

Morphological Changes in Nylon-6/Acrylonitrile–Butadiene–Styrene Reactive Blend

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ABSTRACT: The morphological changes of blends of nylon-6 and acrylonitrile–butadiene–styrene (ABS) with reactive compatibilizer [poly(*N*-phenylmaleimide–styrene–maleic anhydride)] as a function of viscosity ratio of the components, concentration of compatibilizer, and the feed rate have been studied using an intermeshing corotating twin screw extruder. The occurrence of reaction between the amine end group of nylon-6 and maleic anhydride of compatibilizer during melt blending was identified by the solvent extraction and infrared spectroscopy study. It was found that the minimum dispersed phase size occurred at the viscosity ratio (p) = 0.75. Dispersed phase size was decreased significantly by the addition of compatibilizer and tended to equilibrate at about 15 wt % compatibilizer based on the amount of nylon-6. It was observed that the morphology was strongly dependent on the feed rate. The presence of maximum dispersed phase size was observed as a function of feed rate. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 1595–1604, 1997

Key words: morphology; nylon-6/acrylonitrile–butadiene–styrene blend; reactive blend; viscosity ratio; feed rate

INTRODUCTION

In recent years, the development of technology for the blending of established polymer systems has been increased because of the high cost associated with the development of new synthetic polymers. Many blends of interest require compatibilization to obtain a desired property, and it has been suggested that compatibilization can be achieved by the addition of a third component, so-called compatibilizer. The classical compatibilizer is a nonreactive block copolymer: one block of which is identical to or miscible with one blend component; the other block of which is identical or miscible with the other blend component. An attractive alterna-

tive is to form the block or graft copolymer *in situ* during blend via interfacial reaction of added functionalized component and its so-called reactive polymer blend. This copolymer reduces the interfacial tension between two phases, provides for better dispersion, and promotes adhesion between the phases. To achieve reactive polymer blend, the functional group is introduced to one of components or the functionalized compatibilizer is used as a third component. This approach has already been implemented in a number of commercial products. One of these products is a nylon-6/acrylonitrile–butadiene–styrene (ABS) blend. An attractive feature of the nylon-6 for reactive coupling to other polymers is its inherent chemical functionality through the amine end groups. It has been well known that amine end groups on the nylon-6 readily react with anhydride groups.^{1–3}

Levedev et al.⁴ studied temperature and con-

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centration dependences of the dynamic mechanical properties of simple mechanical blends of nylon-6 and ABS. In their study, they did not use modified ABS, but rather commercial ABS. Recently, Lavengood and Silver⁵ and Aoki and Watanabe⁶ investigated the structures and properties of nylon-6/ABS blend using maleic-anhydride (MA)-modified ABS. They mainly studied the effects of nylon-6/ABS composition on the morphology, physical properties, and rheology. Howe and Wolkowicz⁷ studied the structures and physical properties for four nylon-6/ABS blends near the midpoint of the compositions. They found three different kinds of compatibilization structures, such as stratified, droplet/ribbon, and cellular. Styrene/maleic anhydride copolymer (SMA) was also used as a reactive compatibilizer for the nylon-6/ABS blend.^{2,8}

Many attempts have been done to investigate the interrelationship between the material, the processing, the morphology, and the properties of the polymer blends.^{9–15} Material parameters that determine the morphology include the viscosity ratios of the components, interfacial tension, composition, and the elasticities of the components. Processing parameters include shear rate, shear stress, feed rate, time of mixing, and speed of screw rotation. Even though the viscosity ratios^{10–12} and feed rate^{13–15} are important to determine the final morphology of polymer blends, little work has been reported for reactive polymer blends. A goal of this work is to investigate the effect of viscosity ratio, feed rate, and concentration of compatibilizer on the morphology in reactive polymer blend using nylon-6/ABS blend with a reactive compatibilizer.

EXPERIMENTAL

Materials

Table I summarized the sources and some pertinent characteristic information about the materials used in this study. ABS consisted of 80 wt % of matrix poly(acrylonitrile styrene) (SAN) and 20 wt % SAN grafted butadiene rubber (*g*-ABS) (45% butadiene rubber and 55% grafted SAN). Three different molecular weight (MW) matrix SAN were used, and those were designated as SAN-L, SAN-M, and SAN-H with increasing MW. Acrylonitrile content was within the range of 24–28.5%. Compatibilizer used [poly(*N*-phenylmaleimide–styrene–maleic anhydride)] was a

commercially available polymer having reactive maleic anhydride group in the main chain. Antioxidant (Ciba-Geigy, Irgafos 168) was used to prevent degradation of materials during reactive blending.

