAN32.5 blends and the composition prepared in a Brabender batch mixer.
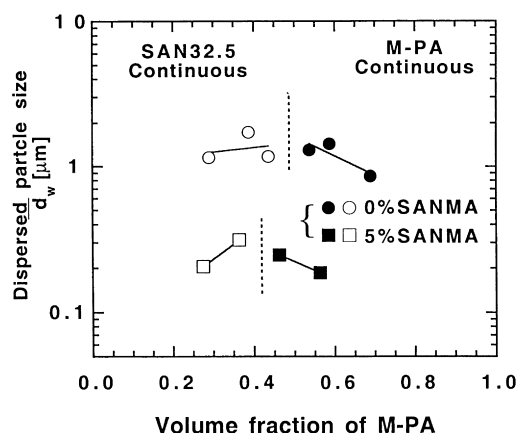
Batch mixing : M-PA / SAN32.5 / SANMA blends

Fig. 8. Effect of the addition of SANMA on the relation between the dispersed phase particle size of M-PA/SAN32.5 blends and the composition prepared in a Brabender batch mixer.

behavior; whereas, blends compatibilized with IA and the M-PA/SAN25 blend compatibilized with SANMA show significant asymmetric behavior. Blends compatibilized with IA show an intense asymmetry regardless of the miscibility between the SAN and IA; thus, miscibility between SAN and compatibilizer does not seem to be a factor. Based on analysis of the data, there is no consistent effect of miscibility on the size distribution or shape of the dispersed phase particles.

2.3. Effect of mixing method

To examine the effect of blend preparation method on the relation between the dispersed particle size and composition, the blends with and without the IA compatibilizer were prepared in a single screw extruder outfitted with an intensive mixing head for a comparison with those prepared in the Brabender batch mixer. The particle size was measured at the center of the extrudate parallel to the flow direction. Results for M-PA/SAN25 blends are shown in Fig. 9. The dispersion of nylon 6 in the SAN25 matrix is quite effective for the compatibilized blends prepared in the extruder, and no asymmetric behavior is seen; this is in strong contrast to results for blends prepared in the Brabender batch mixer. Thus, the blend preparation method significantly affects the relation between the dispersed particle size and composition.

3. Discussion

Possible causes for the asymmetric behavior described above have been considered; however, to date, no single clear-cut reason for this effect has emerged. Thus, the purpose of the following discussion is to propose three factors that together may contribute to this effect. No doubt, other factors may be operative.

Fig. 10 schematically illustrates the idealized structure of the domains in a nylon 6 matrix or an SAN matrix after reactive compatibilization. It shows the graft copolymer, comprised of long nylon 6 side chains attached at a number of points along the IA or SANMA backbone, located at the interface. For blends with a nylon 6 matrix, the side chains of the graft copolymer face toward and expand into the nylon 6 matrix. In these circumstances, there is no crowding problem at the interface. On the other hand, for blend formed with a SAN matrix, the side chains of the graft copolymer are more crowded as they try to extend into the nylon 6 domain phase. From the comparison of these two cases, it is clear that the formation of small SAN domains in a nylon 6 matrix is more favorable in terms of these conformational issues than the reverse case.

Table 2
Asymmetry index obtained from the experiments

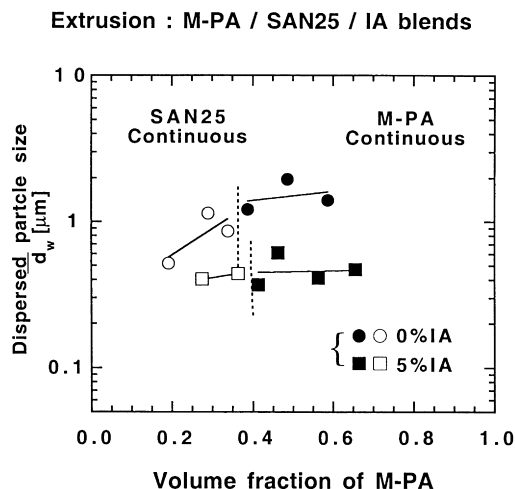| Composition	$\bar{d}_{PA}$ in SAN matrix (μm)	$\bar{d}_{SAN}$ in M-PA matrix (μm)	$\bar{d}_{PA}/\bar{d}_{SAN}$
M-PA/SAN25			
45/55	1.5	–	0.43
50/50	–	3.5	
M-PA/SAN25/IA			
52.5/42.5/5	3.6	–	40
62.5/32.5/5	–	0.09	
M-PA/SAN25/SANMA			
37.5/57.5/5	0.78	–	3.5
47.5/47.5/5	–	0.22	
M-PA/SAN32.5			
45/55	1.2	–	0.92
55/45	–	1.3	
M-PA/SAN32.5/IA			
57.5/37.5/5	1.5	–	15
66.5/28.5/5	–	0.10	
M-PA/SAN32.5/SANMA			
37.5/57.5/5	0.31	–	1.2
47.5/47.5/5	–	0.25	

Extrusion : M-PA / SAN25 / IA blends

Fig. 9. Effect of the addition of IA on the relation between the dispersed phase particle size of M-PA/SAN25 blends and the composition prepared in a single screw extruder.

