

The Phase Inversion and Morphology of Nylon 1010/Polypropylene Blends

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SYNOPSIS

Noncompatibilized and compatibilized blends of nylon 1010/PP blends having five different viscosity ratios were prepared by melt extrusion. Glycidyl methacrylate-*grafted*-polypropylene (PP-*g*-GMA) was used as the compatibilizer to enhance the adhesion between the two polymers and to stabilize the blend morphology. The effect of the viscosity ratio on the morphology of nylon 1010/polypropylene blends was investigated, with primary attention to the phase-inversion behavior and the average particle size of the dispersed phase. The relationship between the mechanical properties and the phase-inversion composition was investigated as well. Investigation of the morphology of the blends by microscopy indicated that the smaller the viscosity ratio (η_{PP}/η_{PA}) the smaller was the polypropylene concentration at which the phase inversion took place and polypropylene became the continuous phase. The compatibilizer induced a sharp reduction of particle size, but did not have a major effect on the phase-inversion point. An improvement in the mechanical properties was found when nylon 1010 provided the matrix phase. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

It is well known that the morphology of immiscible polymer is affected by the blending conditions, interfacial tension between the components, special interaction such as possible covalent or hydrogen bonding, and the viscosity of the components.¹⁻³ Generally, the major component forms the continuous phase.⁴ When the volume fraction of the dispersed phase is increased, the average particle size increases as well. In addition to the composition, the phase-inversion point also depends on the viscosity of the components under the conditions of blending.⁵

The dependence of morphology on the ratio of the viscosity of the dispersed phase to the viscosity of the matrix ($P = \eta_{PP}/\eta_{PA}$) was earlier studied by Wu⁶; he found that the relative influence of interfacial tension and viscosity ratio on phase morphology dimensions can be characterized by a dimensionless Weber number:

$$We = \frac{\eta_m \dot{\gamma} r}{\gamma_{12}} = 4 \left(\frac{\eta_d}{\eta_m} \right)^{\pm 0.84} \quad (1)$$

where $\dot{\gamma}$ is the shear rate; r , the radius of the dispersed particle; and γ_{12} , the interfacial tension. The exponent is positive if the viscosity ratio η_d/η_m is > 1 and negative if the viscosity ratio is < 1 . These equations indicate that the smallest particles are generated when the viscosity ratio is near unity. Serpe et al.⁷ showed eq. (1) to be valid for polyamide/polyethylene blends. In this work, the effect of the viscosity ratio on the phase inversion of nylon 1010/polypropylene blends was studied. The viscosity ratio was varied by using five polypropylenes with different melt viscosities. Both noncompatibilized and compatibilized blends were prepared. A graft copolymer compatibilizer was added to increase interactions between the two phases.

EXPERIMENTAL

Materials

Nylon 1010 was purchased from Jilin Shijinggou Union Co. (China). Polypropylenes (PPs) 1330,

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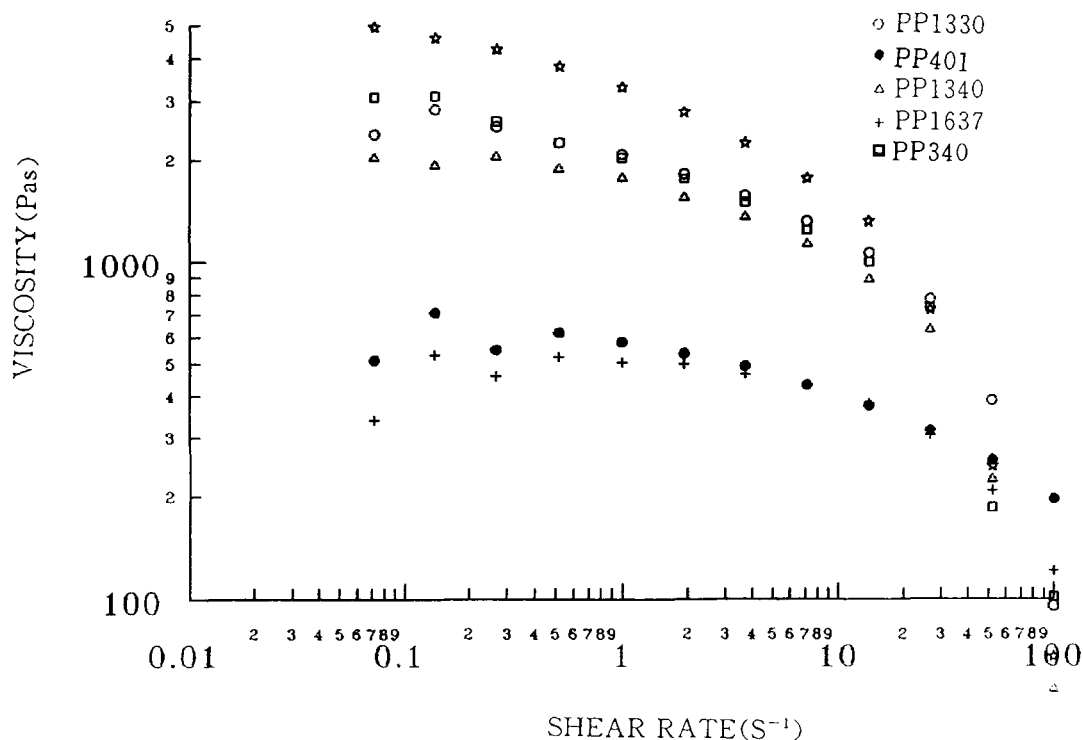