Blending

Nylon-6, SAN, *g*-ABS, compatibilizer, and antioxidant were mixed together for 10 min using a tumbler mixer, and those were fed into extruder using loss-in-weight feeder. Corotating intermeshing twin screw extruder (Berstorff, diameter = 40 mm and L/D = 32) was used for reactive melt blending. Barrel temperature profile was 30/220/250/240/250°C, and screw speed was 300 rpm. Feed rate was varied within the range of 30–60 kg/h. 5–20 wt % compatibilizer based on the amount of nylon-6 was added. Nylon-6 was vacuum dried at 80°C for 24 h to prevent the hydrolytic degradation during blending.

Rheological Analysis

Capillary viscometer (Rosand, diameter = 1 mm and L/D = 16) was used to measure the viscosity of nylon-6s and ABSs. The viscosity curves of nylon-6s and ABSs at 250°C were presented in Figure 1. All measurements were carried out under a dry nitrogen atmosphere, and 0.3 wt % of antioxidant was added to avoid degradation during measurements.

Electron Microscopy and Image Analysis

Pellets from the extrusion were used as samples to examine the morphology of blends. A scanning electron microscopy (Stereoscan 40, Leica Cambridge) was used to examine the size and shape of the dispersed phase. Samples were immersed in formic acid for 10 min to extract the nylon-6, and it was vacuum-dried for 24 h at room temperature, followed by gold coating. Transverse section to machine direction was observed. Both the number-average diameter (d_n) and volume-average diameter (d_v) of dispersed phase were estimated using an image analyzer (Jenaval, Carl Zeiss). More than 120 dispersed phase particles were measured in order to obtain a correct distribution.

Table I Materials Used in This Study

Designation	Material	Molecular Weight and Composition ^a	Source
Nylon-L	Nylon-6	—	Kolon Inc.
Nylon-H	Nylon-6	—	Kolon Inc.
SAN-L	Styrene–acrylonitrile copolymer	$M_n = 53,000$ $M_w = 96,000$ 24% AN	Cheil Inc.
SAN-M	Styrene–acrylonitrile copolymer	$M_n = 56,000$ $M_w = 114,000$ 28.5% AN	Cheil Inc.
SAN-H	Styrene–acrylonitrile copolymer	$M_n = 91,000$ $M_w = 170,000$ 27% AN	Cheil Inc.
RC	<i>N</i> -Phenylmaleimide–styrene–maleic anhydride copolymer	51 wt % imide 46 wt % styrene 3 wt % maleic anhydride	Nippon Denki Kagaku Kogyo

^a From sources.

RESULTS AND DISCUSSION

Identification of Reaction

The solvent extraction of pellets of uncompatibilized and compatibilized nylon-6/ABS blend is carried out to identify the occurrence of reaction

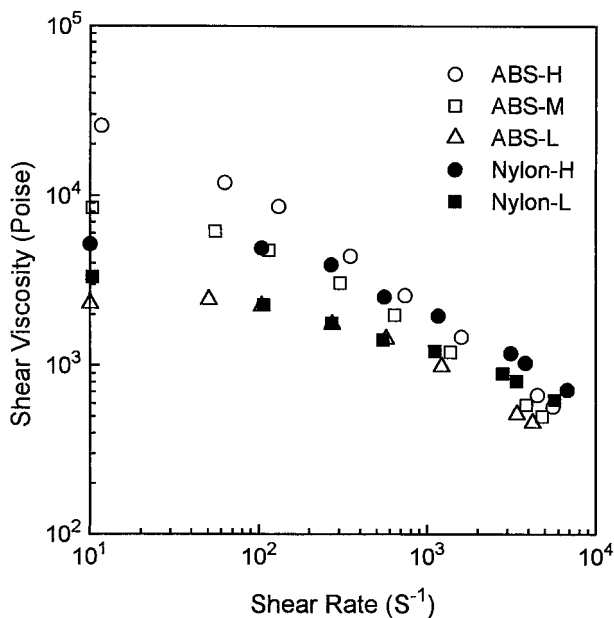


Figure 1 Shear viscosities of nylons and ABSs at 250°C.

between compatibilizer and nylon-6. Figure 2 summarizes the extraction scheme, which is similar to Howe and Wolkowicz.⁷ This method is based on the fact that only nylon-6 is soluble in 90% formic acid and only SAN and compatibilizer are soluble in chloroform. The fractions of the solvent extracted blend are characterized by infrared (IR) spectroscopy (Bio-rad) to identify the occurrence of interfacial reaction between maleic anhydride of compatibilizer and amine end group of nylon-6. The IR analysis of the formic acid soluble fraction is shown in Figure 3. The IR spectrum for the formic acid soluble fraction of uncompatibilized blend is essentially identical to nylon-6, as reported by others.^{16,17} Same experiment has been done for the chloroform soluble fraction. No trace of the presence of nylon-6 is also detected for the chloroform soluble fraction. The effectiveness of the extraction method can be validated from the experiment for the uncompatibilized blend. For the formic acid soluble fraction of compatibilized blend, imide peak at 1714 cm^{-1} (*D*) and nitrile

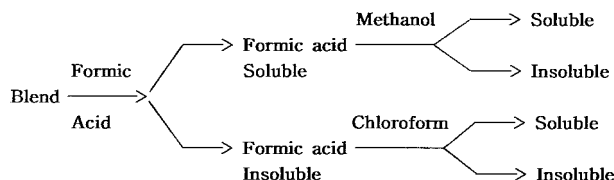


Figure 2 Solvent extraction diagram.

