Relationship Between Morphology and Mechanical Properties of Binary and Compatibilized Ternary Blends of Polypropylene and Nylon 6

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SYNOPSIS

The effect of compatibilization on the morphology, mechanical properties, and dynamic mechanical properties of isotactic polypropylene (IPP)/nylon-6 (Ny-6) binary blends was investigated. Maleic anhydride (MAH) functionalized IPP was used as a compatibilizer in binary blends. The morphological, mechanical, and dynamic mechanical properties of binary and ternary blends were compared. The blends containing IPP-g-MAH showed more regular and finer dispersion of phases, different dynamic properties, and improved mechanical properties due to better adhesion between the two phases. The blends were also characterized for their flow properties and extent of water absorption. The melting peak temperature and percent crystallinity of IPP and Ny-6 phases were decreased in compatibilized blends. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

As a cost effective means, polymer blends are becoming an increasingly important area of polymer science and technology.[1,2] Although most polymers are thermodynamically immiscible, such heterogeneous multicomponent polymer mixtures combine the most desirable properties of both polymeric components and also display some new features due to the particular phase morphology. But improvement of physicomechanical properties of such blends depends to a large extent on the size and shape of the dispersed phase. Therefore, it is of prime importance to control the phase morphology in immiscible blends.

It is well known that this control can be achieved by introducing a graft or block copolymer with segments capable of specific interactions with the blend components. Blending has been done for years to improve the performance of commodity and engineering plastics to achieve wider applications. Isotactic polypropylene (IPP) is the most important

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commodity plastic among the polyolefins because of its intrinsic properties, but its high permeability to organic solvents and vapor limits its potential.[3,4] Nylon-6 (Ny-6) is an engineering plastic of great industrial importance, but it has some limitations in its end uses, such as poor dimensional stability and poor barrier properties to moisture. It is also relatively expensive. Attempts have been made to prepare compatible blends of PP and Ny-6. Ide and Hasegawa[5] achieved compatibility in PP/Ny-6 blends using PP-g-maleic anhydride (MAH) as a compatibilizer. Similar compatibilization by adding functionized PP copolymers was also reported for polyolefin-polyamide blends by other researchers.[6–8]

However, the graft copolymers (PP-g-MAH) used as compatibilizers were with ~ 3% grafting.[9] We report PP-g-MAH with ~ 5% grafting.[10] In this article we examine the potential of PP-g-MAH prepared in our laboratory in PP/Ny-6 blends.

EXPERIMENTAL

Materials

The IPP M 0030 Koylene (density 0.9 g/cm^3 and melt flow index, MFI, 10.0 g/10 min) was supplied

by Indian Petrochemical Co. Ltd. (Vadodara, India). Ny-6 M 28 RC Gujlon with 1.125 g/cm^3 density and MFI 30.0 g/10 min was supplied by Gujarat State Fertilizer Company Ltd. (Vadodara, India). Details about the synthesis of PP-g-MAH used as a compatibilizer in the preparation of blends was reported earlier.[10] Graft copolymer with 5.32 wt % MAH was used as compatibilizer.

Blend Preparation

A Brabender plasticorder system coupled with single screw extruder (L/D = 20) was used for the preparation of blends. Ny-6 granules were dried at 110°C for 3 h prior to blending. The binary and ternary blends (i.e., compatibilized blends) were prepared by the single step melt mixing technique. The temperature of the extruder was maintained at 190, 220, and 235°C and die temperature was at 230°C. The screw speed was maintained at 30 rpm. The various compositions used for the blends under investigation are reported in Table I. The dried compounded pellets were injection molded to obtain test specimens for measurement of tensile properties, Izod impact strength, thermal properties, water absorption, and dynamic mechanical properties.

Measurements

The tensile properties measurements of the dumbell shaped samples were carried out following the ASTM D638 procedure. The flexural measurements were carried out following the procedure discussed in ASTM D790 using the 3-point loading system. The impact strength was measured following the procedure described in ASTM D256.

All the specimens used for the water absorption measurement had dimensions of about 6.1 × 2.0 × 0.3 cm. Test samples were dried prior to measurements and the test was carried out as reported earlier.[11]

The thermal analysis was carried out using a Delta Series DSC-7. To avoid any effect of moisture, all the samples were vacuum dried prior to the measurements. The melting temperatures were determined by performing a temperature sweep from 25 to 250°C at a heating rate of 10°C/min. The percent crystallinity was calculated using the following equation[11]:

$$\% \text{ crystallinity} = \frac{\Delta H_f^*}{\Delta H_f^\circ} \times 100$$

where ΔH_f^* is the heat of fusion for PP or Ny-6 in the corresponding blend and ΔH_f° is the heat of fusion of 100% crystalline PP or Ny-6 and was taken as ΔH_f° (Ny-6) = 45.6 cal/g and ΔH_f° (PP) = 50 cal/g from the literature.[5,12]

A scanning electron (SE) microscope (JEOL JSM 35 C) was used to examine the morphology of the blends. The specimens were broken under liquid nitrogen and fractured surfaces were gold coated and observed under an electron microscope.

The dynamic mechanical analysis was carried out on a Rheometrics Dynamic Spectrometer (RDS, NJ). The testing was carried out in 3-point bending (flexural) mode. The temperature ranges were 20–140°C. The static and dynamic loads were 2 and 1 kg, respectively. The magnitude of dynamic moduli (E'') and tangent of the phase angle (tan δ = E''/E')

Table I Various Compositions of Blends

Code No.	PP (wt %)	Ny-6 (wt %)	PP-g-MAH (wt %)	Code No.	PP (wt %)	Ny-6 (wt %)	PP-g-MAH (wt %)
PP	100	—	—	C$_1$	71.4	23.8	4.8
A$_1$	75	25	—	C$_2$	57.1	38.1	4.8
A$_2$	60	40	—	C$_3$	47.6	47.6	4.8
A$_3$	50	50	—	C$_4$	38.1	57.1	4.8
A$_4$	40	60	—	C$_5$	23.8	71.4	4.8
A$_5$	25	70	—				
Ny-6	—	100	—	D$_1$	68.2	22.7	9.1
				D$_2$	45.5	45.5	9.1
B$_1$	73.2	24.4	2.4	D$_3$	22.7	68.2	9.1
B$_2$	58.5	39.0	2.4				
B$_3$	48.8	48.8	2.4				
B$_4$	39.0	58.5	2.4				
B$_5$	24.4	73.2	2.4				

were measured at every 5°C with increasing temperature.

