

# Polypropylene–Phenol Formaldehyde-Based Compatibilizers. II. Application in PP/PA6 75/25 (wt/wt) Blends

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**ABSTRACT:** A new class of compatibilizers suitable for blends or alloys of polypropylene and engineering polymers having aromatic residues or functionality complementary to hydroxyl were evaluated in blends of isotactic polypropylene (PP) and polyamide 6 (PA6). The compatibilizer consisted of a PP part with a phenol formaldehyde (PF) polymer grafted onto it. In this study, various combinations of the polymer parameter of each compatibilizer building block were examined. Based on the same loading, the compatibilizer with low molecular weight PP and high content of high molecular weight PF was observed to be the most efficient. A compatibilizer content of up to 7.5% by weight gave significant reduction in the average particle size of the dispersed PA phase. Similarly, corresponding improvements in the mechanical properties were observed as the average particle size was reduced. For some of the blends, more than additive improvement in the mechanical properties were achieved. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 75: 355–360, 2000

**Key words:** PP-PA blends; Polypropylene compatibilizers; Polypropylene-Phenol formaldehyde copolymers; Reactive extrusion

## INTRODUCTION

In the first part of this series (I), the synthesis of polypropylene-*graft*-phenol formaldehyde (PP-*g*-PF) copolymers was demonstrated.<sup>1</sup> In this synthesis, it was clearly shown that the component viscosity ratio had a significant effect on the conversions of the reactants. Component viscosity ratios of close to 1 were observed to give optimum reaction conditions. This is also according to earlier stated theories.<sup>2,3</sup>

The present study was aimed at understanding the relationship between the nature of the compatibilizer and the resulting blend properties. In particular, PP-rich PP/polyamide 6 (PA6) blends were investigated using six different PP-*g*-PF compatibilizers with widely different segment structures. For comparison reasons, maleic anhydride (MAH)-functionalized PP was also included in the study. This is a well-known compatibilizer for PP/PA blends.<sup>4,5</sup> Also, a neat PF resin with high functionality and high viscosity was evaluated.

## EXPERIMENTAL

### Materials

One isotactic PP–polyethylene (PE) heterophase block copolymer and one PA6 grade provided the

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**Table I** Compatibilizer Compositions

Compatibilizer Code	PF Content (wt %) <sup>a</sup>	PP $M_n$ (g/mol)	PF $M_n$ (g/mol)
A1	25	52,000	6300
A2	25	52,000	27,550
A3	25	143,000	6300
B1	50	52,000	6300
B2	50	52,000	27,550
B3	50	143,000	6300
C1	0	143,000	—
C2	100	—	27,550

<sup>a</sup> Bound PF after extraction in acetone. Content determined by FTIR.

polymers. PP P 410H was supplied by Borealis, AS, Stathelle, Norway and PA6 Ultramid B3 was supplied by BASF AG, Ludwigshafen, Germany. P 410H had a melt flow index of 0.9 g/10 min (230°C/2.16 kg) and the B3 grade had a melt volume index of 120 mL/10 min (275°C/5 kg). The viscosity ratio between P410 and B3, determined by dynamic rheology, at was about 1 : 1 at a shear rate of 200–500 s<sup>-1</sup>, typical shear rates for reactive extrusion.<sup>6</sup> Six different compatibilizers based on PP–PH were synthesized according to an in-house procedure (PP–g–PF).<sup>1</sup> One high functionality MAH-functionalized PP resin (C1), and one high viscosity PH resin (C2) were also evaluated as compatibilizers. Some properties of the synthesized compatibilizers are given in Table I. Molecular weights of each block of the compatibilizers given Table I are based on GPC analysis of each starting polymer.

Blend compositions used in this study are listed in Table II. The blends were prepared with

0, 2.5, 5, 7.5, 12.5, 17.5, 25, and 35 wt % PP–g–PF compatibilizers. The amount of base polymer (PP) in the blend was adjusted so that PP plus the compatibilizer was equal to 75 wt %, while the PA was constantly kept at 25 wt %. The PP–g–PF compatibilizer and the PA6 were predried at 80°C for 12 h to remove residual monomers and traces of water.