Phase inversion of M-PA / SAN32.5 blends : Batch mixing

Fig. 11. Shift of the phase inversion composition for M-PA blends with SAN32.5 compatibilized with IA or SANMA prepared in a Brabender batch mixer.

As shown in Fig. 11, the addition of IA to nylon 6/SAN blends causes a shift of the phase inversion composition to a higher nylon 6 volume fraction; whereas, the addition of SANMA slightly lowers the nylon 6 volume fraction where the phase inversion occurs. Similar effects were observed for blends of other nylon 6 and SAN materials. The dotted lines show the phase inversion points. Because of the shifts, the addition of IA extends the composition range of the SAN matrix phase; whereas the addition of SANMA slightly extends the composition range of the nylon 6 matrix phase. Concerning the structure of the graft polymer shown in Fig. 10, the formation of the nylon 6 matrix is more preferable to avoid the crowding problem than that of SAN matrix. Therefore, the shift of the phase inversion composition to the higher nylon 6 volume fraction, which is in the case of the addition of IA, has a negative effect for the compatibilization using IA. As illustrated in Fig. 12, the shift of the phase inversion composition to higher or lower nylon 6 volume fraction away from the 50/50 composition, may contribute to the asymmetric trend, since generally the average domain size grows as the volume fraction of the minor phase increases due to the greater possibility of coalescence [13–19]. Ignoring differences in viscosity between phases, the simple
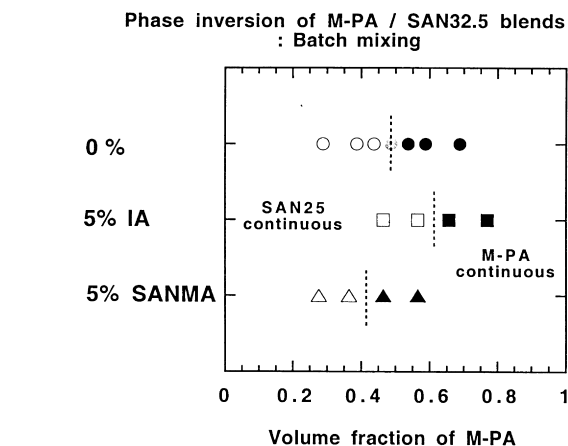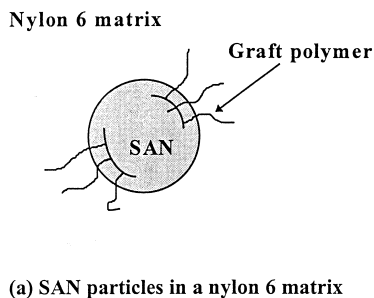
arguments about the rates of coalescence suggest that the dispersed phase particle size should be symmetric about the 50/50 composition as illustrated in Fig. 12 by the line labeled uncompatibilized. Addition of compatibilizer is expected to lower the particle size [12,13,18–34] owing to increased rates of droplet break-up (lower interfacial tension) and a reduced rate of coalescence [18,22]. Ideally the two branches of the curves of particle size versus composition should be symmetrical about 50/50 composition. However, a shift in the phase inversion composition to a higher fraction of nylon 6, as in the case of IA, could then naturally lend to the type of asymmetry observed as suggested by the two lower solid lines in Fig. 12. A shift to lower nylon 6 composition, as in the case of SANMA, would have the opposite effect. These predictions are consistent with the experimental observation. For IA compatibilized blends prepared in an extruder, phase inversion occurs closer to a nylon 6 volume fraction of 0.5 [10], and no asymmetric behavior was observed. This is consistent with the prediction of Fig. 12.

Wu [35] proposed the following equation to predict the particle size for polyamide and polyester blends containing 15% ethylene–propylene rubber as a dispersed phase. The positive exponent is for $\eta_r > 1$, while the negative exponent

Nylon 6 matrix

SAN matrix

(a) SAN particles in a nylon 6 matrix
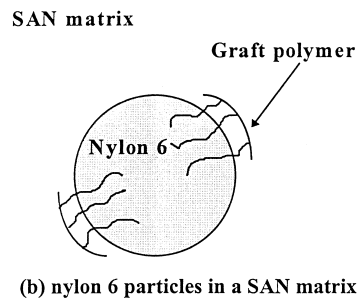
(b) nylon 6 particles in a SAN matrix

Fig. 10. Schematic illustration of the conformation of the graft polymers at the interface between nylon 6 and SAN phase. (a) when nylon 6 forms a matrix, (b) when SAN forms the matrix.
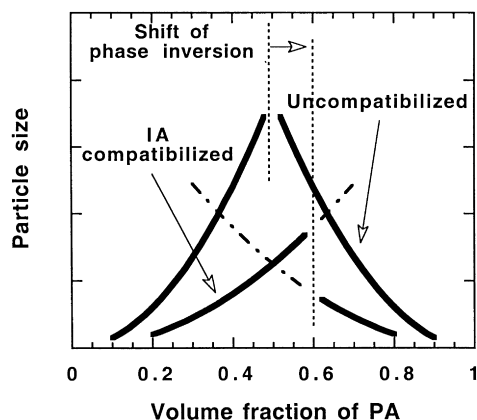
Fig. 12. Schematic illustration of how a shift in the phase inversion point can lead to asymmetric relation between particle size and composition.