RESULTS AND DISCUSSION

PP and Ny-6 are incompatible. When PP-g-MAH is added to PP/Ny-6 blends, the anhydride group of MAH reacts with the terminal amino group of Ny-6 during melt mixing, resulting in the formation of PP-g-Ny-6 copolymer.[13]
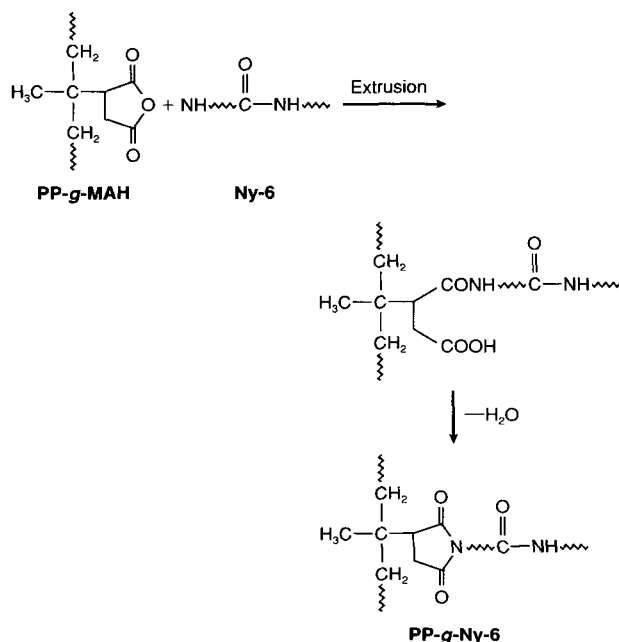
The activity of the PP-g-MAH as a compatibilizer was confirmed by the following tests.

Molau's Test

When formic acid was added to PP/Ny-6 binary blends, the Ny-6 was dissolved completely within 1–3 h while the PP phase separated and floated on the top, indicating poor adhesion between the two phases.[14] The PP/Ny-6/PP-g-MAH blends give rise to a stable emulsion in formic acid. According to Molau,[14] this result can be taken as an indication for the formation of PP-g-Ny-6 in PP/Ny-6/PP-g-MAH blends, which acts as an interfacial agent.

Morphology

SE micrographs of fractured surfaces prepared at a liquid nitrogen temperature show lack of interfacial adhesion in the binary blends of PP/Ny-6 (75 : 25
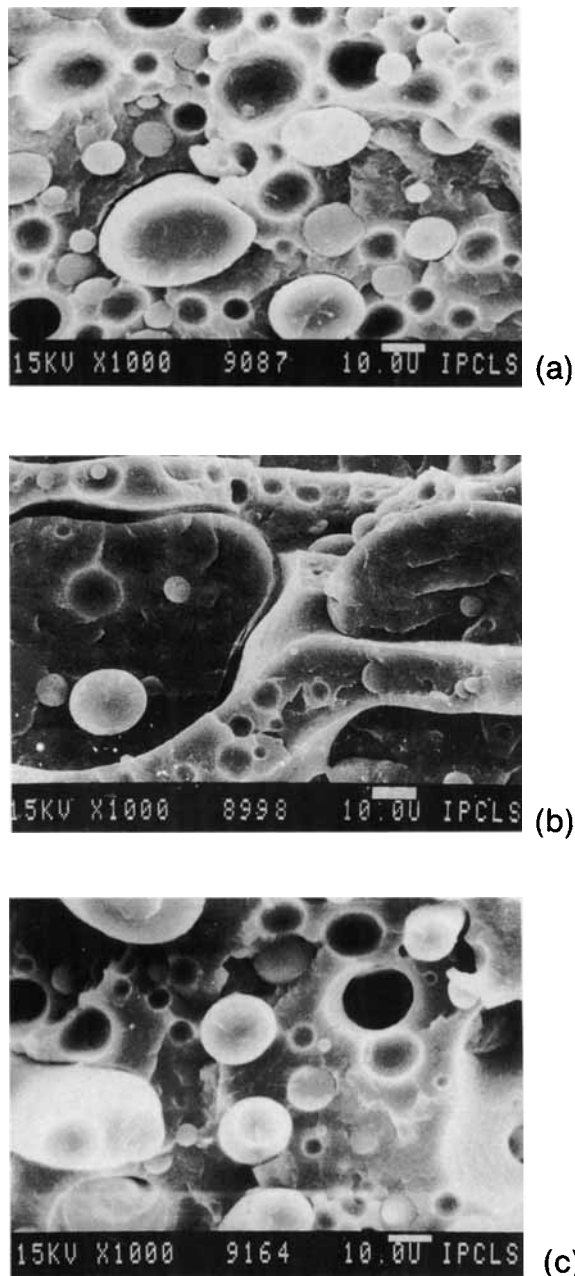
Figure 1 SE micrographs of binary PP/Ny-6 blends: (a) 75 : 25, (b) 60 : 40, (c) 25 : 75 (×1000).

and 25 : 75) as shown in Figure 1 (a,c). In both cases the dispersed phase particles are large and irregularly shaped and have relatively smaller contact areas with the matrix. The PP/Ny-6 blends of 60 : 40 ratio [Fig. 1(b)] show a cocontinuous two-phase interpenetrating morphology. This was also observed in the 50 : 50 blend composition.