### Blending of PP and PA

The preparation of the PP/PA blends was conducted in a 25-mm Clextral BC 21 intermeshing corotating twin-screw extruder (TSE) with an  $L/D$  of 44. PP and the compatibilizer were fed into the main hopper, and PA at 15  $L/D$ , from a side-stream single-screw extruder, at a total throughput of 3 kg/h. The screw rotation speed was 150 rpm and the barrel set temperature 250–265°C. Average residence time at these conditions was 2.5 min. The extruder was equipped with highly efficient vacuum venting to remove unreacted species and reaction by-products. An inert atmosphere was used to reduce polymer degradation. The extrudate was immediately quenched in a water bath and then pelletized.

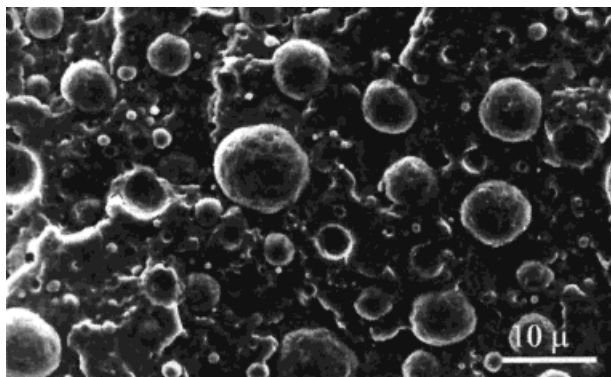
The extruder screw profile was configured to allow good melting of the polymers followed by efficient mixing and high shear, high residence time in the reaction zone, and venting close to the outlet of the extruder. Neutral, 90°, kneading blocks followed by backmixing screw elements were located after 10 and 25  $L/D$ . The remaining elements of the screw profile were semipitch conveying elements. The extruder was equipped with Ktron T20 feeders and a loss-in-weight feeding system for accurate feeding of the raw materials.

**Table II** Measured Average Particle Size of Dispersed Phase at Various Blend Compositions

PP/C/PA6 <sup>a</sup>	A1 $D_p$ ( $\mu\text{m}$ )	A2 $D_p$ ( $\mu\text{m}$ )	A3 $D_p$ ( $\mu\text{m}$ )	B1 $D_p$ ( $\mu\text{m}$ )	B2 $D_p$ ( $\mu\text{m}$ )	B3 $D_p$ ( $\mu\text{m}$ )
75.00/0/25	5.3	5.3	5.3	5.3	5.3	5.3
72.5/2.5/25	2.5	1.9	4.0	2.0	1.7	4.2
70/5/25	1.7	1.5	2.3	1.7	0.7	3.3
67.5/7.5/25	1.4	1.1	1.6	1.3	0.6	1.7
62.5/12.5/25	0.7	0.6	0.9	0.7	0.4	1.0
57.5/17.5/25	0.8	0.5	0.8	0.7	0.3	0.8
50/25/25	0.7	0.4	0.6	0.6	0.3	0.7
40/35/25	0.5	0.4	0.6	0.5	0.3	0.6

Measured by SEM on extruded strand.

<sup>a</sup> C = compatibilizer type; A1 . . . A3 and B1 . . . B3.



**Figure 1** SEM picture of incompatibilized PP/PA system.

### Sample Preparation and Characterization

A systematic chemical and mechanical characterization of the blends was undertaken using rheologic, microscopic, and mechanical testing. Melt viscosity was analyzed using a Bohlin CSM rheometer equipped with 25-mm parallel plates and a 1-mm gap setting. The rheometer was modified to reduce polymer degradation during analysis by applying a nitrogen gas blanket outside the analysis cell.

Blend morphology was investigated with a scanning electron microscope (SEM), JEOL T 300. The micrographs were taken of extrudates collected from the TSE. The samples for SEM were prepared by fracturing at liquid nitrogen temperature and then were gold-plated before microscopy. The average particle size was determined using image analysis techniques.