Figure 1 Melt viscosities of PPs vs. shear rate at 210°C.

1340, 1637, 340, and 401 were supplied by Beijing Yanshan Petroleum Chemical Co. (China). The compatibilizer was PP-grafted with 0.573 wt % glycidyl methacrylate (PP-*g*-GMA); its preparation was reported in a previous article.⁸

Blending Preparation

Nylon 1010 was dried for 12 h at 80°C before melt blending. Blendings were prepared by melt extrusion by a twin-screw extruder. The rotation speed was 51 rpm and melt temperature 200–210°C.

Nylon 1010/PP blends in compatibilized and noncompatibilized forms in the volume ratios 95/5, 85/15, 75/25, 70/30, 65/35, 55/45, 45/55, 35/65, 25/75, and 15/85 were prepared. The amount of the compatibilizer, PP-*g*-GMA, was in all cases 5 wt % of the total blend weight.

Characterization

Melt viscosities were measured at 210°C with a cone-plate viscometer. Nylon 1010 and the blends were predried at 80°C for 12 h. The experiments were carried out under a nitrogen atmosphere.

Blend morphology was investigated by a JXA-840 scanning electron microscope (SEM). The sam-

ples for SEM were prepared by etching the extrudate in boiling xylene for 40 min to remove the polypropylene phase and were golden-coated before microscopy. The phase-inversion region of these samples were investigated by a Universal R Pol light microscope with a hot stage. The melting of each polymer phase was observed and continuous and dispersed phases were characterized.

Injection-molded samples were injection-molded into the form of test specimens after drying with a JSWJ17SA injector. Blends were injection-molded at a melt temperature of 190–210°C; other injection-molding conditions were kept constant for all blends. Tensile properties were measured with an Instron 1121 testing machine at room temperature; the strain rate was 50 mm/min. The flexural strength was determined with the same testing machine as was the tensile strength.

RESULTS AND DISCUSSION

Viscosity of Component Polymers

The melt viscosity of the polymers are reported as a function of shear rate in Figures 1 and 2. Because the measuring temperature was the same as the