For PP/Ny-6/PP-g-MAH (2.4 wt %) blends a drastic reduction in particle size of the dispersed phase was observed [Fig. 2(a,c), Table II] that
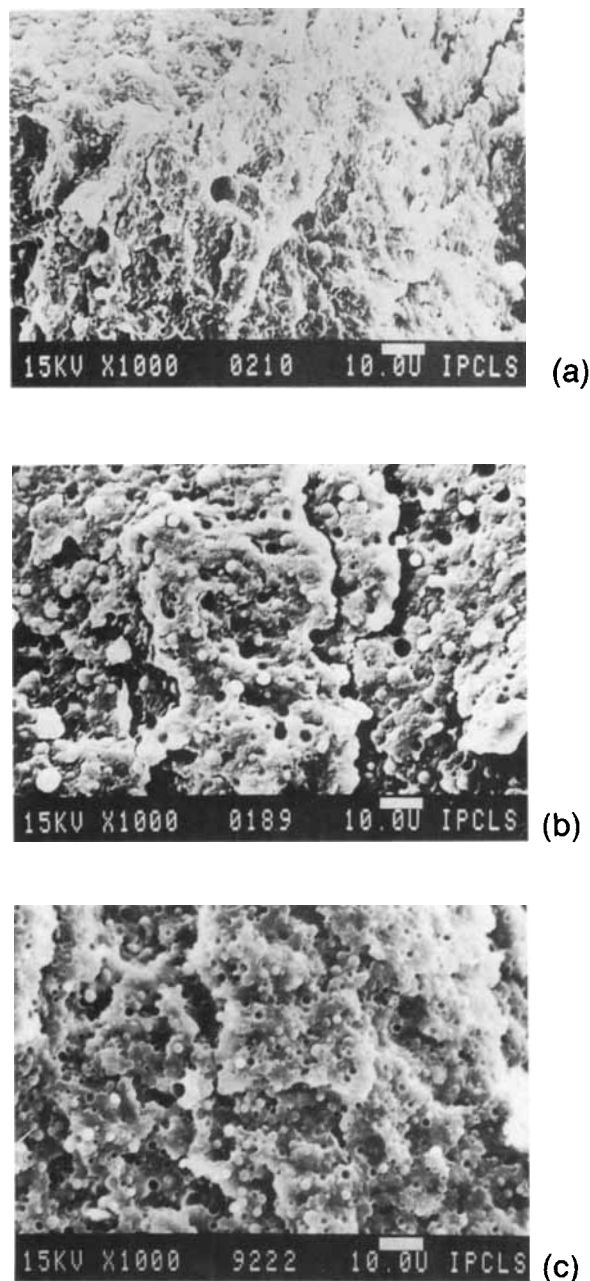
(a)

(b)

(c)

Figure 2 SE micrographs of ternary PP/Ny-6/PP-g-MAH blends: (a) B_1, (b) B_2, (c) B_5 ($\times 1000$).

shows increased adhesion between the PP and Ny-6 phases. Homogenity of dispersion and decreased size of the dispersed phase in ternary blends increases the surface area in contact with the matrix, resulting in better adhesion of the dispersed phase and the matrix. In 60/40 (PP/Ny-6) blends the cocontinuous structure changes to two-phase morphology with a reduction in the disperse phase size [Fig. 2(b)]. In the blends containing 4.8 and 9.1 wt % PP-g-MAH copolymer at the 1,000$\times$ magnifica-

Table II Accuracy and Precision of SEM Results

Code No.	30 Measurements for		
	Mean Diameter of Domains	Average Deviation	Standard Deviation
A_1	25.40	0.012	3.126
A_5	20.42	0.052	2.590
B_1	0.89	0.089	0.368
B_5	0.54	0.024	0.148
D_3	1.5	0.017	0.246

The particle size measurement for C_1 and C_5 were not possible.

tion, dispersed particles are not seen [Figs. 3(a,b), 4]. The morphology of these ternary blends looks very homogeneous, indicating the strong interaction and adhesion between the PP and Ny-6 phases due to the presence of reactive MAH groups.

For the measurement of actual partical size of the dispersed phase, the PP phase from the binary and ternary blends was selectively extracted with hot xylene in Ny-6 rich blends. Figure 5(a-d) shows the SE micrographs of PP/Ny-6 binary (25/75)
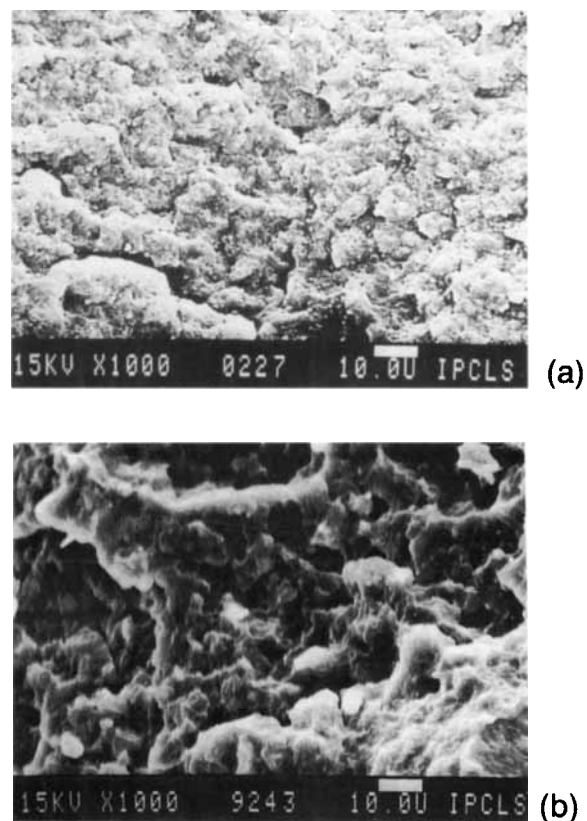

(a)

(b)

Figure 3 SE micrographs of ternary PP/Ny-6/PP-g-MAH blends: (a) C_1, (b) C_5 ($\times 1000$).
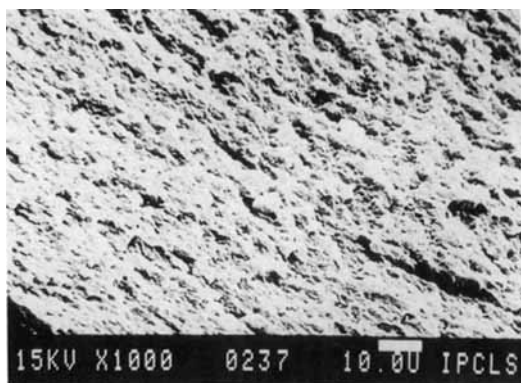
**Figure 4** SE micrographs of ternary PP/Ny-6/PP-*g*-MAH blend D$_3$ (×1000).

blends and corresponding ternary blends with 2.4, 4.8, and 9.1 wt % PP-*g*-MAH copolymer, respectively. The holes in the figures are the areas from which the PP was extracted and remaining material is Ny-6. The particle size dimensions are given in Table II.