Test samples for tensile and some of the impact testing samples were injection-molded on an Arburg 150-45 allrounder 170 CMD injection-molding machine. Molding temperature was 250–280°C, and all samples were molded at the same conditions. The samples were dried at 80°C for 12 h prior to injection molding. Tensile specimens of a dogbone type and impact testing discs of 2 mm were molded.

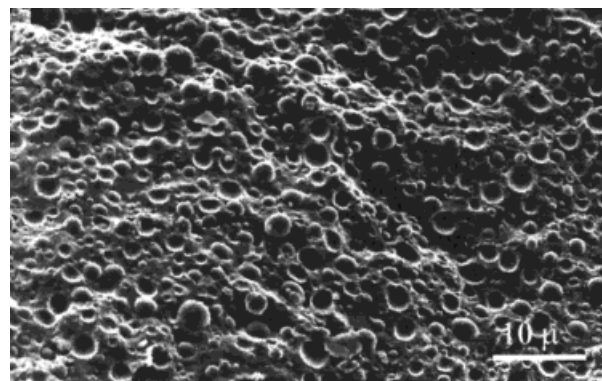
Tensile testing was performed with a Zwick tensile tester 1445 according to ISO R 527. Test temperature was 23°C. Impact testing was conducted on a Rosand instrumented falling weight impact tester, type 5, according to ISO 6603/1. Samples were tested at 0°C. The injection-molded samples were dried at 80°C for 12 h prior to testing and stored in sealed bags until testing.

## RESULTS AND DISCUSSION

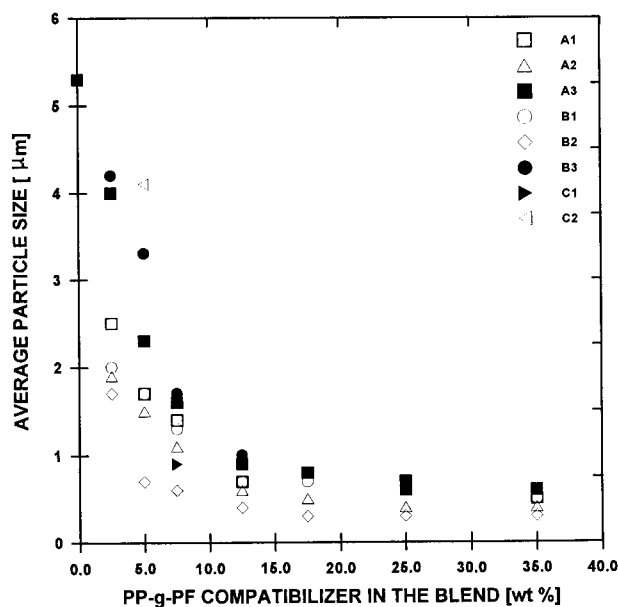
### Particle Size of Different PP/PA Blends

The uncompatibilized blend of PP/PA had a coarse morphology with an average particle size of 5.3 microns (Fig. 1). Some very large particles were also observed in the micrograph. The SEM micrograph was taken on fractured surfaces of the extrudate before undergoing any postprocessing. This large average particle size confirmed the incompatibility of the two components. In the compatibilized blends, the PA was well dispersed into the PP phase as small spherical particles. Blends prepared with a 2.5 wt % PP-*g*-PF compatibilizer resulted in fairly uniform PA particles ranging from 1.7 to 4.2  $\mu\text{m}$ , depending on the type of compatibilizer. Further increase in either compatibilizer concentration gave a pronounced decrease in the PA particle size, until a plateau of 0.3–0.6  $\mu\text{m}$  was reached. Further increase in the compatibilizer had no effect on the PA particle size.

Figure 2 shows a PP/PA blend compatibilized with 7.5 wt % of the compatibilizer B1. The particle-size development for each compatibilizer is summarized in Figure 3. It is evident that there was an effect of the type of compatibilizer. According to Figure 3, the most efficient compatibilizer was B2, having a low molecular weight PP backbone and a high content of the high molecular weight PF polymer part. Also, A2 and C1 were observed to be efficient compatibilizers for this PP/PA system, the first one (A2) being a low molecular weight PP backbone with a low content of high molecular weight PF, and the second a PP with high functionality and high viscosity. Further interpretation of the figure also shows that



**Figure 2** SEM picture of compatibilized PP/PA system.



**Figure 3** PA average particle size as a function of PP-g-PF content in the blend.

compatibilizers consisting of low molecular weight PF did not work as efficiently as did those based on high molecular weight PF. PF (C2) alone did not work very well.