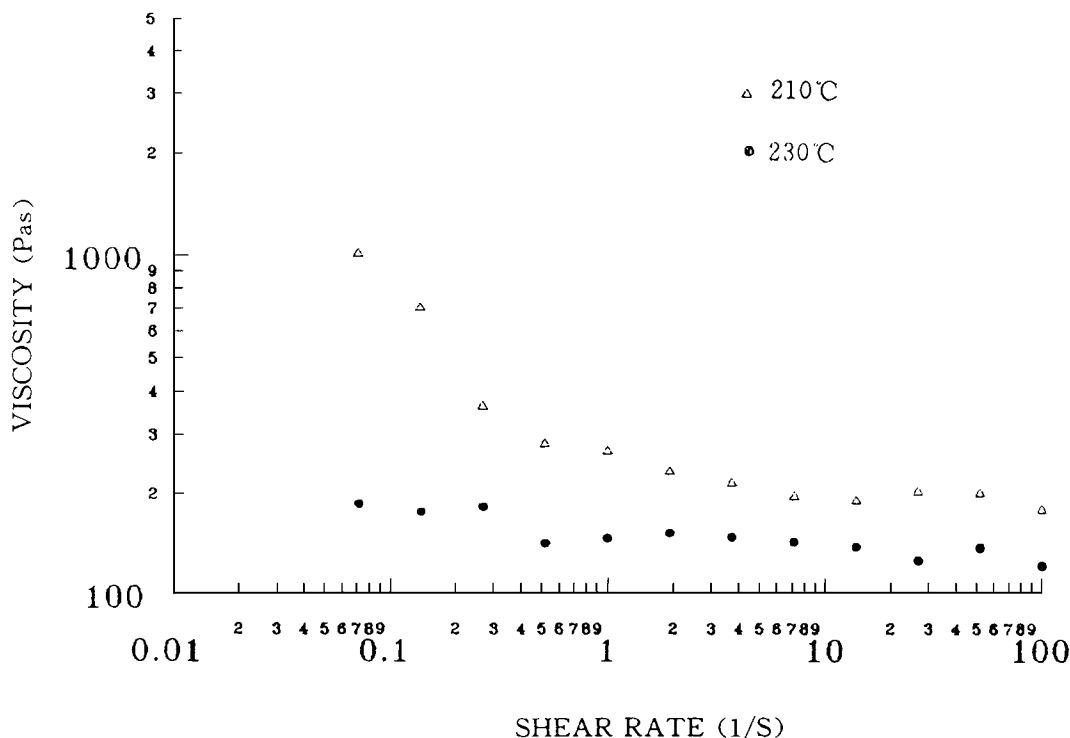


Figure 2 Melt viscosities of nylon 1010 vs. shear rate at 210°C.

blending temperature, 210°C, the measured viscosities indicate the viscosities that dominated under the processing conditions. The shear thinning behavior of PP was more noticeable than that of nylon 1010. At higher investigated shear rates, the viscosities of nylon 1010 used in this work are higher than those some of PPs. The viscosity ratios of PP to nylon 1010 varied from about 0.8 to 2.0 in the range of shear rate studied. It was very difficult to determine any exact shear rate for the applied processing conditions; the shear rate of 51 S^{-1} was selected, calculated by the method proposed by Wu.⁶ The value is assumed to best describe the average shear rate during the corotating screw extrusion.

Effect of Viscosity Ratio on the Phase Inversion

The phase inversion of the noncompatibilized blends could be determined with the help of an optical microscope and a hot stage. The melting of the individual phases was observed and whether the melting first took place in the dispersed particle or in the matrix was clarified. The temperature of the samples was increased to 185°C by using the hot stage. At this temperature, PP was melted and nylon 1010 did not melt. The observed dark part is the PP phase and the light part is the nylon 1010 phase. The

phase-inversion behavior can be determined by observing morphologies of nylon 1010/PP blends with a series of compositions. For the nylon 1010/PP340 blend, it was found that PP was a continuous phase when its volume fraction was ≥ 0.75 and nylon 1010 became a continuous phase when the volume fraction of PP was ≤ 0.7 . From these features, it could be concluded that the phase inversion for the nylon 1010/PP340 blends occurred at the PP volume fraction of about 0.7–0.75. The phase-inversion behavior of other noncompatibilized blends also could be obtained by the same procedures, as shown in Figure 3(a). The viscosity ratio was determined from Figures 1 and 2 at an estimated average shear rate 51 S^{-1} . The smaller the viscosity ratio, the smaller PP concentration at which phase inversion occurred.

PP-*g*-GMA was used as a compatibilizer. The phase-inversion of the compatibilized blends could not be determined by the optical microscope because of the good adhesion; we, therefore, used SEM to define the phase-inversion regions of the compatibilized blends. The SEM samples were etched by xylene; the dark holes were the PP phase. By examining the morphologies of the investigated blends, one could determine which phase was continuous at various PP volume frac-