It is observed from Figure 5(a) that in case of 25/75 PP/Ny-6 binary blend, the holes are of ir-

regular shape and size. The observed average particle size was ∼ 20–30 µm. In blends compatibilized with 2.4 wt % [Fig. 5(b)] PP-*g*-MAH copolymer, the particle size was drastically decreased due to the strong adhesion between PP and Ny-6. The average diameter was ∼ 1–2 µm. In the blends containing 4.8 wt % PP-*g*-MAH copolymer [Fig. 5(c)], no such holes were observed at 1,000× magnification; in blends containing 9.1 wt % PP-*g*-MAH [Fig. 5(d)], holes were observed with average diameter of ∼ 1.5 µm. These results confirm the interaction between PP, Ny-6, and PP-*g*-MAH during melt mixing; and the extent of the interaction is maximum at 4.8 wt % concentration of PP-*g*-MAH compatibilizer. Compatibilizer acts as a bridge between two incompatible phases at the interface. Hence for compatibilizer effectiveness optimum concentration is required. As the concentration increases from 2.4 to 4.8%, the extent of compatibilization and hence dispersion increases; but at 9.1% concentration, the excess compatibilizer does not find a place at the interface of PP and Ny-6 and hence remains either in PP or Ny-6 alone. Hence effective concentration
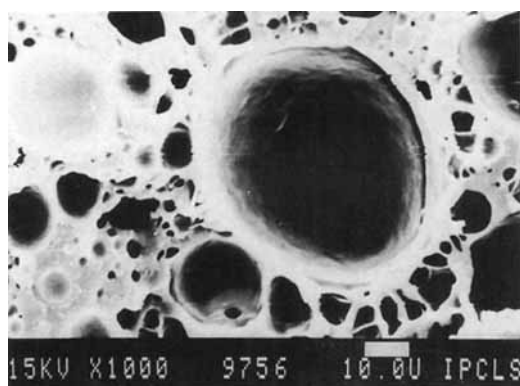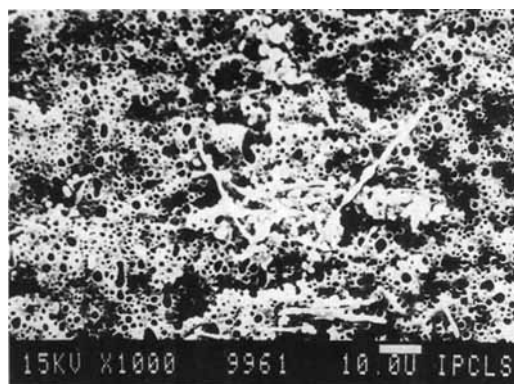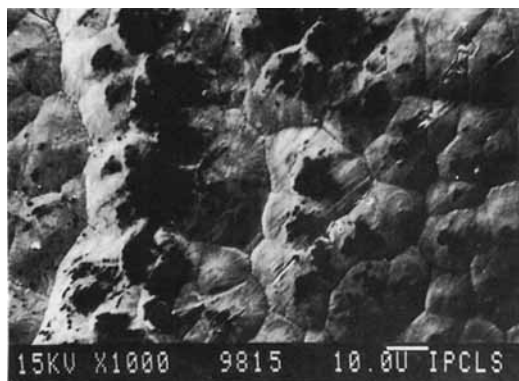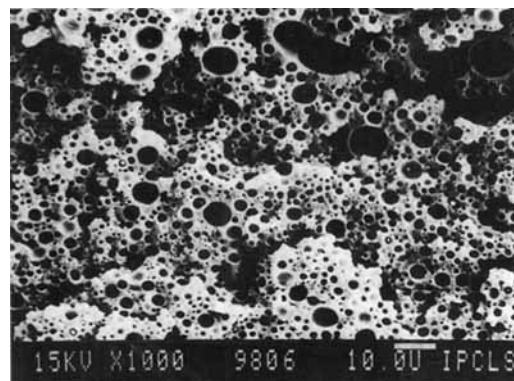

Figure 5 SE micrographs of blends etched with hot xylene: (a) A$_5$, (b) B$_5$, (c) C$_5$, (d) D$_3$ (×1000).

available for the compatibilization decreases, affecting the overall dispersion.

Tensile Mechanical Properties

Typical stress–strain curves for PP and Ny-6 homopolymers and for binary PP/Ny-6 and ternary PP/Ny-6/PP-g-MAH blends are given in Figure 6. From the figure it can be inferred that necking behavior was decreased in binary and ternary blends. Figures 7–9 show the effect of blend composition on the tensile modulus, tensile strength, and flexural strength of binary PP/Ny-6 blends and ternary PP/Ny-6/PP-g-MAH (2.4, 4.8, and 9.1 wt %) blends, respectively. It was observed that the performance of PP/Ny-6 blends is strongly influenced by the addition of PP-g-MAH (2.4, 4.8, and 9.1 wt %). In general, improvement in all these properties was observed for ternary blends containing PP-g-MAH copolymer when compared with the corresponding binary PP/Ny-6 blends. On comparison with corresponding PP/Ny-6/PP-g-BA blends,[15,16] it was observed that PP/Ny-6/PP-g-MAH blends show higher tensile modulus, tensile strength, and flexural strength. This may be attributed to improved homogeneity due to the presence of the more reactive MAH groups of the PP-g-MAH copolymer. Improved homogeneity is also seen from the SE micrographs (Figs. 2, 3).