#### Mechanical Properties of Different PP/PA Blends

The mechanical properties of the starting PP polymers and the compatibilizers are not very different. Therefore, when replacing PP with up to 35 wt % PF, only minor changes in the mechanical properties will take place. This was also observed in a PP/PP-g-PF system. The elastic modulus of an extruded neat PP P 410 H was 1050 MPa, and of a similar PP with 25 wt % PP-g-PF of B3 grade, 1107 MPa.

In Figure 4, the impact strength is plotted as a function of the average particle size for various types of PP-g-PF compatibilizers. The calculated impact strength from the "rule of mixture" for a PP/PA 75/25 blend is also included in the figure. Normally, with such immiscible blends, the impact strength is the weakest property due to the lack of sufficient dispersivity and interface adhesion. The PA particles behave as voids without any stronger interaction at the particle interface. The role of the blend composition and compatibilization is therefore essential for the final mechanical properties. The observed impact strength (Fig. 4) is very dependent on the average particle size at least up to 4–5 microns. Further

increase in the particle size seems to have less effect on the impact strength. The particle size of 5.3 microns corresponds to the incompatibilized blend.

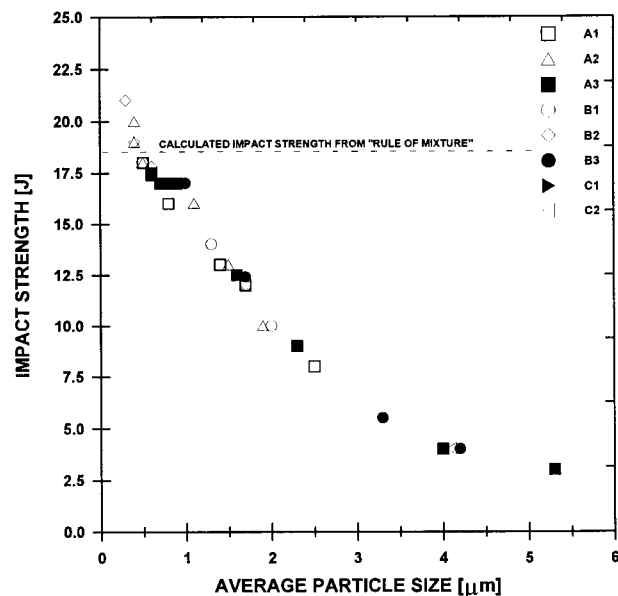
Two of the compatibilizers gave improved impact strength as compared to the calculated additive impact strength. In this case, the compatibilizers created an ideal polymer alloy with synergistic behavior in a property. In the best cases, an impact strength of more than 20 J, measured as total energy by the falling weight method, was achieved.

In Figure 5, the tensile modulus is similarly plotted as a function of the average particle diameter. The calculated tensile modulus for PP/PA 75/25 is also included in the figure. It is evident that the tensile modulus was determined by the PA particle size. In this case, almost all blends gave higher than the calculated tensile modulus. All recipes except the incompatibilized blends, having the particle size of 5.3 microns, had higher tensile stiffness than that of the additive relationship.

