

Compatibilization of Polypropylene/Nylon 6 Blends with a Polypropylene Solid-Phase Graft

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ABSTRACT: The compatibilization of polypropylene (PP)/nylon 6 (PA6) blends with a new PP solid-phase graft copolymer (gPP) was systematically studied. gPP improved the compatibility of PP/PA6 blends efficiently. Because of the reaction between the reactive groups of gPP and the NH₂ end groups of PA6, a PP-g-PA6 copolymer was formed as a compatibilizer in the vicinity of the interfaces during the melting extrusion of gPP and PA6. The tensile strength and impact strength of the compatibilized PP/PA6 blends obviously increased in comparison with those of the PP/PA6 mechanical blends, and the amount of gPP and the content of the third monomer during the preparation of gPP affected the mechanical properties of the compatibilized blends.

Scanning electron microscopy and transmission electron microscopy indicated that the particle sizes of the dispersed phases of the compatibilized PP/PA6 blends became smaller and that the interfaces became more indistinct in comparison with the mechanical blends. The microcrystal size of PA6 and the crystallinity of the two components of the PP/PA6 blends decreased after compatibilization with gPP. The compatibilized PP/PA6 blends possessed higher pseudoplasticity, melt viscosity, and flow activation energy. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 420–427, 2004

Key words: poly(propylene) (PP); nylon; blends; compatibilization

INTRODUCTION

As a cost-effective method, polymer blending is an increasingly important area of polymer science and technology. It is attracting growing interest for the preparation of new materials.^{1–3} However, most polymers are thermodynamically immiscible, so the desired properties cannot be obtained by a simple combination of two incompatible polymers. It is obvious that the proper choice of a suitable compatibilizer plays an important role in the improvement of material properties, and the compatibilization of immiscible blends has been the subject of research activity.^{4–6}

The role of a compatibilizer is especially important in the combination of a polar polymer and a nonpolar polymer, such as polypropylene (PP) and nylon 6 (PA6). PP and PA6 are two important classes of thermoplastics; blending PP with PA6 can overcome their drawbacks and lead to improved properties.^{7,8} However, the blending of PP and PA6 usually leads to macrophase separation, and the desired properties cannot be achieved without a compatibilizer. Blends of PP and PA6 can be compatibilized with polypropylene-graft-maleic anhydride (PP-g-MAH), polypro-

pylene-graft-acrylic acid, ethylene/butylene acrylate-graft-fumaric acid, and ethylene/ethyl acrylate-glycidyl methacrylate by reactive extrusion; PP is used to form a copolymer that improves the compatibility between the two components.^{9–12} In the interface, PA6 end groups are chemically reacted with functional groups on functionalized PP during melt mixing. The grafted copolymers that are formed *in situ* during compounding processes preferentially reside at the interface, improve interfacial adhesion through chemical linkages, and allow a finer dispersion and more stable morphology to be created.

One successful approach to the compatibilization of PP and PA6 blends is the use of PP-g-MAH as a compatibilizer.^{13–16} However, maleic anhydride (MAH) has a low boiling point and is toxic, so preparing PP-g-MAH by melt grafting can be difficult. The content of MAH in PP-g-MAH prepared by melt grafting is low because of bad self-polymerization; therefore, the use of PP-g-MAH as a compatibilizer for PP and PA6 blends has some limitations.

Solid-phase grafting, which has been widely used for the grafting modification of polymers, has many advantages over melt grafting.¹⁷ For example, to obtain high PP-graft-MAH copolymers, Xingwang¹⁸ and Yanmei¹⁹ studied the solid-phase grafting of mixed monomers, MAH and methyl methacrylate (MMA), onto PP. These PP solid-phase grafts have high levels

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of grafting and may be used as compatibilizers of PP/PA6 blends. However, there have been very few studies in which PP solid-phase grafts have been used as compatibilizers of PP/PA6 blends. In this work, the compatibilization of PP/PA6 blends with new PP solid-phase graft copolymers (gPP), PP-*graft*-MAH, MMA, and a third monomer, which was used to improve the mechanical properties of the PP/PA6 blends, was systematically investigated.

EXPERIMENTAL

Materials

PP was purchased from Panjin Chemical Factory (China). PA6 was purchased from Allied Signal Corp (USA). Blends of PP and PA6 were compatibilized with gPP, PP-*graft*-MAH, MMA, and a third monomer. gPP was synthesized in our laboratory, and the grafting percentage of gPP was measured by chemical analysis.²⁰ The grafting degree of gPP used in this study was 13.16%.