Also observed from Figures 7–9 is that the tensile mechanical properties go on increasing with increasing concentration of compatibilizer up to 4.8
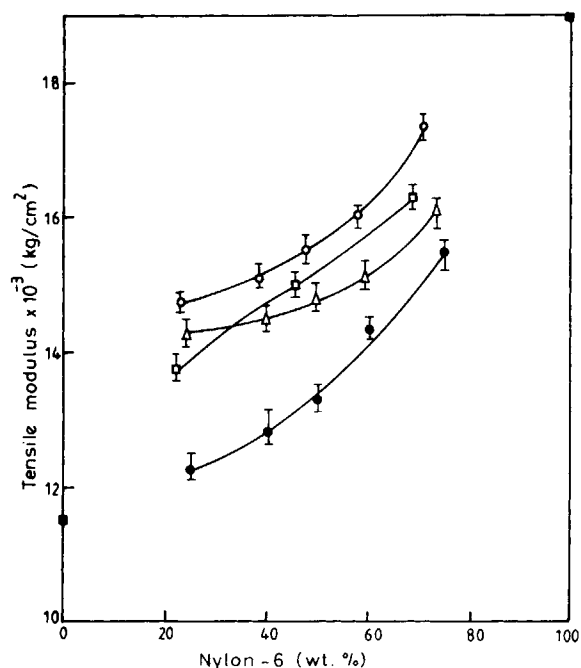

Figure 7 Tensile modulus versus weight percentage of Ny-6: (●) PP/Ny-6; (△) PP/Ny-6/PP-g-MAH (PP-g-MAH = 2.4 wt %); (○) PP/Ny-6/PP-g-MAH (PP-g-MAH = 4.8 wt %); (□) PP/Ny-6/PP-g-MAH (PP-g-MAH = 9.1 wt %).

wt %. On further addition of the compatibilizer (9.1 wt %), a relative decrease in these properties was observed. This may be due to the plastisization effect at higher concentration of compatibilizer due to de-
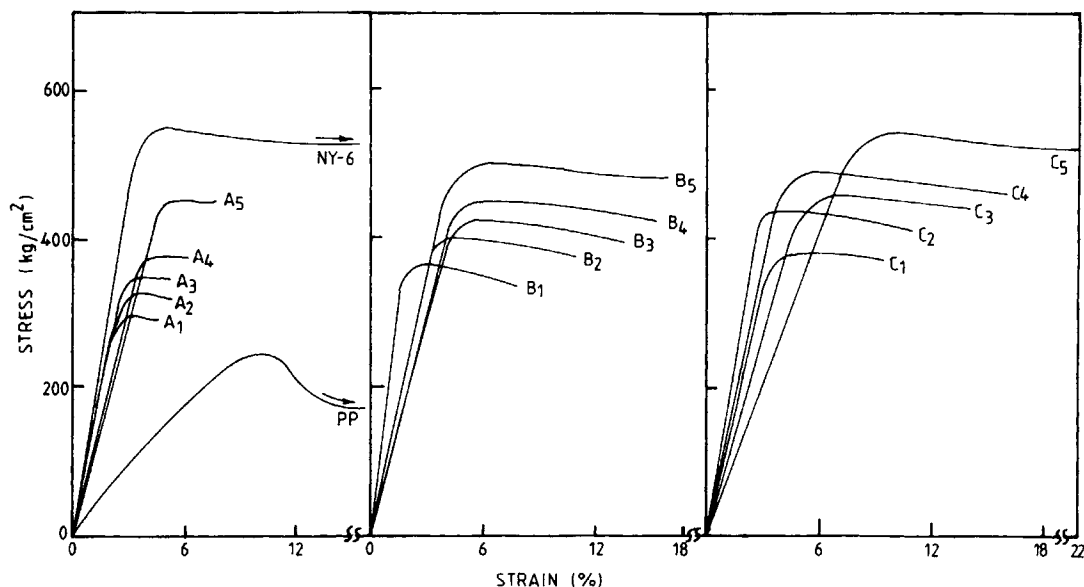

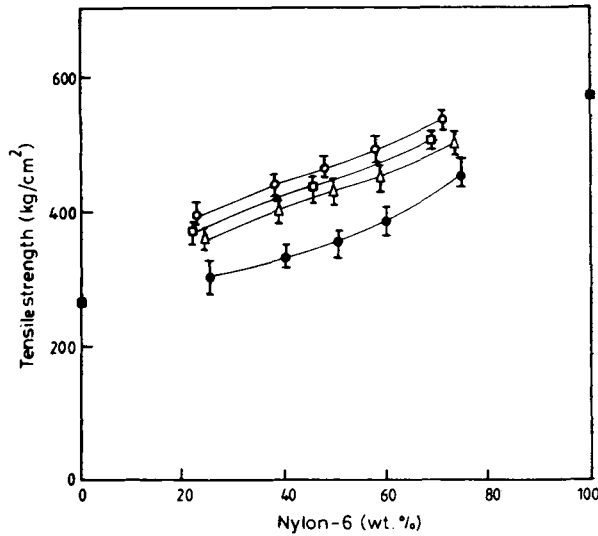**Figure 6** Stress–strain curves for binary and ternary blends.

Figure 8 Tensile strength versus weight percent of Ny-6: (●) PP/Ny-6; (△) PP/Ny-6/PP-g-MAH (PP-g-MAH = 2.4 wt %); (○) PP/Ny-6/PP-g-MAH (PP-g-MAH = 4.8 wt %); (□) PP/Ny-6/PP-g-MAH (PP-g-MAH = 9.1 wt %).

Figure 9 Flexural strength versus weight percent of Ny-6: (●) PP/Ny-6; (△) PP/Ny-6/PP-g-MAH (PP-g-MAH = 2.4 wt %); (○) PP/Ny-6/PP-g-MAH (PP-g-MAH = 4.8 wt %); (□) PP/Ny-6/PP-g-MAH (PP-g-MAH = 9.1 wt %).

creased availability of compatibilizer as discussed earlier.

It was observed from stress–strain curves that the percentage elongation values of all the ternary blends are considerably higher than the corresponding PP/Ny-6 binary blends. The above observation may be ascribed to the fact that in the PP/Ny-6 blends the components are incompatible, with almost no mutual adhesion. Furthermore, the large size of dispersed particles probably hinders cold drawing of PP or Ny-6 matrix, causing the premature rupture of the material and lowering of the elongation values. The observed higher values of elongation of PP/Ny-6/PP-g-MAH blends can be explained on the basis of formation of PP-g-Ny-6 copolymer during melt blending, which is mostly located at the interface of PP/Ny-6, acting as an interfacial agent. Thus higher homogeneity is achieved with respect to PP/Ny-6 binary blends. This overall morphology probably contributes to a decrease of the high stress concentration around the dispersed particles by local plastic deformation and by making the system more efficient for cold drawing.