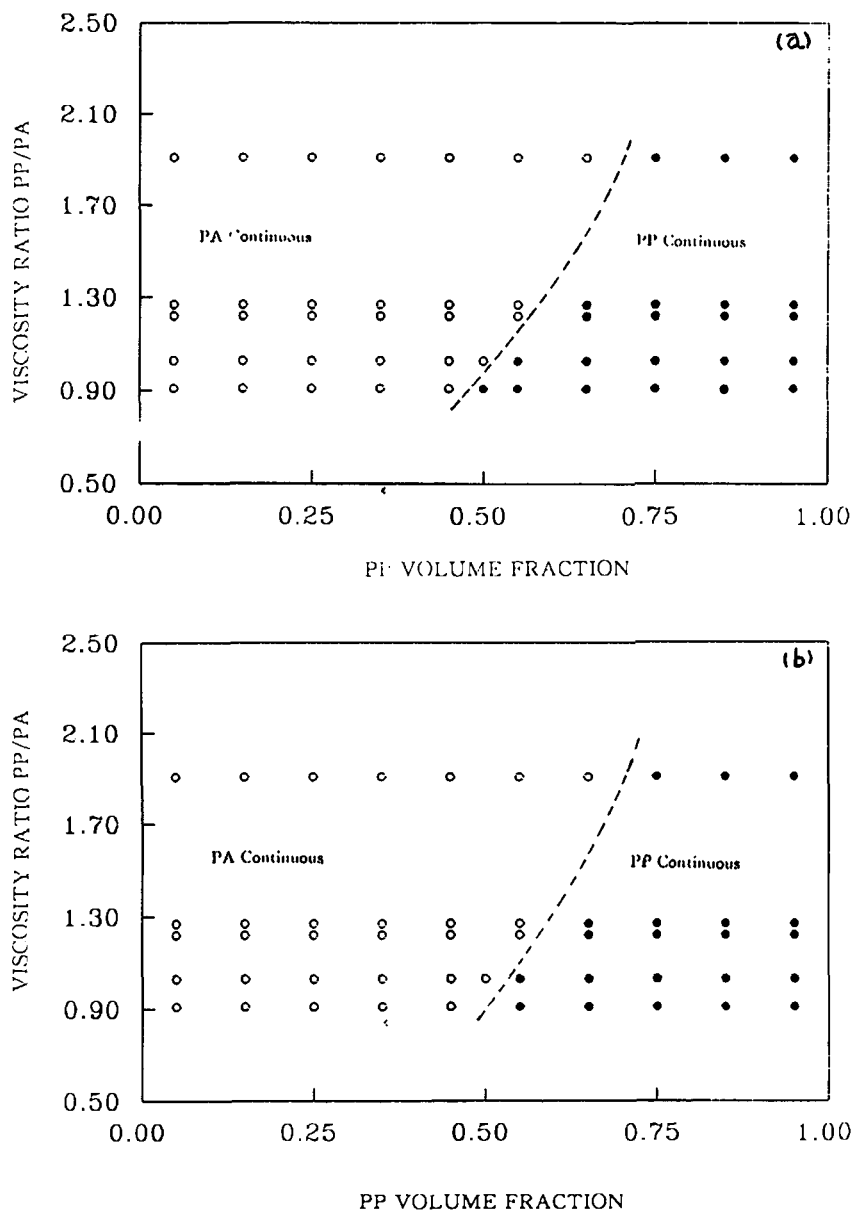


Figure 3 The phase-inversion regions of the blends as a function of the viscosity ratio and PP composition containing (a) 0 wt % compatibilizer and (b) 5 wt % compatibilizer. The continuous phase is (●) PP or (○) nylon 1010. (---) Jordhamo et al.'s model.

tions. The phase-inversion behavior of the compatibilized blends is depicted in Figure 3(b). Addition of the compatibilizer changed the phase-inversion range only a little for the nylon 1010/PP blends. In this case, dual-phase continuity for different compatibilized blends was seen at nylon 1010 concentrations of 41.5, 46.4, 51.4, 51.4, and 61.7 wt %, respectively. Compared with uncompatibilized blends, it is evident that the compatibilization does not have a pronounced effect on the composition of the phase inversion.

Jordhamo et al.⁹ developed an empirical model for predicting the phase-inversion region of immiscible polymer blends; according to the model, phase inversion occurs when the following equation holds:

$$\frac{\eta_m}{\eta_d} \cdot \frac{\Phi_d}{\Phi_m} = 1 \quad (2)$$

where η_m and η_d are the viscosities of the matrix and dispersed phase and Φ_d and Φ_m represent the

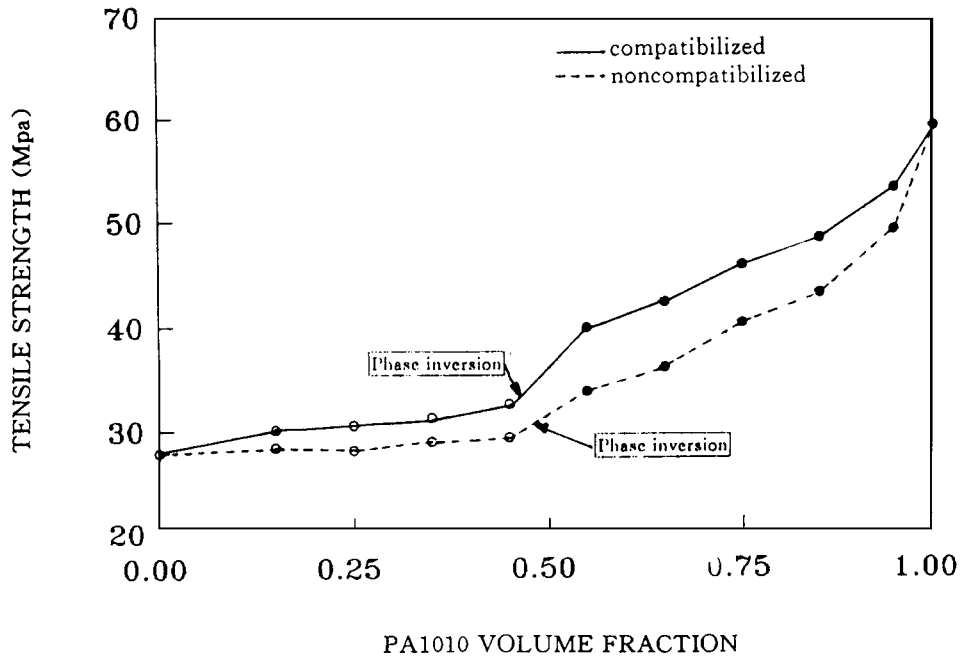


Figure 4 The tensile strength of compatibilized and noncompatibilized nylon 1010/pp 340 blends. Continuous phase is (O) PP or (●) nylon.

