

Pan-Milling Preparation of Polypropylene-*graft*-Maleic Anhydride and Its Compatibilizing Effect on Polyamide 6/Polypropylene Blend

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ABSTRACT: By pan-milling at ambient temperature, maleic anhydride (MAH) was mechanochemically grafted onto polypropylene (PP) in solid state without the aid of initiator. FT-IR confirmed the formation of PP-*g*-MAH. The obtained PP-*g*-MAH was applied as compatibilizer for polyamide 6/PP blend. Morphological analysis shows that the microstructure was well modified by incorporating PP-*g*-MAH into PP/PA6. PP phase has a dimension reduced a lot and more uniform dispersion in PA6 matrix. The equilibrium torque of compatibilized blend increased too. Mechanical tests show that PP-*g*-MAH substantially improved the mechanical properties of PA6/PP blend. For PA6/PP (80/20) blend compatibilized by 11 v% PP-*g*-MAH, the tensile strength at break attained 57.56 MPa and the Izod notched impact strength was 108.9 J m⁻¹, increased by 8.87 MPa and 45.4 J m⁻¹ respectively. Mechanism studies show that the improvement of microstructure and mechanical structure was caused by the formation of PP-PA6 copolymer through the reaction of reactive groups on PP-*g*-MAH and PA6.

KEY WORDS Polypropylene / Polyamide 6 / Polypropylene-*graft*-Maleic Anhydride (PP-*g*-MAH) / Pan-Milling / Compatibilization /

Blending of polyolefin with engineering plastics has been one of the focuses of polymer engineering for many years. For instance, polypropylene (PP) and polyamide 6 (PA6) have many complementary properties.^{1,2} By blending PP and PA6, it is hopeful to obtain a product with balanced properties including low moisture absorption, reasonable mechanical and thermal properties, improved processability as well as acceptable price.³

Nevertheless, the inherent immiscible properties of PA6 and PP made it impossible to achieve the desired properties without using interfacial modifiers.⁴ Many previous studies have showed that microstructure, phase stability and interfacial adhesion are of crucial importance with respect to the properties of polymer blends.⁵ Therefore, more attentions in this field are focused on seeking economic approaches to introduce some reactive monomers containing polar groups onto PP. The formed blocking or graft copolymers can serve as compatibilizers to reduce the interfacial tension, modify the microstructure or provide steric hindrance protecting the dispersed phase from coalescence during melt blending.^{6—8}

Several methods have been developed to graft reactive polar monomers onto polypropylene. For instance, PP and reactive monomers can be dissolved in solvent and initiated to form copolymer.⁹ The product obtained has high yield and grafting rate, but it is difficult to avoid byproduct and the solvent recycling also made

it impractical for large-scale production. This reaction can also be conducted in melt state by using extruder or internal mixer as the reactor.^{10,11} This method requires no solvent and is convenient to process. However, PP suffers severe degradation at the processing temperature often higher than 200°C. It is also a problem to remove the remnant monomer and initiator. In recent years, an alternative approach, solid phase grafting, was introduced to prepare PP co-polymer.^{12,13} In this process, polypropylene in powder state was mixed with monomer assisted by small amount of interfacial wetting agent (< 10%, often solvent of PP). The reacting temperature can be reduced to 100—130°C. Hence, the degradation degree is greatly lessened. But this approach also needs initiator and small amount of organic solvent. Besides, the homogeneity of the graft product depends a lot on the particle size of PP powder. Reactive extrusion offers another way to form PA6/PP blend by initiating graft polymerization reaction of ϵ -caprolactam onto PP chains. The microstructure of the blend can be well controlled during this process and nano-dispersed PA6/PP blend can even be obtained.¹⁴ While the slow reaction rate made it still far from general use. So, in spite of thousands of related articles in the research literature, no polymer blend compatibilized by addition of low levels of block or graft copolymers has been commercialized.¹⁵

Here a novel method was reported to prepare polypropylene-*graft*-maleic anhydride (PP-*g*-MAH) by pan-milling at ambient temperature and without using initiators. In our previous works, a novel equipment,