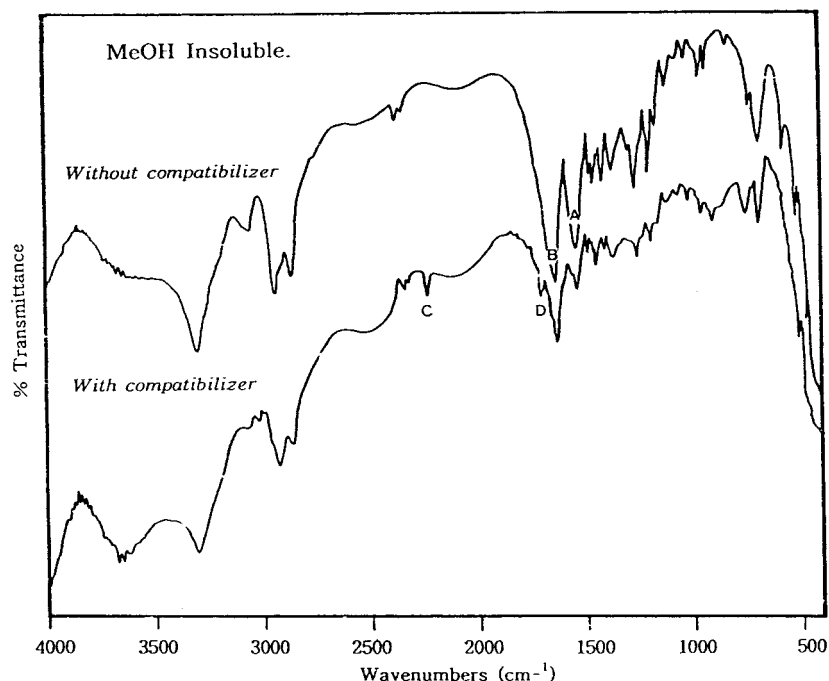


Figure 3 IR spectra of the formic acid soluble-methanol insoluble fraction of the blend.

peak at 2238 cm^{-1} (C) are observed. The imide peak can come from the compatibilizer itself and the result of reaction between maleic anhydride and amine end group of nylon-6. Though it is difficult to measure the extent of interfacial reaction from the IR analysis, the presence of imide peak for compatibilized blend indicates the occurrence of reaction between the compatibilizer and nylon-6. The nitrile peak indicates the presence of SAN in this fraction. It has been known that SAN is miscible with poly(*N*-phenylmaleimide-*co*-styrene) within specific ranges of copolymer composition,¹⁸ and the SAN and the compatibilizer used in this experiment fall into that range. Thus, the compatibilizer reacted with nylon-6 probably brings the SAN into formic acid soluble fraction.

Effect of Viscosity Ratio of Components

Figure 4 shows the scanning electron micrographs for all uncompatibilized 20 wt % nylon-6/80 wt % ABS blends. Figure 5 also shows the scanning electron micrographs for 20 wt % nylon-6/80 wt % ABS blends with 10 wt % compatibilizer based on the amount of nylon-6. For these blends, two phases are observed with nylon-6 dispersed phase composed of spherical domains. It has been observed that the dispersed phase size is strongly

dependent on the viscosity ratio of nylon-6 and ABS for uncompatibilized blends. In Figure 6, the variation of dn of the dispersed phase size with the viscosity ratio (nylon-6/ABS) for the uncompatibilized and compatibilized systems are presented. The main problem in this case is the determination of viscosity ratio since it is not easy to estimate a single and significant value for the deformation rate in a twin screw extruder. Exact temperature and strain rate of each phase inside the extruder are essential to find out the effect of viscosity ratio of nylon-6/ABS on the morphology of blend. However, it is very difficult to characterize the temperature and the magnitude of the strain rate in the extruder by a single number because the materials are subjected to complex shear and elongational deformations and complex temperature profiles along the extruder. Thus, the viscosity and viscosity ratio of the two phases vary, along with the temperature and strain rate in the extruder, and dispersion of minor phase can occur at any stage during the extrusion. In this study, the effective shear rate is assumed close to the screw speed as in the work of Wu.¹⁰ Viscosities of nylon-6s and ABSs at shear rate 300 s^{-1} are shown in Table II. Viscosity ratio of nylon-6/ABS varies from 0.3 to 2.0.