volume fractions of two phases. Jordhamo et al.'s model is limited to low shear rate. The shear rate of 51 S^{-1} , chosen as an estimate of the shear rate,

correlates fairly well with the model. If a higher value of the shear rate is chosen, the correlation between the observed phase-inversion composi-

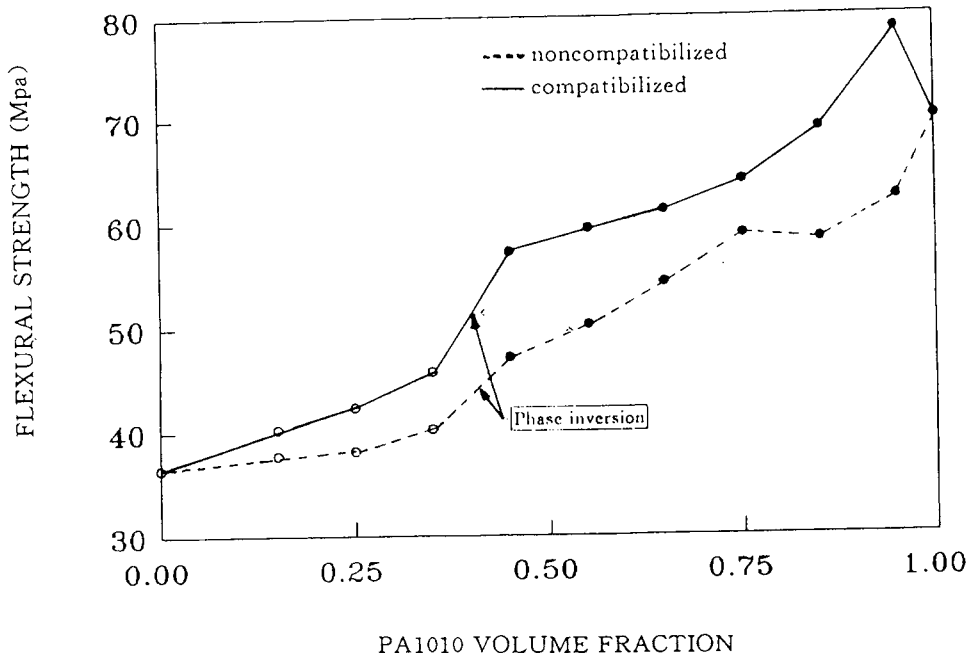


Figure 5 The flexural strength of the compatibilized and noncompatibilized nylon 1010/PP 340 blends. Continuous phase is (O) PP or (●) nylon.