Preparation of the blends

PA6 was dried in a vacuum oven for 16 h at 80°C before blending. Blending was performed with a twin-screw extruder; the temperatures of the extruder were kept at 200, 210, 220, 230, 235, 240, and 240°C, temperature of the die was 235°C, and the screw speed was 240 rpm. The components were fed simultaneously. The dried compounded pellets were injection-molded to obtain test specimens.

Blend characterization

A systematic characterization of the blends was undertaken with mechanical, microscopic, and rheological analysis. Tensile tests were performed on an Instron 1122 universal testing machine according to GB1040-79. Impact strength tests were carried out with an X CJ-40 impact tester (Chengde, China) according to GB1043-79.

The IR spectrum of the compatibilized blends was monitored with a Nicolet 760 (USA). After the PA6 phase of the PP/PA6 (20/80) blend was selectively extracted with formic acid, the residue was pressed into a thin film with the addition of KBr for the measurements. The absorption spectrum was recorded in the form of wave numbers.

The blend morphology was studied with a Hitachi 510 scanning electron microscope (Japan) and a TEM-100 CXII transmission electron microscope (Japan). Samples for scanning electron microscopy (SEM) were prepared by the fracturing of the extrudate at the temperature of liquid nitrogen, and they were gold-coated before the microscopy observations. Specimens

for transmission electron microscopy (TEM) were obtained with an LKB-2088 razor (Sweden), and the thickness of the thin sections was less than 80 nm. Before the TEM observations, the specimens were stained with OsO₄.

Wide-angle X-ray diffraction (WAXD) patterns of the blends were obtained with a Y-4Q X-ray spectrometer (Japan); the measurement conditions were Cu K α , 1.54046 Å, 40 kV, 30 mA, $\Delta\theta = 0.2^\circ$, and $20^\circ/\text{min}$.

Thermal analysis was performed under a nitrogen atmosphere with a differential scanning calorimeter (TA DSC 2910; Thies Technology, Inc., USA). The temperature was raised from 30 to 260°C at a rate of 10°C.

Dynamic mechanical thermal analysis (DMA) was performed with a TA Instruments DMA2980 (USA) under a nitrogen atmosphere with the temperature increasing at a rate of 30°C/min from -120 to +150°C. The frequency was 10 Hz. Samples were prepared by compression molding, and the dimensions between the clamps were 1 mm \times 4 mm \times 40 mm.

The apparent melt viscosity was measured with an XYZ-II capillary rheometer (Instruments Factory of Jilin University, China) with a capillary length/diameter ratio of 20.

RESULTS AND DISCUSSION

Characterization of the copolymer formation

PP and PA6 are immiscible. When gPP is added to PP/PA6 blends, the reaction groups of gPP and the terminal amino groups of PA6 may react during the melt mixing of gPP and PA6, and this can result in the formation of the PP-g-PA6 copolymer. PP-g-PA6 acts as an interfacial agent in the PP/PA6 blend system. The data for the PP-g-PA6 copolymer was confirmed with Molau's test.²¹ When formic acid was added to PP/PA6 binary blends, PA6 dissolved completely, whereas the PP phase-separated and floated on top. The compatibilized PP/PA6 blends gave rise to a stable emulsion in formic acid. According to Molau, this result can be taken as a proof of the formation of PP-g-PA6 in compatibilized PP/PA6 blends. For further confirmation of the data for PP-g-PA6, the PP phase of a compatibilized PP/PA6 (80/20) blend was selectively extracted with hot xylene. The residue of the Soxhlet extraction of the mechanical blend was about 22% after the entire PP phase was extracted. The residue of the Soxhlet extraction of the compatibilized blends increased in proportion to the amount of gPP added to the blend. The result can be explained as follows: increasing the amount of gPP in the blend results in an increasing amount of PP-g-PA6, which cannot be extracted by xylene, and the residue of the PP phase increases. This was also proved by the IR spectrum of the residue of a PP/PA6 (20/80) blend after extraction with formic acid. In the mechanical

blend of PP/PA6, PA6 could almost be completely extracted by formic acid, so there were only very weak NH_2 group peaks at 3300, 1640, 1530, and 1260 cm^{-1} in the IR spectrum of the residue. However, for the compatibilized blend, very strong NH_2 group peaks were observed in the IR spectrum of the residue. This demonstrated that the interaction between gPP and PA6 made it impossible to extract all the PA6 components from the compatibilized PP/PA6 blend with formic acid, and a significant amount of PA6 was in the residue.