In Figure 6, dn of nylon-6 as a function of vis-

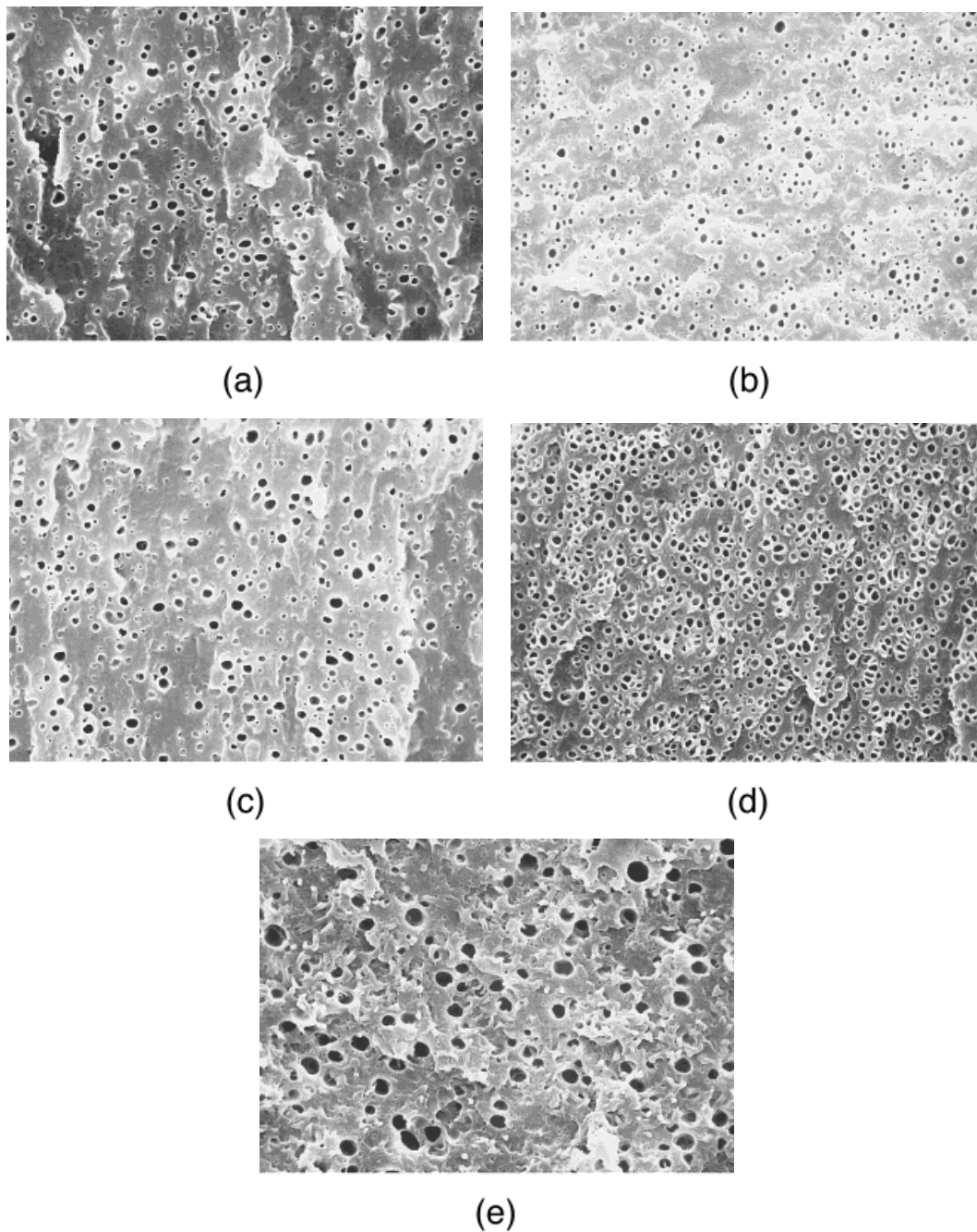


Figure 4 SEM photomicrographs of 20 wt % nylon-6/80 wt % ABS blends without compatibilizer: (A) nylon-L/ABS-H ($p = 0.35$), (B) nylon-H/ABS-H ($p = 0.75$), (C) nylon-L/ABS-L ($p = 0.96$), (D) nylon-H/ABS-M ($p = 1.21$), and (E) nylon-H/ABS-L ($p = 2.0$).

cosity ratio shows a typical V-shape appearance for uncompatibilized blend. The compatibilized systems show the significant drop in dispersed phase size and also show less dependence on the viscosity ratio than the uncompatibilized systems. The minimum dispersed phase size is observed at

approximately $p = 0.75$ for the uncompatibilized and the compatibilized blends. Wu¹⁰ and Serpe et al.¹⁹ have found that minimum dispersed phase size is obtained about $p = 1$, while Gonzalez-Nunez et al.¹² observed the minimum size at $p = 0.15$ for nylon-6/high density polyethylene blend. The