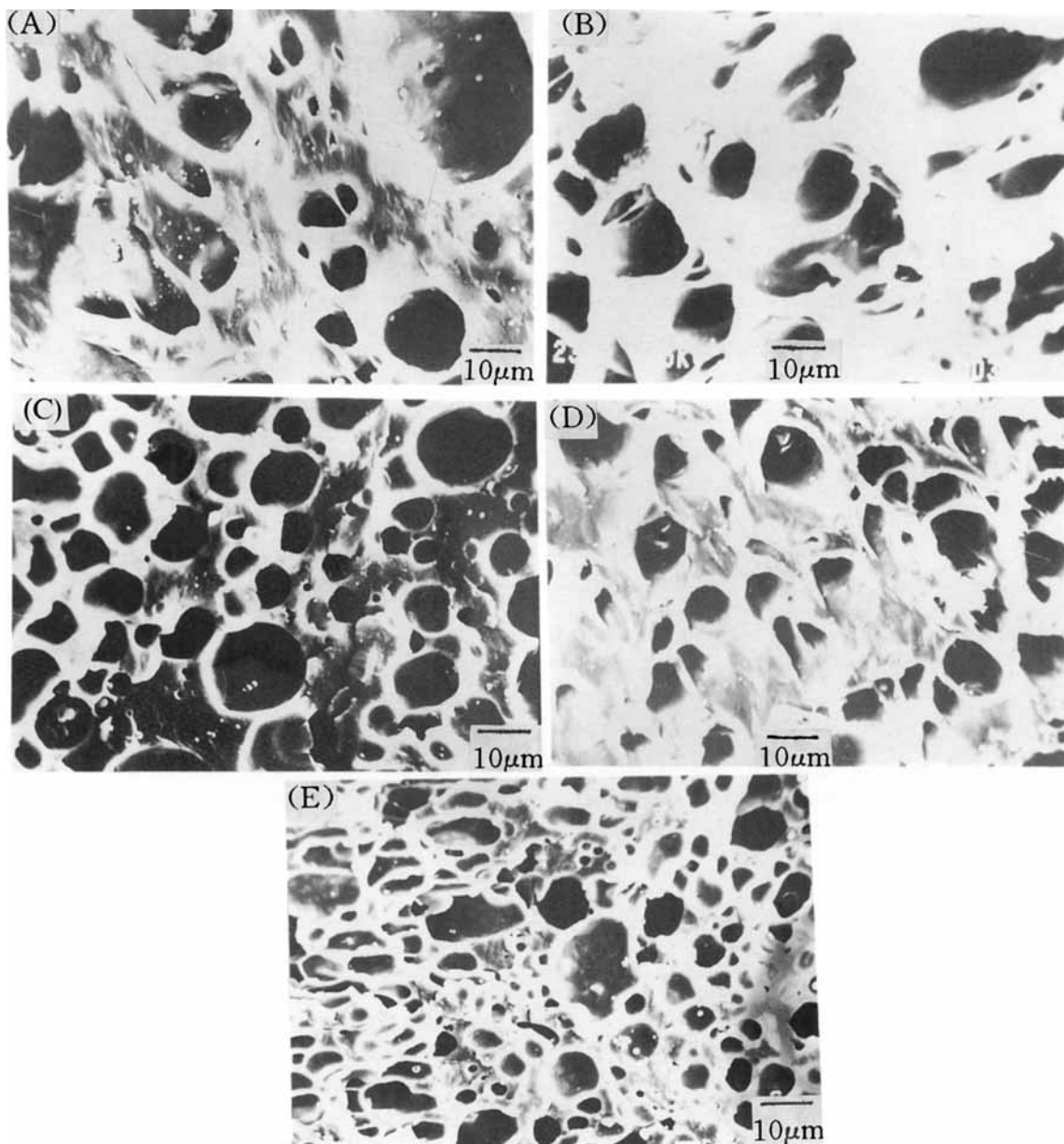


Figure 6 SEM photographs of noncompatibilized nylon 1010/PP blends in the weight ratio 70/30 for (A) nylon 1010/PP 1330, (B) nylon 1010/PP 401, (C) nylon 1010/PP 1340, (D) nylon 1010/PP 340, and (E) nylon 1010/PP 1637.

tion and the Jordhamo et al. equation becomes weaker, in agreement with some previous investigations.^{10,11}

Effect of Phase Inversion on the Mechanical Properties

Mechanical properties of blends are expected to be determined mainly by the continuous phase. Improvement in the mechanical properties as a func-

tion of nylon concentration may take place when the continuous PP phase is replaced by the continuous nylon 1010 phase. The results of tensile-strength measurements and the flexural strength are reported in Figures 4 and 5. It was found that the tensile and flexural properties improved remarkably when the continuous PP phase was replaced by the nylon 1010 phase. On the other hand, the mechanical properties of the compatibilized blends are better than those of noncompatibilized blends; this should