Morphology

SEM and TEM observations

Figure 1 shows the SEM micrographs of cryogenically fractured extrudate surfaces for PP/PA6 (80/20) blends. The morphology of the mechanical blend is particle-in-matrix, the major phase forms the matrix, and the minor phase is segregated into spherical domains. The dispersed-phase particles are large and have smooth surfaces. We believe that during the fracturing process, many domains were pulled away from their previous position and empty holes were formed; this indicated poor adhesion at the interphase between the matrix and domains. The morphology of the compatibilized blends was homogeneous, and no similar domain particle was observed. The dispersed-phase domains decreased with increasing gPP. The compatibility of the blends was improved with increasing gPP according to SEM because with more gPP added, more PP-g-PA6 formed and interfacial adhesion increased. In the blend compatibilized with 6.25% gPP, spherical particles were not observable in the micrographs even under higher magnification, and it was difficult to identify one component as the continuous phase and the other as the dispersed phases.

TEM images of PP/PA6 (80/20) blends are shown in Figure 2. In Figure 2(a), the TEM image of the mechanical blend shows a lack of interfacial adhesion. The two components are easily distinguished, and the spherulite structure of PA6 can be clearly observed. The dispersed-phase particles were too large for thin samples to be prepared for TEM observation. The compatibilizer caused increased adhesion between the dispersed phase and the matrix because the surface area between the dispersed phase and the matrix increased. In Figure 2(b), the TEM image shows strong interfacial adhesion in the compatibilized blend. After compatibilization with gPP, the particle sizes of the dispersed phase of the compatibilized PP/PA6 blends became smaller, and the interfaces became more indistinct; obvious interfaces between PP and PA6 phases could be observed. The SEM and TEM results show that gPP can strengthen the interfacial adhesion between PP and PA6 phases and improve the compatibility of PP/PA6 blends efficiently.

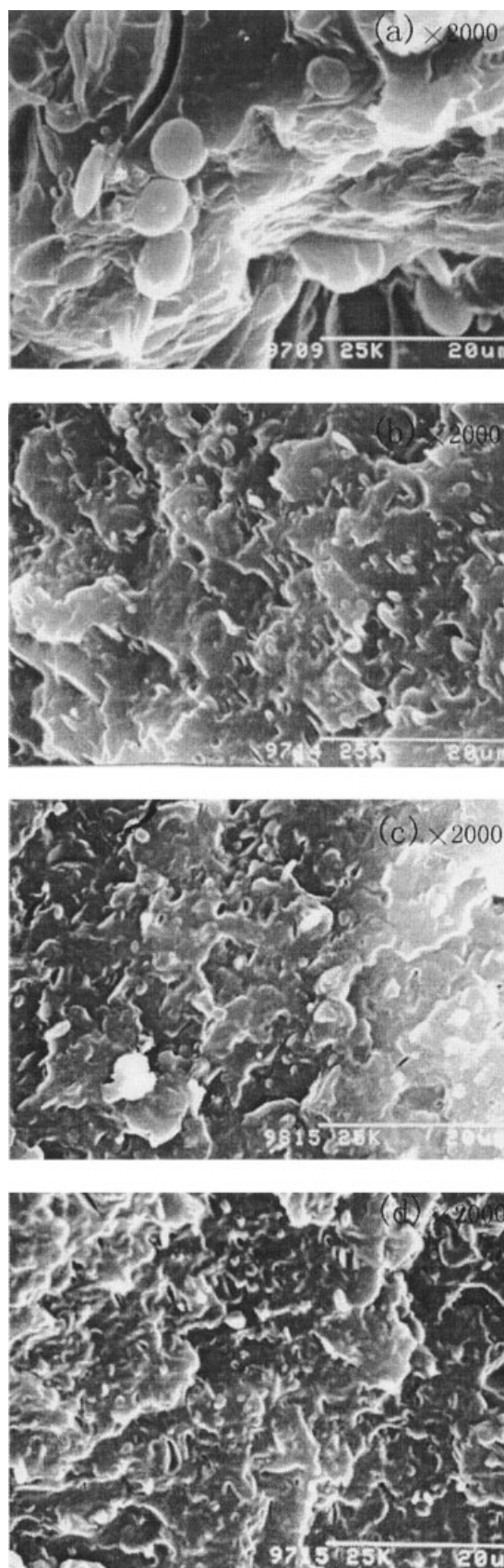


Figure 1 SEM micrographs of PP/PA6 (80/20) blends with (a) 0, (b) 2.5, (c) 5, and (d) 6.25% compatibilizer.