Impact Properties

From Figure 10 it is observed that all the blends of PP/Ny-6/PP-g-MAH have higher impact strength than corresponding PP/Ny-6 binary blends. Figure 1(a,c) shows the large size of the disperse phase with-
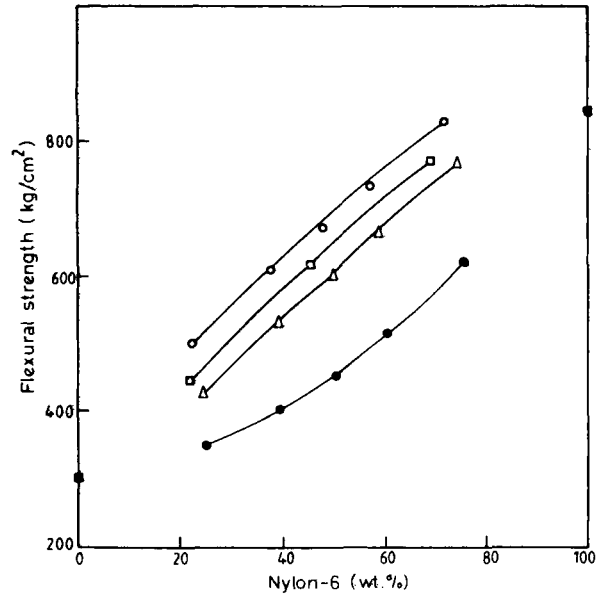

Figure 10 Impact strength versus weight percent of Ny-6: (●) PP/Ny-6; (△) PP/Ny-6/PP-g-MAH (PP-g-MAH = 2.4 wt %); (○) PP/Ny-6/PP-g-MAH (PP-g-MAH = 4.8 wt %); (□) PP/Ny-6/PP-g-MAH (PP-g-MAH = 9.1 wt %).

Figure 11   Melt flow index versus weight percent of Ny-6: (●) PP/Ny-6; (△) PP/Ny-6/PP-*g*-MAH (PP-*g*-MAH = 2.4 wt %); (○) PP/Ny-6/PP-*g*-MAH (PP-*g*-MAH = 4.8 wt %); (□) PP/Ny-6/PP-*g*-MAH (PP-*g*-MAH = 9.1 wt %).
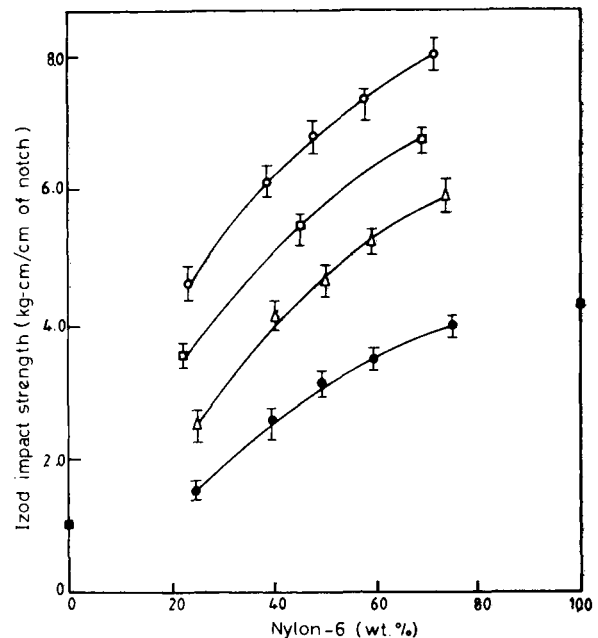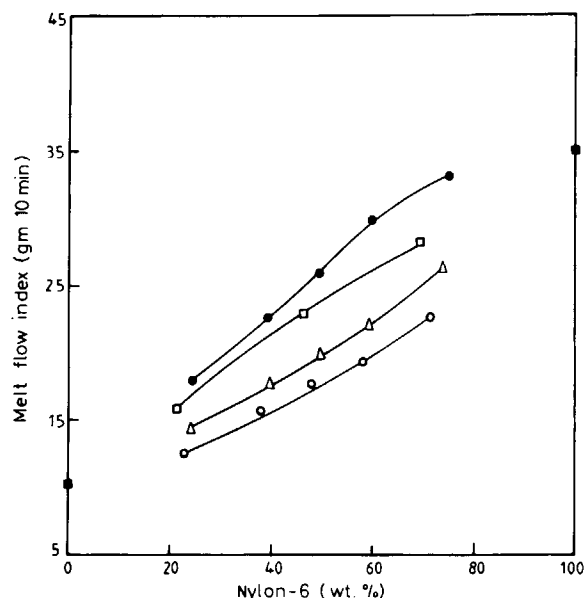
out any adhesion to matrix in PP/Ny-6 blends. Due to this morphology, a decrease in impact strength was observed. From Figures 2 and 3 it may be noted that addition of PP-*g*-MAH copolymer to a PP/Ny-6 blend results in almost homogeneous phase morphology [Figs. 3, 5(b,c)] with drastic reduction in the average dimension of the dispersed phase particles, causing an increase in the impact strength. But further increase in the compatibilizer concentration (9.1 wt %) decreases the impact strength due to the decreased availability of the compatibilizer for the compatibilization of PP and Ny-6.

MFI

From Figure 11 it can be inferred that all the blends have lower MFI than Ny-6. MFI of ternary blends (i.e., blends containing 2.4 and 4.8 wt % of PP-*g*-MAH copolymer) decreased with respect to the corresponding binary blends. The decrease in MFI can be attributed to the higher reactivity of MAH resulting in formation of higher PP-*g*-Ny-6 copolymer in the blends. However, the higher concentration of compatibilizer (9.1 wt %) shows an increase in MFI values than for 2.4 and 4.8 wt % compatibilized systems, emphasizing the optimum concentration of the compatibilizer in the blends.

Water Absorption

Figure 12 shows that all the ternary blends have lower percentage water absorption values than Ny-6 and PP/Ny-6 blends. Water susceptibility of Ny-6 is mainly due to the presence of amide/amine groups. In PP/Ny-6/PP-*g*-MAH blends, the AH groups of MAH interact with the amide/amine groups of Ny-6. As a result the number of free amide groups in PP/Ny-6/PP-*g*-MAH is reduced, which reduces the water susceptibility of Ny-6. When the water absorption of PP/Ny-6/PP-*g*-MAH blends is compared with that of previously reported PP/Ny-6/PP-*g*-BA blends,[15,16] it is observed that in PP/Ny-6/PP-*g*-MAH blend, although the highly water susceptible MAH is present, lower water absorption is observed than in PP/Ny-6/PP-*g*-BA blends. This can be attributed to the higher reactivity of MAH for Ny-6 resulting into the decreased availability of amine/amide groups from Ny-6 for water absorption.