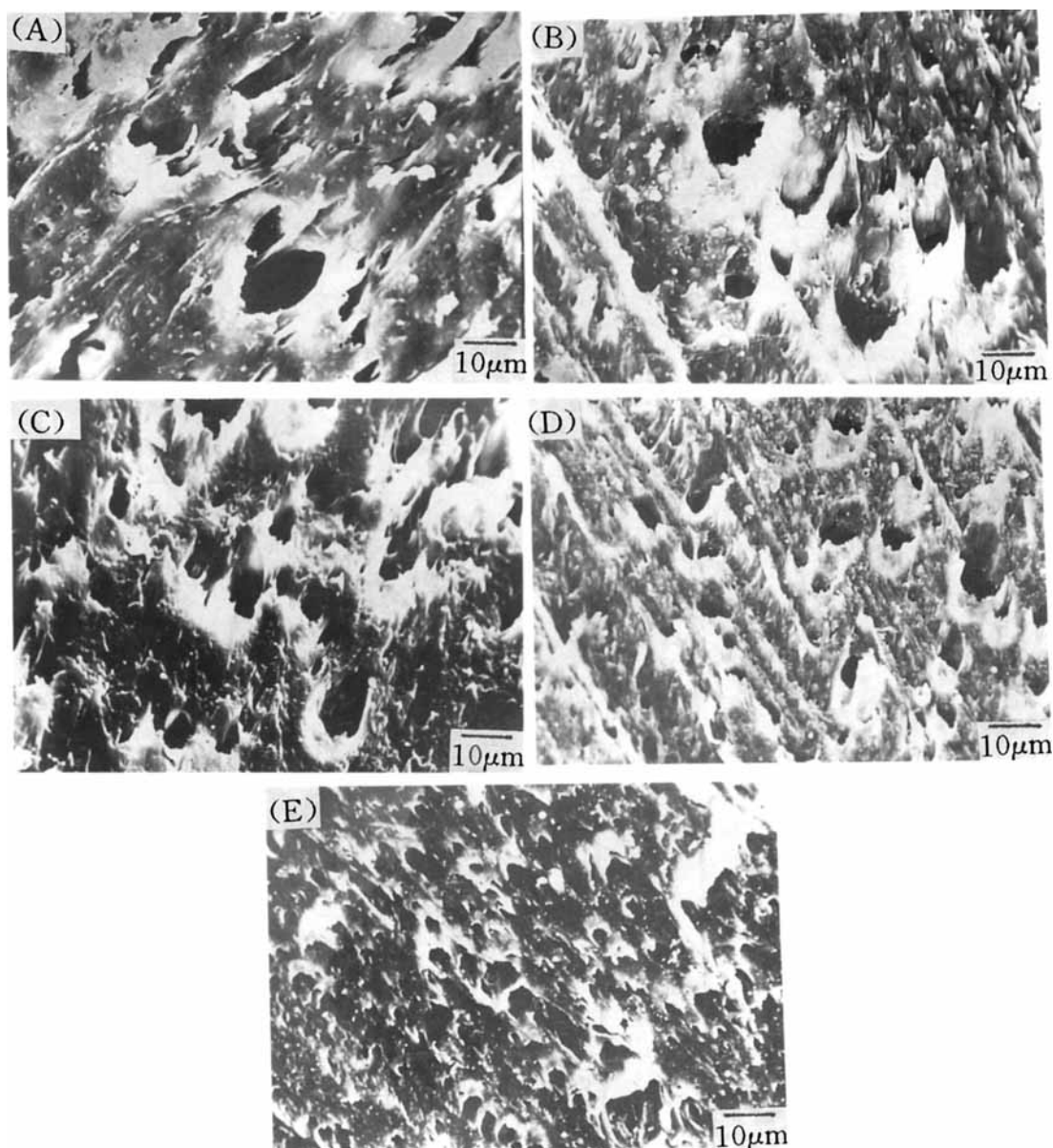


Figure 7 SEM photographs of compatibilized nylon 1010/PP blends in the weight ratio 70/30 for (A) nylon 1010/PP 1330, (B) nylon 1010/PP 401, (C) nylon 1010/PP 1340, (D) nylon 1010/PP 340, and (E) nylon 1010/PP 1637.

be attributed to the good compatibility and adhesion of the two phases in the compatibilized blends.

Morphology

The addition of the compatibilizer changed the morphology of the blends considerably. Typical SEM pictures are shown in Figures 6 and 7. The dark hole is the PP phase, which was removed by xylene. The PP domains of the noncompatibilized blends have a diameter which ranges between 3 and

30 μm . The domain surface appears to be very smooth; the large particle size with no evidence of adhesion between the matrix and dispersed confirmed the incompatibility of the two components in the noncompatibilized blends. Some differences are clearly visible between the morphologies of the compatibilized and noncompatibilized blends. Figure 7 shows that the average size of the second component of the nylon 1010/PP compatibilized blends decreased remarkably compared with that of noncompatibilized blends; the diameter in this case was