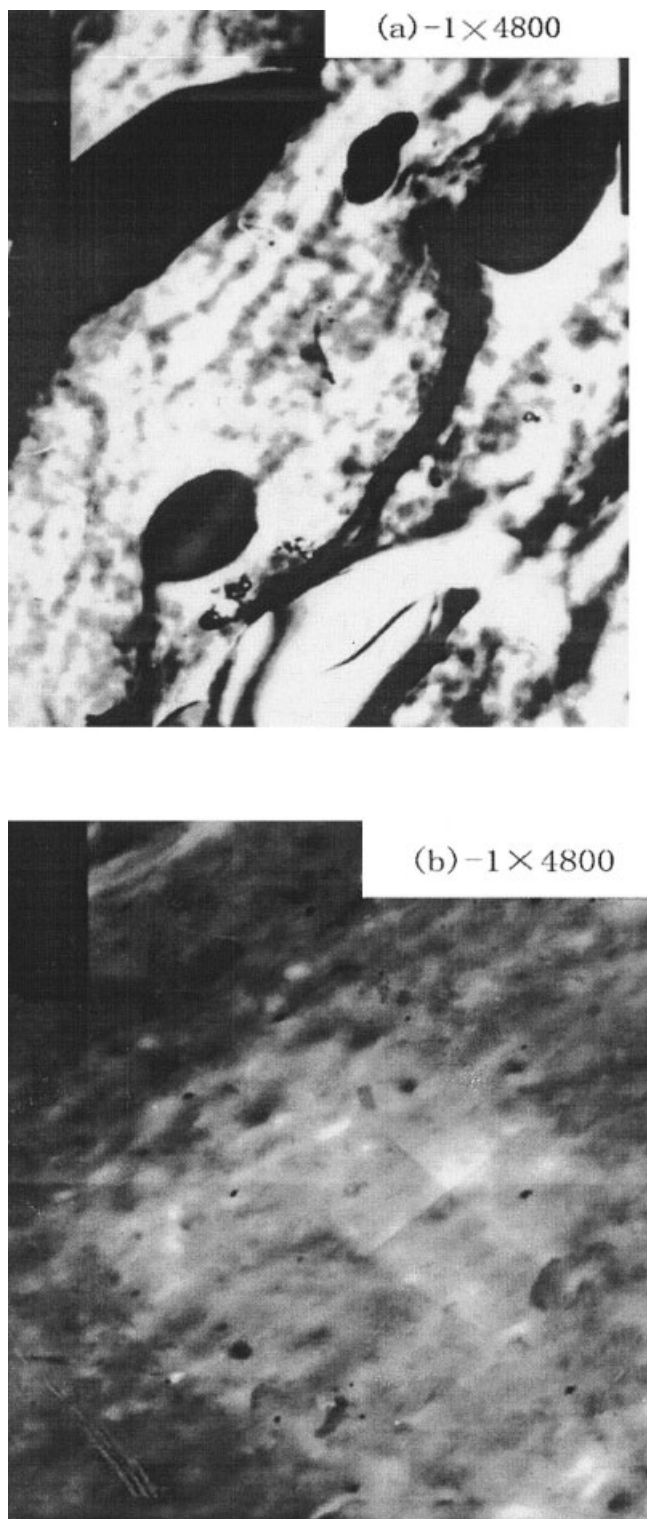


Figure 2 TEM micrographs of PP/PA6 (80/20) blends (a) without a compatibilizer and (b) with 5% gPP.

WAXD, differential scanning calorimetry (DSC), and DMA analysis

The WAXD pattern of the PP/PA6 mechanical blends shows four main diffraction peaks: one is attributable

to PA6, and the others are attributable to PP.²² The WAXD pattern of the compatibilized blend is similar to that of the mechanical blends, including the shape, location, and crystal parameters of the peaks.²³ The results indicate that after compatibilization by gPP, the crystal structures of PP and PA6 were not changed, and no new crystal structures appeared. However, the microcrystal size of PA6 in the compatibilized blend was much smaller than in the mechanical blend. Crystallite size (L_{hkl}) of PA6, calculated from the WAXD pattern of a PP/PA6 (80/20) mechanical blend, was 430.64 Å; after compatibilization with 5% gPP, L_{hkl} of PA6 decreased from 430.64 to 205.67 Å because PP-g-PA6 was formed, which hindered the increment of PA6 microcrystals.