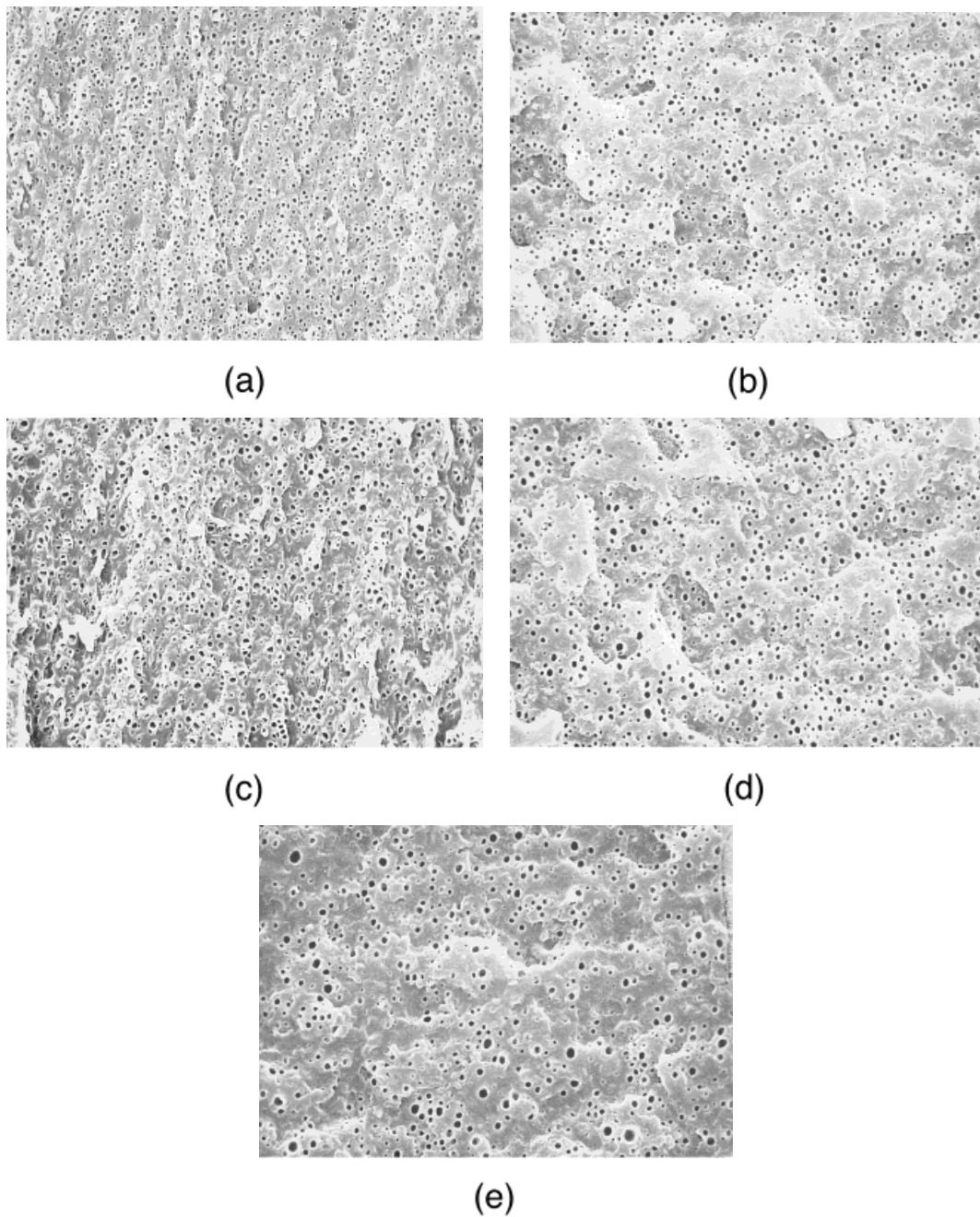


Figure 5 SEM photomicrographs of 20 wt % nylon-6/80 wt % ABS blends containing 10 wt % compatibilizer based on the amount of nylon-6: (A) nylon-L/ABS-H ($p = 0.35$), (B) nylon-H/ABS-H ($p = 0.75$), (C) nylon-L/ABS-L ($p = 0.96$), (D) nylon-H/ABS-M ($p = 1.21$), and (E) nylon-H/ABS-L ($p = 2.0$).

variation of p value for the minimum particle size illustrates that not only the viscosity ratio but also the elasticity ratio can profoundly affect the morphology. The dispersed particle size distributions for nylon-H/ABS-L are shown in Figure 7. Reactive blends show narrower dispersed particle size distribution than in the non-reactive blends.