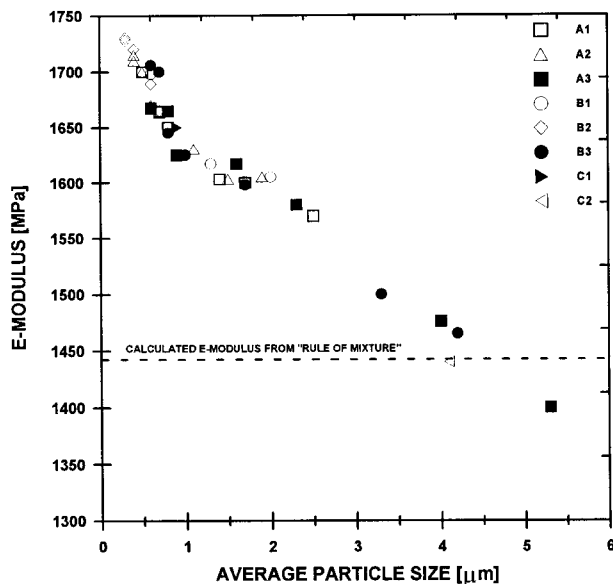
Both mechanical results indicate that the average particle size is important for performance. No direct effect of the type of compatibilizer was observed and only indirectly by compatibilizers having different abilities to stabilize.

#### Critical Surface Concentration

By *critical surface concentration* (CSC) is meant the necessary amount of compatibilizer for ad-



**Figure 4** Impact strength as a function of particle size for various compatibilizers.



**Figure 5** Elasticity modulus as a function of particle size for various compatibilizers.

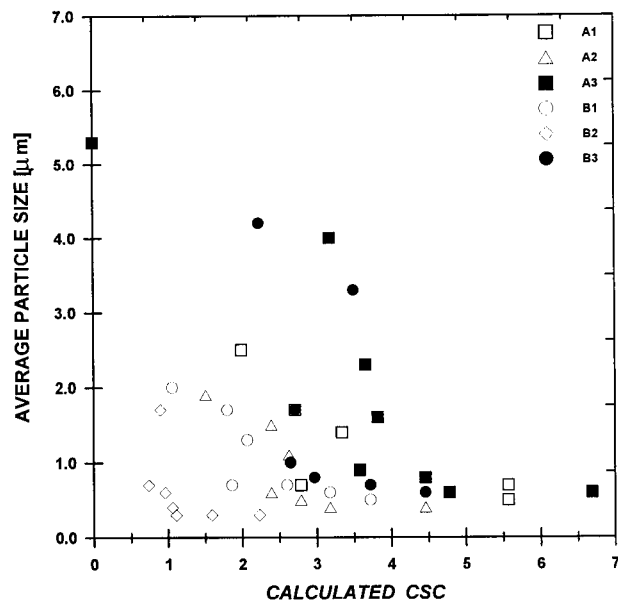
sorption of one *monolayer* of compatibilizer molecules on the dispersed polymer surface. Such calculations are very common in the science of surface and colloid chemistry. The calculations are based on the effective area of adsorption for the compatibilizer molecule calculated from the hydrodynamic radius ( $r_h$ ) and the total area to be stabilized. Examples of the calculation of the hydrodynamic radius and relevant input data for the calculations can be collected from the *Polymer Handbook*.<sup>7</sup> Characteristic data at  $\theta$  conditions were used for the calculations. A CSC of 1 means that the PA surface is being 100% covered by the compatibilizer molecules. A CSC of  $> 1$  means more than 100% is covered or more than monolayer adsorption. Similarly, a CSC  $< 1$  means that the surface is not completely covered or stabilized. In the calculations used in this article, all compatibilizers are considered to be at the PP/PA interface and not as clusters or micelles distributed in the PA or PP phase. This will, of course, represent a simplification of the system.

The average PA particle size is plotted versus the calculated CSCs in Figure 6. By this method, efficient compatibilizers is located in the lower left corner, where smaller particle sizes are achieved at lower calculated levels of the compatibilizer at the surface. Similarly, the least efficient ones are found in the upper-right corner. For these compatibilizers, finer morphology is only obtained at higher compatibilizer loadings. Ac-