Figure 3 depicts the DSC curves of PP/PA6 (80/20) blends, and the DSC results are listed in Table I. The melting temperature and crystallization of PP and PA6 of the mechanical blend were similar to those of the compatibilized blend. After compatibilization with gPP, the crystallization peaks and fusion peaks of the components changed; the fusion peaks of PA6 almost disappeared, and the melting enthalpy and crystallization enthalpy of PP and PA6 decreased significantly. The melting enthalpy could lead to crystallinity of the components with the quoted value of fully crystalline materials.²⁴ The crystallinity of PP in the mechanical blends was 57.70%, but in the compatibilized blends, it decreased to 38.85%. Correspondingly, the crystallinity of PA6 was 7.70 and 6.41% in the mechanical and compatibilized blends, respectively. The compatibilizer affected the crystallization and the fusion of the components of the PP/PA6 blends. We believe that the formation of PP-g-PA6 during blending affected the crystallization and the size of the dispersed phase.

The glass-transition temperature (T_g) of the components can give expression to the compatibility of a blend. From the DMA spectra of a PP/PA6 (80/20) blend, we found that T_g of PP in the compatibilized blend with PP-g-MAH was higher than in the mechanical blend, and T_g of PA6 in the compatibilized blend was lower than that in the mechanical blend. This means that the two T_g 's of the components in the compatibilized blend were adjoined, and the storage modulus of the compatibilized blend with PP-g-MAH was higher than that of the mechanical blend because of the compatibility improvement.²⁵ The DMA spectrum of the compatibilized PP/PA6 blend with gPP was similar to that of the compatibilized blend with PP-g-MAH, and the storage modulus of the compatibilized blend with gPP was higher than that of the blend with PP-g-MAH. The results indicate that gPP improved the compatibility of PP/PA6 blends efficiently, similarly to PP-g-MAH.