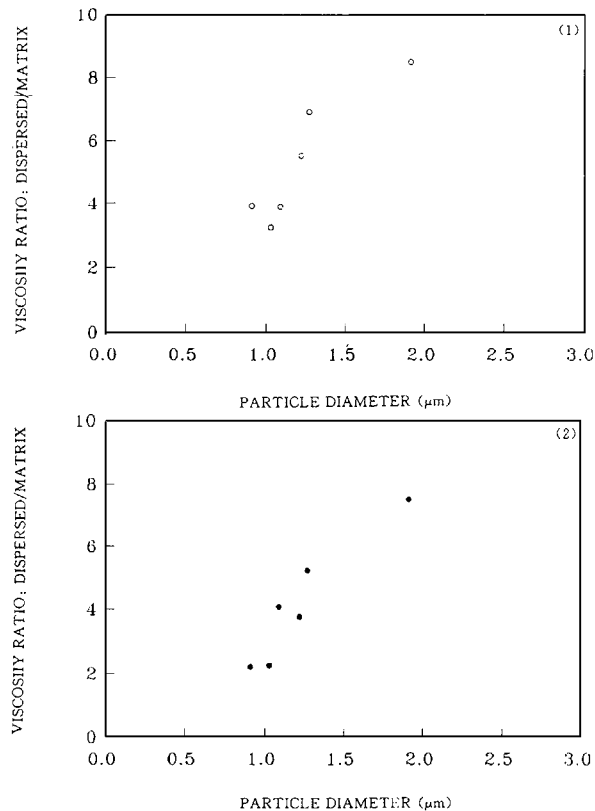


Figure 8 Dependence of the number-average diameter on the viscosity ratio of PP/nylon 1010 blends in the weight ratio 30/70: (1) noncompatibilized blend; (2) compatibilized blend.

between 1 and 15 μm . It was evident that the compatibilizer PP-*g*-GMA had a very large effect on the particle size.

The average particle size of the dispersed sizes was determined manually. The number-average particle size as a function of the viscosity ratio is depicted in Figure 8. At the composition ratio of nylon 70/PP 30, PP was the dispersed phase. The number-average particle size varied from 1 to 10 μm and the viscosity ratio range was 0.9–2.0. Curve 1 is for the noncompatibilized blend series; the matrix viscosity and the interfacial tension are the same, but the PP viscosities are different. From curve 1, we found that the number-average diameter appears to have the smallest particles when the viscosity ratio is about 1. As the viscosity ratio increases above unity or decreases below unity, the dispersed particles become larger. The matrix viscosities for the compatibilized blend are the same but interfacial tensions are different in curve 2. Different dependencies of the number-average particle diameter on the viscosity for the compatibilized blends were found.

Rheology of the Blends

The rheology properties are associated with the phase morphology. An approach is to consider the mean shear rate in a volume element as the sum of the rates of the individual fractions^{12,13}:

$$\dot{\gamma} = \Phi_m \dot{\gamma}_m + \Phi_d \dot{\gamma}_d \quad (3)$$

On the assumption that stresses will be the same in all layers, the viscosity of the blend can be expressed as

$$\frac{1}{\eta} = \frac{\Phi_m}{\eta_m} + \frac{\Phi_d}{\eta_d} \quad (4)$$

This model, proposed by Lees,¹² predicts a monotonic variation of the reciprocal viscosity with volume fraction of the reciprocal viscosity with volume fraction.

Figure 9 depicts the viscosity as a function of PP volume fraction at two shear rates. In the noncompatible blends, viscosity showed a negative deviation from Lees' rule, indicative of noncompatibilized blends.¹⁴ In the case of compatibilized blends, viscosities increased over the entire composition range; the viscosity–composition curves showed a clear positive deviation at a shear rate of 50 S^{-1} . The increase in viscosities demonstrates the reduction in interfacial mobility, caused by the chemical reaction between the amine end group of nylon and the GMA group of the PP-*g*-GMA. At higher shear rate (100 s^{-1}), the viscosity–composition curves became more negative; similar behavior was reported by Park et al.¹⁵

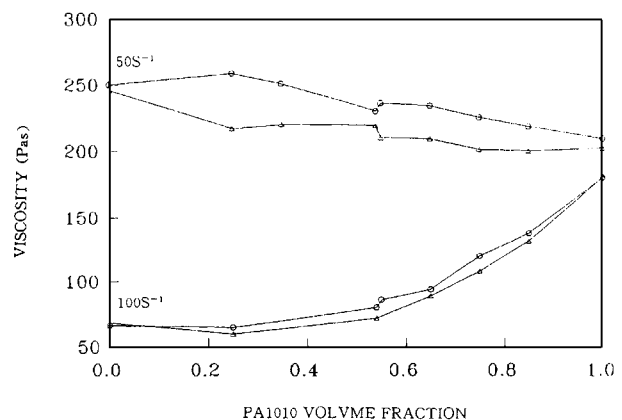


Figure 9 Composition dependence of the viscosity for nylon 1010/PP 340 blends containing (Δ) 0% compatibilizer and (\circ) 5 wt % compatibilizer at two shear rates.

CONCLUSIONS

Jordhamo et al.'s model⁹ can be used to predict the continuous phase. The viscosity ratio in nylon 1010/PP blends had only a limited effect on phase inversion. Compatibilization of the blends with PP-*g*-GMA did not cause significant change in the phase-inversion point, although the average particle size was greatly reduced. Correlation was found between the mechanical properties of the blends and the phase inversion; the mechanical properties appear to critically depend on the continuous phase.

This research was supported by Department of Materials Sciences, National Nature Sciences Foundation of China, Project No. 59433010.

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Received January 3, 1996

Accepted March 12, 1996