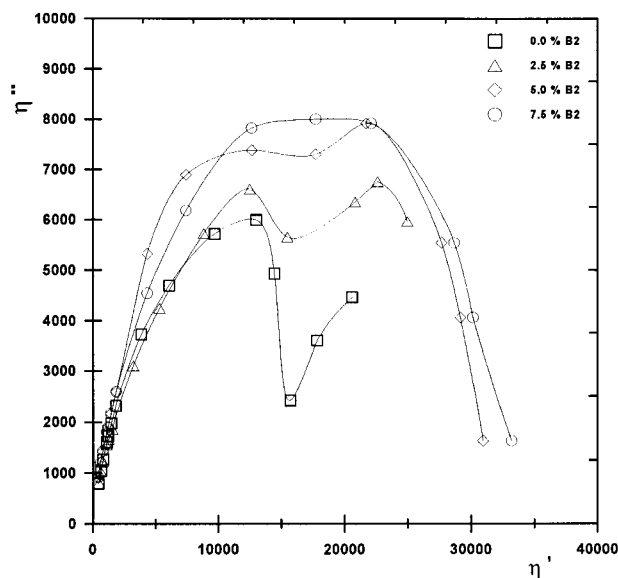
ording to this, it is evident that the most efficient PP-g-PF compatibilizer is B2, as described earlier. The second best are B1 and A2.

### Rheology of PP/PA Blends

The rheological properties of a blend are associated with the phase morphology. Rheological Cole–Cole plotting is method of presenting and determining the compatibilizer efficiency.<sup>8–10</sup> By this method, the loss modulus ( $G''$ ) is plotted as a function of the elastic modulus ( $G'$ ) or, more commonly, the imaginary viscosity ( $\eta'' = G''/\omega$ ) is plotted as a function of the real part,  $\eta' = G'/\omega$ , where  $\omega$  is the angular frequency. A continuous or homogeneous system is represented as one uniform half-circle. For immiscible blends, the continuity is broken and more than one circle may be observed. A Cole–Cole plot for PP/PA with 0, 2.5, 5, and 7.5 wt % of the compatibilizer is presented in Figure 7. Compatibilizer B2 was used. The effect of compatibilization on the rheological behavior was significant. Without the compatibilizer, the Cole–Cole curve is almost like two half-circles, while the half-circle uniformity was more pronounced with increasing compatibilizer content. This result is consistent with the observed reduction in particle size for increased PP-g-PF content and also indicates that the system will be near-homogeneous when the particle size is reduced to a level of less than 1 micron.



**Figure 6** Average particle size as a function of the calculated CSC.



**Figure 7** Cole–Cole plot of PP/PA (75/25) at various PP-g-PF concentrations.

The observed effect of the compatibilizer could be explained by the compatibility of the PF part with the polar group containing polymers like polyamide. This miscibility with PA is due to stronger interactions; covalent bonding is possible between the PA end-group carboxylic acids and the PF end-group hydroxyls. In addition, due to the high content of —OH in the PF backbone, hydrogen bonding is also possible.

## CONCLUSIONS

Compatibilizers based on PP and PF (PP-g-PF) were suitable for blends or alloys of PP and PA6. Blends of isotactic PP and PA6 were well compatibilized by PP-g-PF. The PP-g-PF compatibilizer consisting of a low molecular weight PP backbone and with a high content of the high molecular weight PF part was observed to be the most efficient combination. A significant reduction in the average particle size was observed, and, correspondingly, the mechanical properties were improved. The effect of the compatibilizer was also observed by a rheological Cole–Cole plot.

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## NOMENCLATURE

### Symbol

### Abbreviation Description

PP	polypropylene
PF	phenol formaldehyde resin
PA	polyamide
PA6	polyamide 6
MAH	maleic anhydride
GMA	glycidyl methacrylate
PP-g-MAH	MAH-grafted PP
PP-g-GMA	GMA-grafted PPT
PP-g-PF	PP-graft-PF compatibilizer
A1	PP-g-PF; low $M_n$ PP and low content of low $M_n$ PF
A2	PP-g-PF; low $M_n$ PP and low content of high $M_n$ PF
A3	PP-g-PF; high $M_n$ PP and low content of low $M_n$ PF
B1	PP-g-PF; low $M_n$ PP and high content of low $M_n$ PF
B2	PP-g-PF; low $M_n$ PP and high content of high $M_n$ PF
B3	PP-g-PF; high $M_n$ PP and high content of low $M_n$ PF
C1	PP-g-MAH; high MAH content and high $M_n$
C2	PF; high $M_n$ PF

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