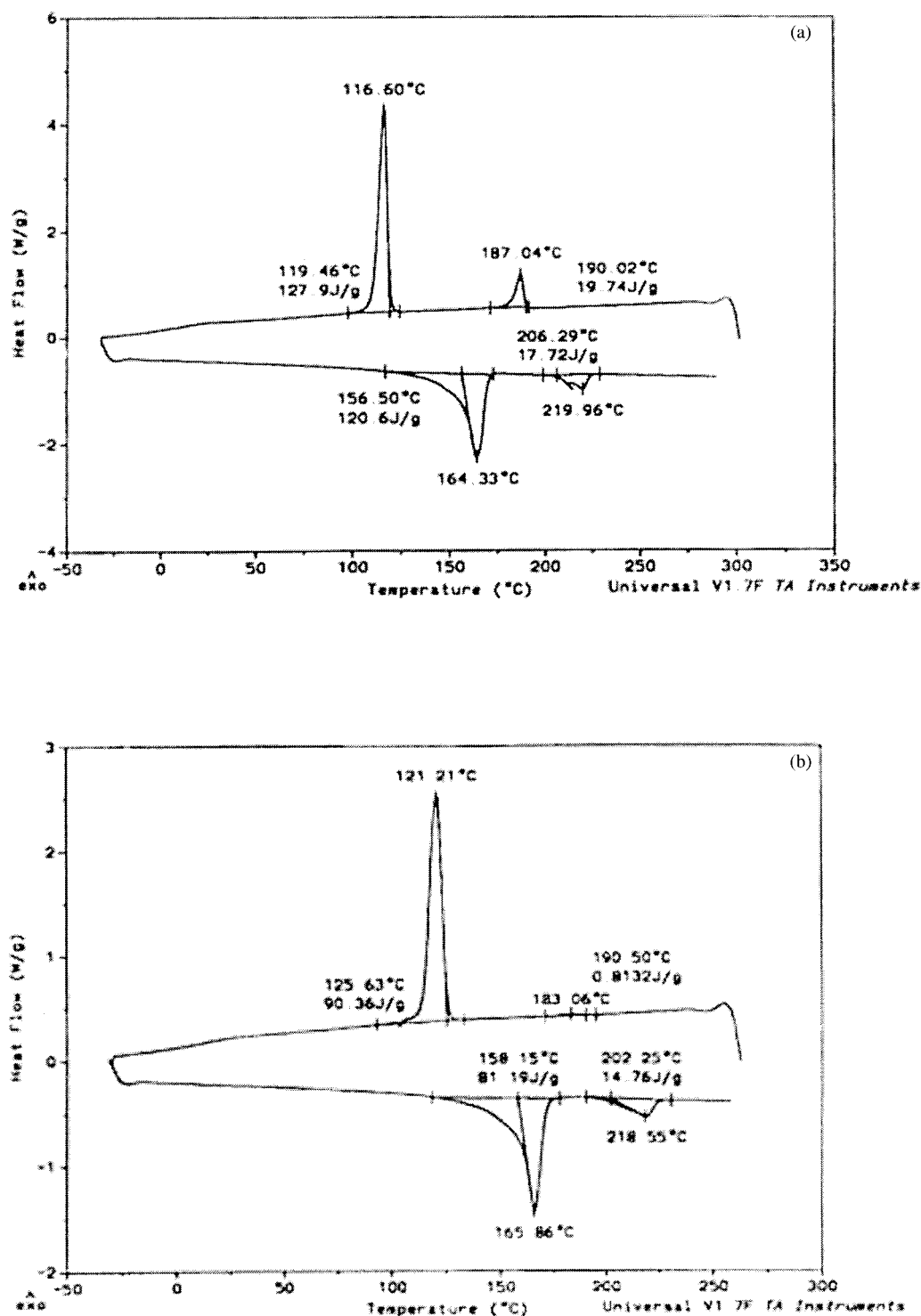


Figure 3 DSC traces of PP/PA6 (80/20) blends: (a) a mechanical blend and (b) a blend compatibilized with 5% gPP.

Mechanical properties

The results of the mechanical testing of the compatibilized blends are shown in Figure 4. Figure 4 shows the impact strength and tensile strength of the blends as a function of the composition. The impact strength and tensile strength of all the compatibilized blends with gPP were higher than those of the mechanical

blends without a compatibilizer. This was due to the improved adhesion between the components, which improved the homogeneity and reduced the size of the dispersed particles. The increased impact strength and tensile strength of all the compatibilized blends suggested that even a small amount of the compatibilizer could improve the interfacial strength significantly.

TABLE I
DSC Results for the PP/PA6 (80/20) Blends

	Mechanical blend	Compatibilized blend
PP		
T_m	164.33	165.85
ΔH_f	120.60	81.19
T_c	116.60	121.21
ΔH_c	127.90	90.36
X	57.70	38.35
PA6		
T_m	219.96	218.55
ΔH_f	17.72	14.74
T_c	187.04	190.50
ΔH_c	19.74	0.843
X	7.70	6.41

T_m = melting temperature; ΔH_f = enthalpy of fusion; T_c = crystallization temperature; ΔH_c = enthalpy of crystallization; X = crystallinity.

The compatibilizer acted as a bridge between two incompatible phases at the interface, and so the optimum concentration of compatibilizer effectiveness