Thermal Properties

The melting temperatures, determined from DSC thermograms, for binary PP/Ny-6 and ternary PP/Ny-6/PP-*g*-MAH blends are given in Table III. In binary PP/Ny-6 blends a decrease in melting point was not observed for the PP and Ny-6 components.
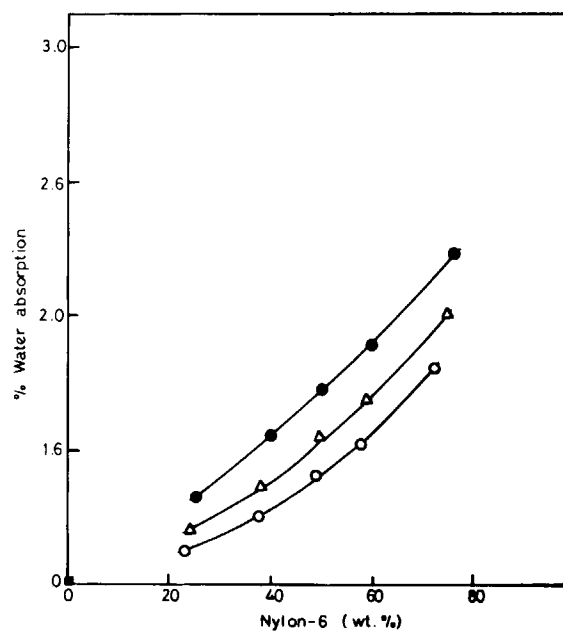

Figure 12   Percentage water absorption versus weight percent of Ny-6: (●) PP/Ny-6; (△) PP/Ny-6/PP-*g*-MAH (PP-*g*-MAH = 2.4 wt %); (○) PP/Ny-6/PP-*g*-MAH (PP-*g*-MAH = 4.8 wt %).

Table III Melting Temperature (T_m) and Percent Crystallinity of PP and Ny-6 Phases in Various Blends

Blend Code	T_m (°C)		% Crystallinity	
	PP	Ny-6	PP	Ny-6
PP	164.5	—	49.0	—
A_1	164.5	225.1	48.1	43.4
A_3	164.2	225.0	49.0	43.3
A_5	164.2	224.6	49.2	43.2
Ny-6	—	225.1	—	43.4
B_1	162.8	222.3	47.0	41.0
B_3	160.3	221.8	46.3	40.0
B_5	159.0	221.7	46.0	41.1
C_1	159.6	220.6	45.5	37.5
C_3	158.4	220.8	44.8	38.1
C_5	156.1	219.0	44.0	39.0

But in compatibilized blends, the melting temperatures of PP and Ny-6 components shifted to lower temperatures. This decrease is more pronounced in blends containing 4.8 wt % of PP-g-MAH copolymer.

The percent crystallinity of PP and Ny-6 phases in the blend is given in Table III. It is observed from Table III that the percent crystallinity of PP and Ny-6 phases in binary blends remains unaltered. But in ternary PP/Ny-6/PP-g-MAH blends, the percent crystallinity was lower than that in binary blends. As discussed earlier, PP-g-Ny-6 copolymer formed

during melt mixing hinders the polymer chain packing, resulting into reduced percent crystallinity. The observed higher reduction in the percent crystallinity of PP and Ny-6 phases in the blends containing 4.8 wt % of PP-g-MAH, can be attributed to the increased formation of graft copolymer and hence greater hindrance.

Dynamic Mechanical Properties

The temperature dependence of the dynamic loss moduli (E'') and loss factor (tan δ) at 6.3 rad s^{-1} for the binary (noncompatibilized) PP/Ny-6 blends (A_1, A_3, and A_5) are given in Figure 13(a,b), respectively, along with Ny-6 curves. The E'' and tan δ curves shown in Figure 13 for noncompatibilized blends exhibit fairly sharp relaxation peaks at 60°C as in virgin Ny-6, corresponding to the glass transition temperature of Ny-6. This indicates the weak mechanical interaction between PP and Ny-6 phases in binary blends.

Figure 14(a,b) summarizes the loss modules (E'') and tan δ data for blends containing 2.4 wt % PP-g-MAH copolymer. It is observed from the figure that the β relaxation (glass transition temperature) peak of the Ny-6 phase in the ternary blends tends to be broader. But in the blends containing 4.8 wt % PP-g-MAH copolymer [Fig. 15(a,b)] the β-transition peaks almost disappear, indicating the improvement in the compatibility between the PP and Ny-6 phases in the ternary blends.
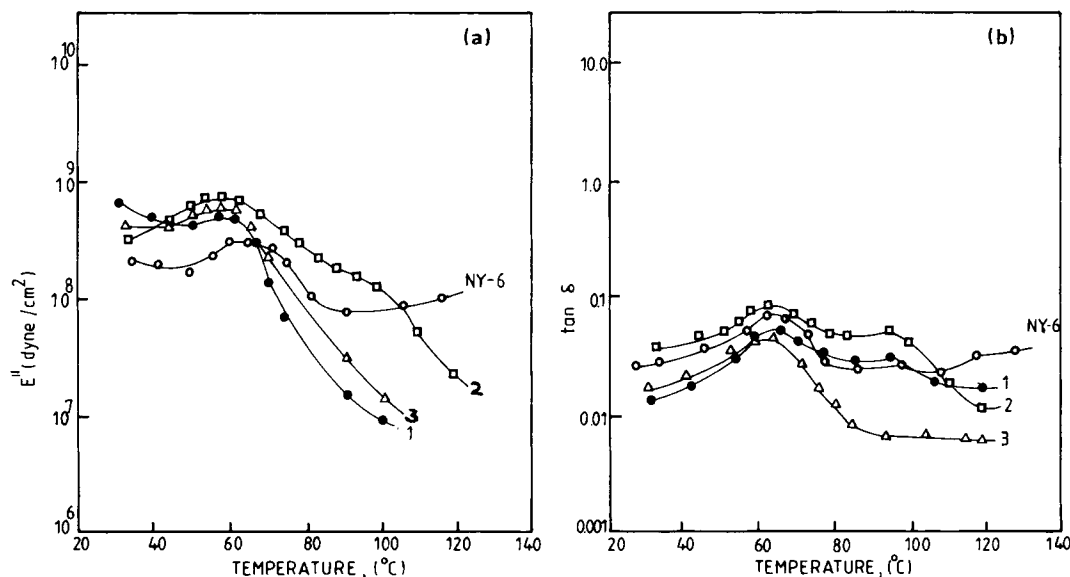