The major effects of the chemical reaction at the interface by the reactive compatibilizer are a reduction in the average size of the dispersed phase particles and a narrowing of the size distribution. The smaller size and narrower distribution of dispersed phase size in the reactive blends compared to non-reactive blends can be related to the reduc-

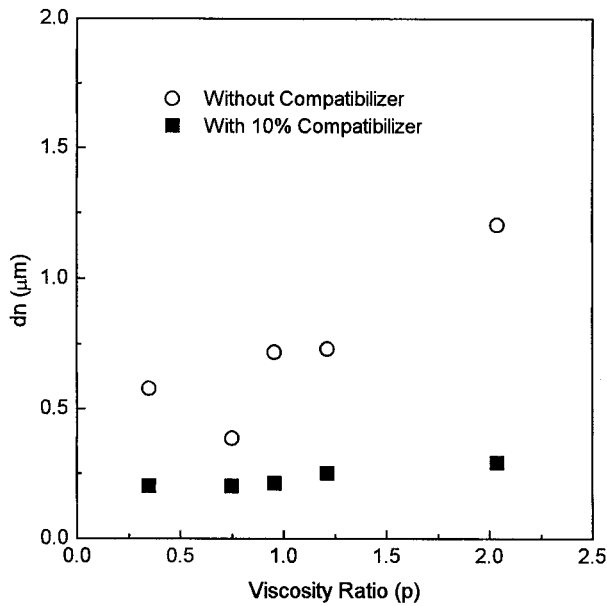


Figure 6 Number-average diameter of the dispersed phase versus the viscosity ratio for blends containing 20 wt % of nylon-6.

tion of the interfacial tension between the phases and inhibition of dispersed phase coalescence by the presence of the copolymer at the interface.^{3,12}

Effect of Feed Rate

The dispersed phase size measurement for the 20 wt % nylon-6/80 wt % ABS blends with 10 wt % compatibilizer based on the amount of nylon-6 as a function of feed rate is shown in Figure 8. The presence of the maximum dispersed phase size is observed at 40 kg/h for nylon-H/ABS-H ($p = 0.75$) and 50 kg/h for nylon-H/ABS-L ($p = 2.0$) blend when the flow rate is varied from 30 to 60 kg/h. These results are in disagreement with previous results. Several investigators studied the effect of feed rate on the morphology of polymer blends, and results are often contradictory. Willis et al.¹³ and Bartilla et al.²⁰ observed an increase

Table II Viscosities at Shear Rate 300 s^{-1}

Material	Designation	Viscosity (Poise)
Nylon-6	Nylon-L	1700
Nylon-6	Nylon-H	3630
ABS	ABS-L	1780
ABS	ABS-M	2990
ABS	ABS-H	4820

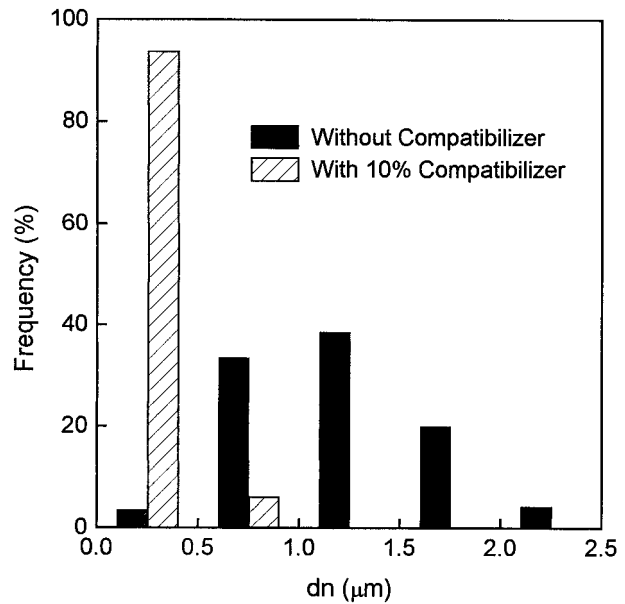


Figure 7 Effect of compatibilizer on the distributions of dispersed phase diameter for nylon-H/ABS-L blends.

of the dispersed phase size as the feed rate increased, while Bordereau et al.¹⁴ and De Loor et al.¹⁵ reported a decrease of the the dispersed phase size with increasing feed rate. However, they did not report the presence of maximum or minimum size of the dispersed phase like our re-