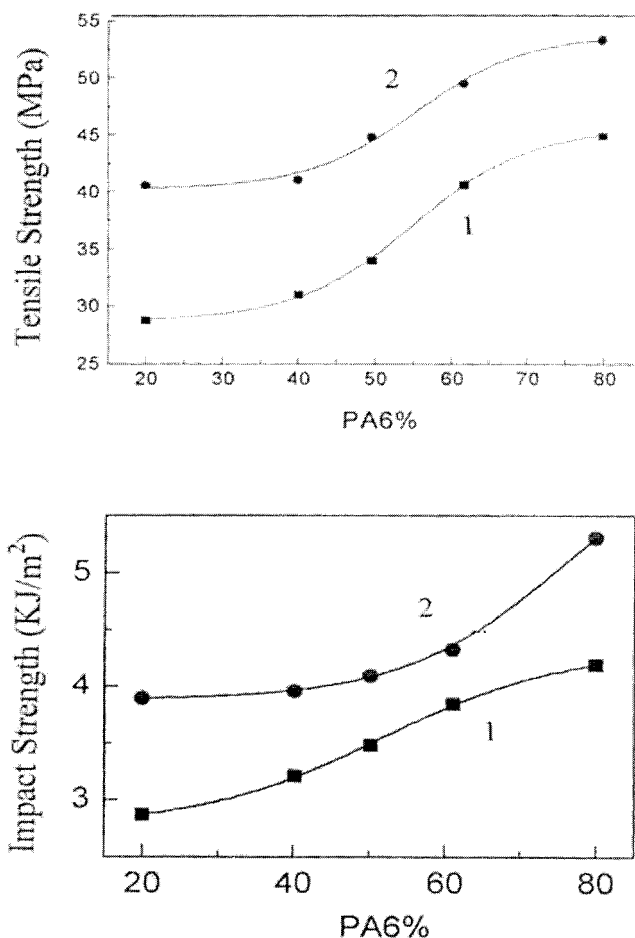


Figure 4 Mechanical properties of PP/PA6 blends: (1) with 5% gPP and (2) without a compatibilizer.

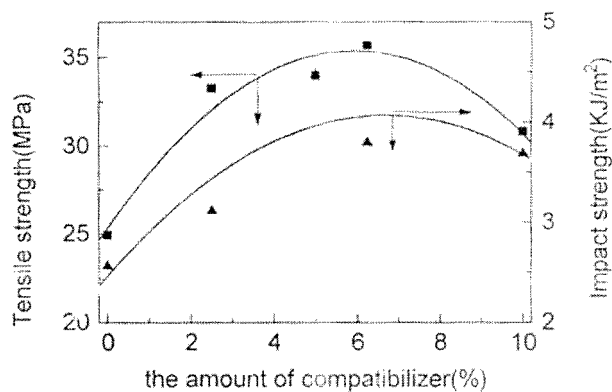


Figure 5 Mechanical properties of PP/PA6 (80/20) blends versus the weight percentage of the compatibilizer.

was always required. The effect of the concentration of the compatibilizer on the impact strength and tensile strength of the blends is shown in Figure 5. At low concentrations of gPP, the impact strength and tensile strength of the blends increased when the concentration of gPP increased. However, when the concentration of gPP was greater than 6.25 wt %, the impact strength and tensile strength of the blends decreased because of the increased plasticization effect of low-molecular-weight gPP. Moreover, the content of the third monomer, when gPP was being prepared, also affected the mechanical properties of PP/PA6 (80/20) blends, as shown in Figure 6. The impact strength and tensile strength of the blends increased while the content of the third monomer in gPP increased, but when the content of the third monomer in gPP was greater than 15 wt %, the impact strength and tensile strength of the compatibilized blends decreased with increasing gPP. The reason was that the content of the third monomer, when gPP was being prepared, affected the grafting percentage of gPP, which affected the compatibilization of PP/PA6.

Rheological properties

Figure 7 shows the apparent melt viscosities of blends at 270°C. The mechanical and compatibilized blends both possessed pseudoplasticity, but the compatibilized PP/PA6 blends possessed higher pseudoplasticity, and the apparent melt viscosities of the compatibilized blends were higher than those of the mechanical blends with gPP. This may have been due to enhanced interactions in the blend, especially the formation of new graft copolymers in the amine-ester reaction between the compatibilizer and PA6. That is, in the case of the mechanical blends, there was only a weak interaction between PA6 and PP; in the compatibilized blends with gPP, there was a strong interaction between these different polymer chains.

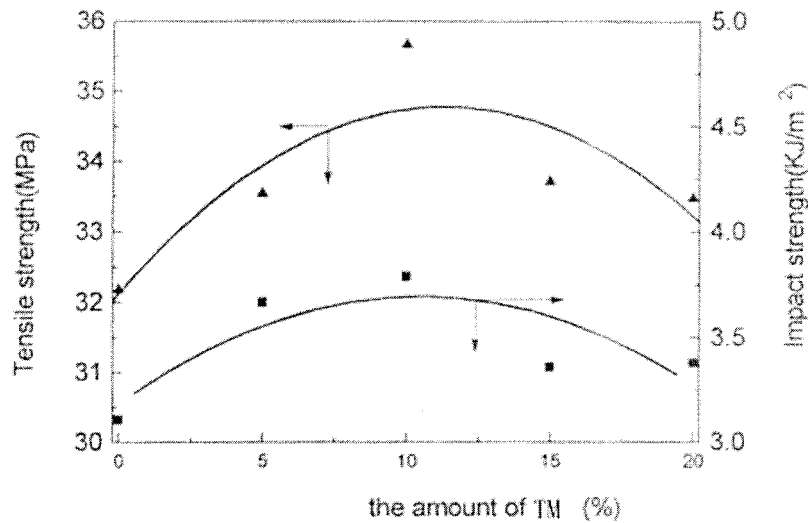


Figure 6 Effect of TM (wt %) on the mechanical properties of PP/PA6 (80/20) blends with 6.25% compatibilizer.