is for $\eta_r < 1$.

$$\bar{d} = 4\gamma \eta_r^{\pm 0.84}/G\eta_m \qquad (2)$$

where $\bar{d}$ is the diameter of the droplet, G the shear rate, γ the interfacial tension, and η_r the viscosity ratio $= \eta_d/\eta_m$ (η_d is the dispersed phase viscosity and η_m is the matrix phase viscosity). In the previous paper [10], we discussed the increase of the nylon 6 phase viscosity due to the formation of the graft polymers [19,36,37]. Since Eq. (2) gives a qualitative relationship between dispersed phase particle size and the viscosity of the components, the increase of the nylon 6 phase viscosity caused by the grafting reaction can be accounted for in predicting domain size. As an example of the prediction using Eq. (2), the predicted particle sizes were evaluated for the nylon 6 blends with SAN25, and the asymmetry index was subsequently calculated. The results are summarized in Table 3. The increase of the nylon 6 phase viscosity was estimated in accordance with the ratio of IA to nylon 6 in the blend. The detailed information on how to evaluate the increase of the nylon 6 phase viscosity due to the formation of the graft polymer is elsewhere [10]. The asymmetry index of the uncompatibilized blend is 0.91, which represents that near the phase inversion point, the dispersed SAN particles in the nylon 6 matrix is similar to the dispersed nylon 6 particles in the SAN matrix. On the other hand, for blends compatibilized with IA or SANMA, the asymmetry index is 1.5–1.8, which indicates that the dispersed nylon 6 particles in the SAN matrix are larger than the dispersed SAN particles in nylon 6 matrix.

Accordingly Eq. (2) suggests the generation of the asymmetric trend for the compatibilized blends; however, the degree of the asymmetry evaluated using Eq. (2) is much smaller than the experimentally observed asymmetry (see Table 2).

4. Conclusion

The relation between the dispersed particle size and blend composition has been examined for blends of nylon 6 and SAN materials over a wide range of compositions that traverse the phase inversion points for simple binary blends and those reactively compatibilized by the addition of IA or SANMA.

For uncompatibilized blends, the relationship between particle size and composition is symmetric about the phase inversion composition. However, blends compatibilized with IA show an intense asymmetric behavior, i.e. SAN dispersed particles in a nylon 6 matrix are quite small, while nylon 6 particles in a SAN matrix are much larger and are elongated. On the other hand, the blends compatibilized with SANMA show a weak asymmetry. This asymmetry is seen for three nylon 6 materials of differing molecular weight. Possible causes for the asymmetric behavior have been considered.

Concerning the structure of graft polymer formation, the side chains of the graft copolymer face toward and expand into the nylon 6 matrix for blends with a nylon 6 matrix. In these circumstances, there is no crowding problem at the interface. On the other hand, for blend formed with a SAN matrix, the side chains of the graft copolymer are more crowded as they try to extend into the nylon 6 domain phase. From the comparison of these two cases, it is clear that the formation of SAN domains in a nylon 6 matrix is easier in terms of these conformational issues than that of nylon 6 domains in a SAN matrix. However, the addition of IA to nylon 6/SAN blends causes the phase inversion composition to shift to a higher nylon 6 volume fraction; whereas, the addition of SANMA slightly lowers the nylon 6 volume fraction where the phase inversion occurs. Because of these shifts, addition of IA extends the composition range where a nylon 6 dispersion, containing intrinsic crowding problem, occurs in a SAN matrix; whereas, the addition of SANMA extends the composition range where a SAN dispersion, containing less crowding problem, forms in a nylon 6 matrix. The shift of the phase inversion

Table 3
Predicted particle sizes using Wu's equation (η_d and η_m are estimated from Brabender torque values (N m) from Ref. [10])

Composition	SAN continuous phase			Nylon 6 continuous phase			$\bar{d}_{PA}/\bar{d}_{SAN}$
	η_d	η_m	$\eta_r^{\pm 0.84}/\eta_m$	η_d	η_m	$\eta_r^{\pm 0.84}/\eta_m$	
M-PA/SAN25	6.0	6.6	0.16	6.6	6.0	0.18	0.91
M-PA/SAN25/IA	12	6.6	0.25	6.6	11	0.14	1.8
M-PA/SAN25/SANMA	10	6.6	0.22	6.6	9.0	0.14	1.5

composition, to higher or lower nylon 6 volume fraction away from the 50/50 composition, may also directly contribute to the asymmetric trend, since generally the average domain size grows as the volume fraction of the minor phase increases due to the greater possibility of coalescence. Using Wu's equation, predicting the dispersed phase particle size, it is suggested that the viscosity increase of a nylon 6 phase due to the formation of graft polymers may affect the asymmetric behavior. However, the predicted asymmetry was less pronounced than the experimentally observed asymmetry.

Acknowledgements

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