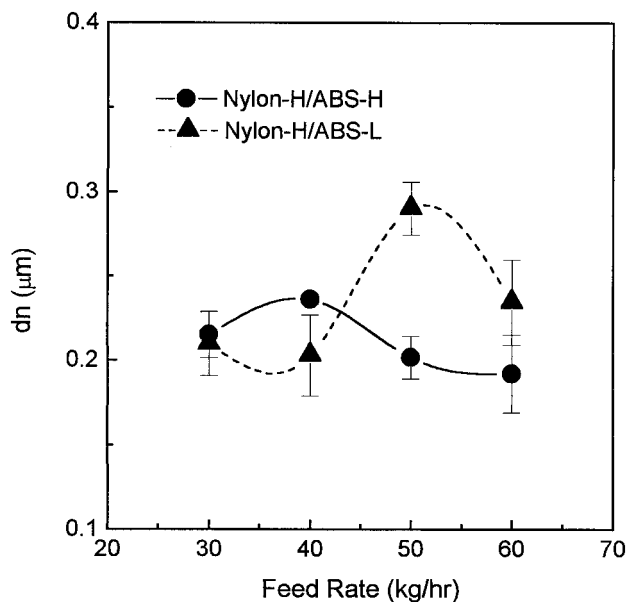


Figure 8 Effect of feed rate on the dispersed phase size of nylon-H/ABS-H and nylon-H/ABS-L blends containing 10 wt % compatibilizer based on the amount of nylon-6.

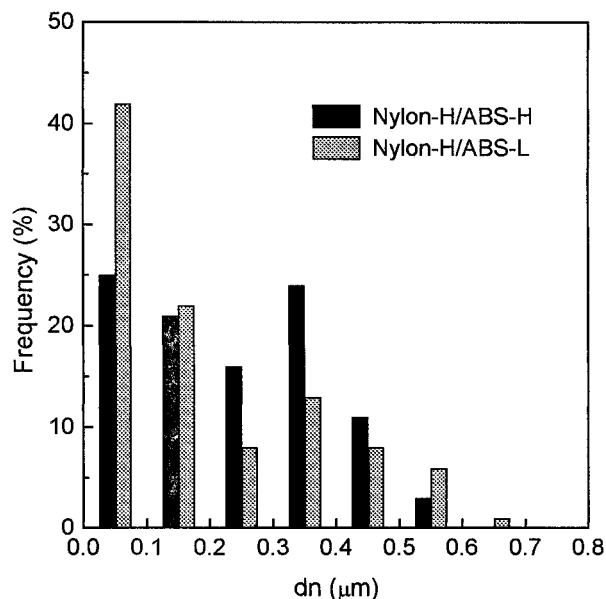


Figure 9 Dispersed phase size distributions at 40 kg/h.

sults. The maximum variation of dispersed phase size is observed as 20% for nylon-H/ABS-H ($p = 0.75$) and 40% for nylon-H/ABS-L ($p = 2.04$). The dispersed phase size distributions at 40 kg/h are shown in Figure 9. It shows that the dispersed phase size distribution of nylon-H/ABS-H is narrower than that of nylon-H/ABS-L. Same phenomena are observed at the other feed rate.

Though it is not clear for the presence of maximum dispersed phase size as a function of feed rate, several explanations can be proposed. Specific energy consumption (SEC) represents the amount of energy required to extrude per unit mass of material; and it can be expressed by the stress, strain rate, and the residence time in the extruder. The shear stress is an important parameter in dispersive mixing, and strain is an important parameter in distributive mixing. Therefore, SEC has been known as an important parameter to determine the measure of the total deformation that the material is exposed to during the extrusion process.²¹ Higher SEC should produce more particle breakdown. A decrease of SEC with increasing feed rate was reported, and it caused the increase of dispersed phase size in polymer blend.^{13,21}

Depending on the feed rate, the filling ratio of the screws varied, also influencing the melting mechanism, the degree of deformation, and the coalescence and breakup of the dispersed phases. Yang et al.²² found that the increase of percent fill

in a non-intermeshing twin screw extruder enhanced the dispersion of polymer blends as a result of more stretch and the high degree of deformation on the minor phase. A similar result has been reported by Bigio and Erwin²³ in their mixing study of two miscible fluids in a corotating twin screw extruder. Such an improvement of mixing will encourage the reduction of dispersed phase size in polymer blend. Also, higher feed rate will reduce the dispersed phase size by lowering a probability of the coalescence between dispersed phases or enhanced breakup mechanism due to the lower residence time and higher shear rate at the die.¹⁵

In addition to the above reasons, the melting behavior during blending can also affect the morphology of polymer blend. Sundararaj and Macosko²⁴ observed the major morphological changes during the initial softening stage. De Loor et al.¹⁵ observed the long fibrilla instead of spherical droplets after the melting for higher feed rate in PP/EVA/EMA blends. Scott and Macosko²⁵ reported the major reduction in dispersed phase size in conjunction with melting or softening of the components, and a further process primarily reduced the size of the large particles in the size distribution. Though an information for the melting mechanism in blend systems is not yet known clearly, the formation of a different morphology during the initial blending stage by different melting behavior can be deduced, and it will affect the final morphology.

As discussed above, the formation of morphology of a blend is the result of complex processes, and no general rule concerning the effect of feed rate on the morphology of a blend in a twin screw extruder can be precisely defined yet. However, the results of this study validate that the feed rate in the twin screw extrusion can strongly affect the dispersed phase size of polymer blend.