The temperature has an important effect on the viscosity of blends, and the dependence of the viscosity on the temperature can be expressed by an Arrhenius equation. The value of the flow activation energy (ΔE_η) expresses the influence of temperature on the viscosity of blends. The correlation of viscosity and temperature for the blends is presented in Figure 8. Calculated from the plots, the ΔE_η values of the mechanical and compatibilized blends were 15.22 and 18.58 kcal/mol, respectively. ΔE_η of the compatibilized blends was higher than that of the mechanical blends; this meant that the sensitivity of the viscosity of the mechanical blends to temperature was higher than that of the mechanical blends. This was because the PP-g-PA6 copolymer was produced in the interface between the PP and PA6 phases after compatibilization with gPP, and it prevented the flow of the molten blend.

CONCLUSIONS

gPP, PP-graft-MAH, MMA, and a third monomer were demonstrated to improve the compatibility of immis-

cible PP/PA6 blends efficiently. Molau testing, solvent extraction, and IR spectra of the residue after extraction with formic acid indicated the formation of PP-g-PA6 in the vicinity of the interfaces during the melt extrusion of gPP and PA6 due to the reaction between the reactive groups of gPP and the NH_2 end groups of PA6. In the presence of the compatibilizers, the particle sizes of the dispersed phases of the PP/PA6 blends were drastically reduced, and they became too small to be identified even with magnification. In compatibilized PP/PA6 blends, the interfaces between the PP and PA6 phases became more indistinct in comparison with the mechanical blends. The microcrystal size of PA6 and the extent of the crystallinity of the two components of the PP/PA6 blends decreased after compatibilization with gPP. The tensile strength and impact strength of the compatibilized PP/PA6 blends were obviously increased over those of the mechanical blends. The amount of gPP and the content of the third monomer during the preparation affected the mechan-

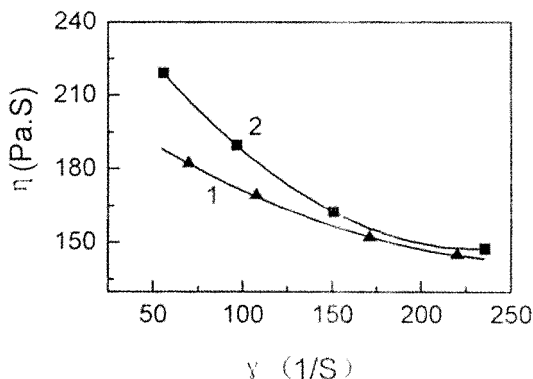


Figure 7 Shear viscosity of PP/PA6 (80/20) blends as a function of the shear rate (270°C): (1) a mechanical blend and (2) a blend compatibilized with 5% gPP.

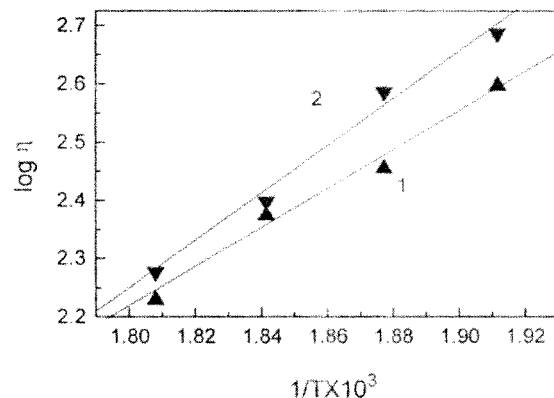


Figure 8 Shear viscosity of PP/PA6 (80/20) blends versus the temperature (shear rate ($\dot{\gamma}_a$) = 157 S^{-1}): (1) a mechanical blend and (2) a blend compatibilized with 5% gPP.

ical properties of the compatibilized PP/PA6 (80/20) blends. The compatibilized PP/PA6 blends possessed higher pseudoplasticity, melt viscosity, and ΔE_{η} values because of the formation of the PP-g-PA6 copolymer.

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