Figure 13 Temperature dependence of dynamic mechanical data for binary PP/Ny-6 blends: (a) loss modulii (E''): 1, A_1; 2, A_3; 3, A_5. (b) tan δ: 1, A_1; 2, A_3; 3, A_5.
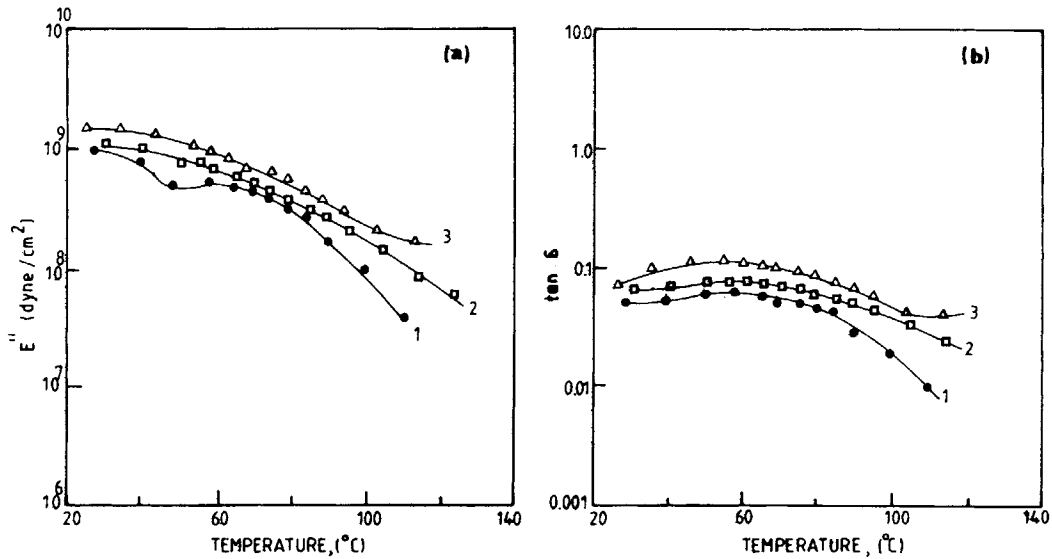
Figure 14 Temperature dependence of dynamic mechanical data for ternary PP/Ny-6/ PP-g-MAH (PP-g-MAH = 2.4 wt %) blends: (a) loss modulus (E''): 1, B_1; 2, B_3; 3, B_5. (b) tan δ: 1, B_1; 2, B_3; 3, B_5.

It is also observed from these figures that the loss modules (E'') and loss tangent (tan δ) are higher for the compatibilized blends than for mechanically blended polymers (binary blends). This may be due to the decrease in crystalline properties as discussed earlier. This suggests the good dispersibility of two phases in the amorphous areas in compatibilized blends. Similar results were obtained by Ide and Hasegawa.[5]

CONCLUSION

In this study it was observed that blending PP and Ny-6 with small amounts of PP-g-MAH copolymer (up to 10 wt %) as compatibilizer markedly influences the tensile modulus and strength of the blends. The morphology of blends indicates no phase separation, and finer dispersion and good adhesion was obtained for compatibilized blends. This resulted in
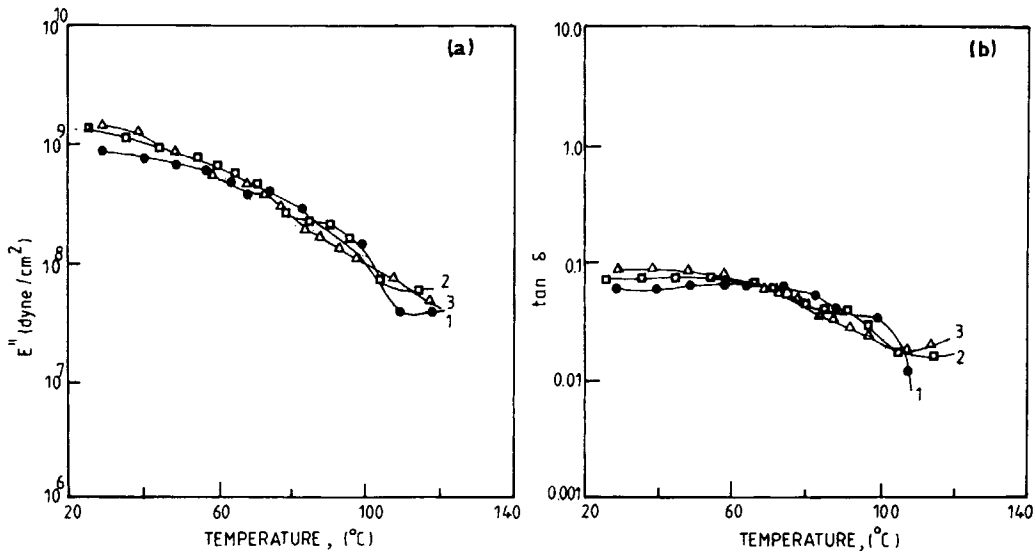

Figure 15 Temperature dependence of dynamic mechanical properties for ternary PP/ Ny-6/PP-g-MAH (PP-g-MAH = 4.8 wt %) blends: (a) loss moduli (E''): 1, C_1; 2, C_3; 3, C_5. (b) tan δ: 1, C_1; 2, C_3; 3, C_5.

lower MFI and water absorption properties due to formation of PP-g-Ny-6 copolymer during melt mixing. This was further confirmed by Molau's test. The 4.8 wt % PP-g-MAH was observed to be the optimal concentration for the PP/Ny-6 blend system.

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