Effect of Concentration of Compatibilizer

Figure 10 shows the number-average and volume-average dispersed phase diameter determined as a function of concentration of compatibilizer for nylon-H/ABS-L ($p = 2.0$) and nylon-H/ABS-H ($p = 0.75$). It is evident that the dispersed phase size decreases as the concentration of compatibilizer increases. Especially, dispersed phase size decreases significantly even for a small amount of compatibilizer addition. Also, the dispersed phase size appears to equilibrate towards larger concentration of compatibilizer. Such trends have also been observed for other interfacially modified

polymer blend systems.¹³ Figure 10 also shows that the value of number-average and volume-average dispersed phase diameter tend to be close to each other. It indicates that the homogeneous dispersed phase size distribution is obtained by the reduction of large dispersed phase, and it is represented in Figure 11 for nylon-H/ABS-L blend. Also, it indicates that the minimum dispersed phase size is dependent on the viscosity ratio of nylon-6/ABS.

CONCLUSIONS

The dispersed phase morphology as a function of viscosity ratio of components, concentration of compatibilizer, and the feed rate is investigated for nylon-6 and ABS blends with reactive compatibilizer [poly(*N*-phenylmaleimide-styrene-maleic anhydride)] using an intermeshing corotating twin screw extruder. The solvent extraction and IR spectroscopy study indicate the occurrence of reaction between maleic anhydride of compatibilizer and amine end group of nylon-6. For 20 wt % nylon-6 and 80 wt % ABS, nylon-6 is a dispersed phase; and it is found that the minimum dispersed phase size occurred at the $p = 0.75$ for both uncompatibilized and compatibilized systems. Dispersed phase size is decreased significantly by the

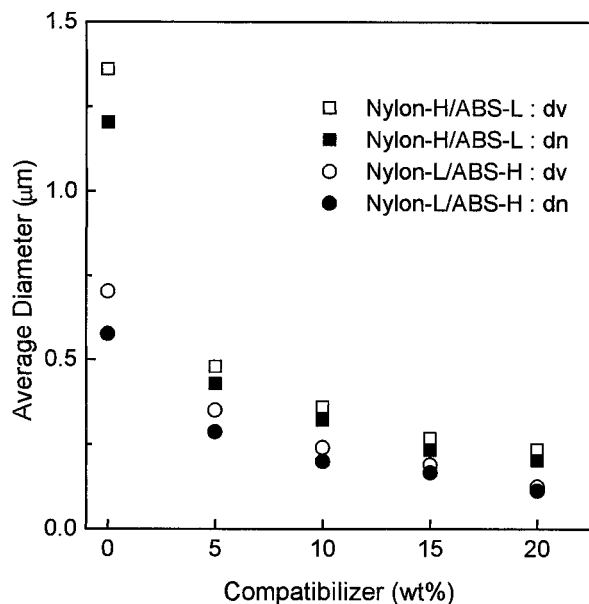


Figure 10 Effect of concentration of compatibilizer on the dispersed phase diameter for nylon-H/ABS-L and nylon-L/ABS-H blends for blends containing 20 wt % of nylon-6.

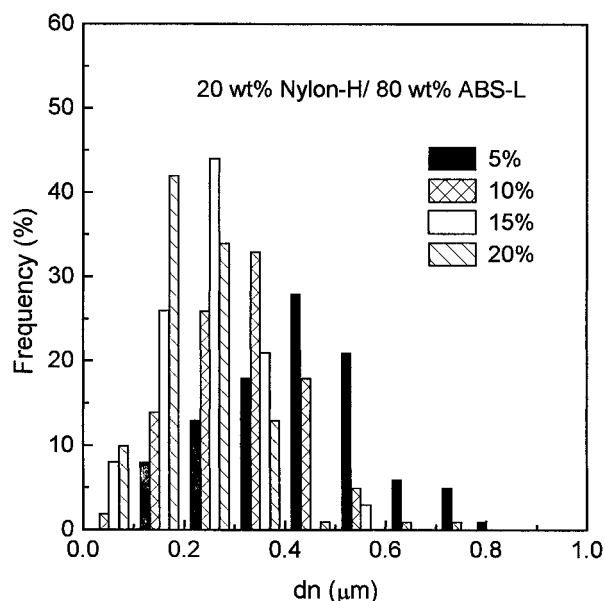


Figure 11 Dispersed phase size distributions of nylon-H/ABS-L blends as a function of concentration of compatibilizer for blends containing 20 wt % of nylon-H.

addition of compatibilizer and tends to equilibrate at about 15 wt % compatibilizer based on the amount of nylon-6. The final dispersed phase size at the equilibrium state is dependent on the viscosity ratio of nylon-6/ABS. The presence of maximum dispersed phase size is observed by changing the feed rate.

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