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Pan-type mill, specially designed for polymers pulverization and mechanochemical reaction has been developed.^{16,17} Theoretical analysis demonstrate that this equipment has excellent pulverizing and mixing effect on polymeric materials due to the ingenious design derived from traditional Chinese stone-mill. Functioning like a pair of three-dimensional scissors, it can exert on materials fairly strong squeezing force in normal direction and shearing force in both radial and tangential directions. Both particle size reduction and chain scission of polymers will occur during pan-milling process. The formed macromolecular radicals can initiate graft polymerization of polar monomers onto polymer chains. Solid-state graft polymerization of hydroxymethyl acrylamide onto polypropylene has been realized in our laboratory.¹⁸

In this paper, the preparation of PP-g-MAH *via* pan-milling at ambient temperature and its compatibilizing effect on PA6/PP blend are reported. By employing the mechanochemical reaction occurred during pan-milling, MAH can react with the macro-radicals resulting from chain scission induced by the high stress inside the equipment. The formed PP-g-MAH was used to compatibilize PA6/PP blend and exhibit rather positive effect on its mechanical properties. For this novel approach is free of organic solvent or chemical initiators and can be conducted at ambient temperature, it is very hopeful to be commercialized in the future.

EXPERIMENTAL

Materials

PA6 in pellet form (Relative viscosity = 3.2, in 98% H₂SO₄ solvent, diameter = 2–3 mm) was supplied by Yingshan Petro-Chemical Engineering Factory, China. PP (T30S) with a pellet diameter of 3–4 mm and MI of 3.4 g/10 min was supplied by Dushanzi Petro-Chemical Co., China. Maleic anhydride of reagent grade was supplied by Jinyu Chemical Reagent Factory, China. Formic acid of reagent grade was supplied by Tianjin Chemical Reagent Factory, China.

Sample Preparation

PP-g-MAH. Polypropylene pellets and maleic anhydride were fed into pan-mill together through the hopper in the middle of the milling pans at certain rotating speed and space between two pans. Milled materials were discharged from the brim of pans. The discharged powders were collected for next milling cycle. The operation was performed at ambient temperature and the produced heat during milling was removed by cooling water. The milled product was extracted with water for 72 h to remove the remnant monomer. Then,

the extracted product was dried in vacuum at 60°C.

PP-g-MAH Compatibilized PA6/PP Blend. PA6 was dried at 100°C for 48 h in vacuum prior to blending. PA6, PP, and PP-g-MAH at certain content were melt blended by using a twin screw counter rotating extruder at process zone temperature between 235–250°C. The rotating speed of screws was kept at 50 rpm. The extruded blend were stranded, water-cooled and pelletized. Blend pellets were dried at 100°C for 48 h in vacuum and injection molded into standard tensile and impact specimens at process zone temperature between 220–250°C.

Test and Characterization

The formation of PP-g-MAH was characterized with a Nicolet 20 SXB FT-IR Spectrometer. The sample was prepared by thermal press molding PP-g-MAH into thin film on a compression machine at 190°C under a pressure of 100 kg cm⁻².

The viscosity average molecular weight of PP was measured with an Ubbelohde viscometer according to the following equation:

$$PP : [\eta] = 1.9 \times 10^{-2} \overline{M}_v^{0.725} \quad (1)$$

(solvent: 1,2,4-trichlorobenzene, 135°C).

Melt index was measured by a CS-127 Melt Index Instrument (Testing temperature: 230°C, load: 2.16 kg).

The graft rate of PP-g-MAH was determined by chemical titration. The samples were dissolved in boiling toluene and superfluous ethanol solution of KOH was added under stirring and heating. Then, the system was titrated by isopropanol solution of HCl.

The torque at equilibrium was determined with a Haake Torque Rheometer. Tensile properties were tested following ASTM D-638 with a material tester (Instron 4302). Izod notched impact strength was tested according to ASTM D-256 with an impact strength tester (XJ-40A).

The blend morphology was characterized with a SEM (HITACHI X-650). Standard specimens were cryogenically fractured in liquid nitrogen. The fracture surface was sputter-coated with gold before observation.

RESULTS AND DISCUSSION

Pan-Milling Preparation of PP-g-MAH

Figure 1 shows the variation of viscosity average molecular weight of PP during pan-milling. The change in melt index of PP during pan-milling was also listed in Table I. The results indicate that the viscosity average molecular weight decreases with increasing the number of milling cycles. After 14 milling cycles, the

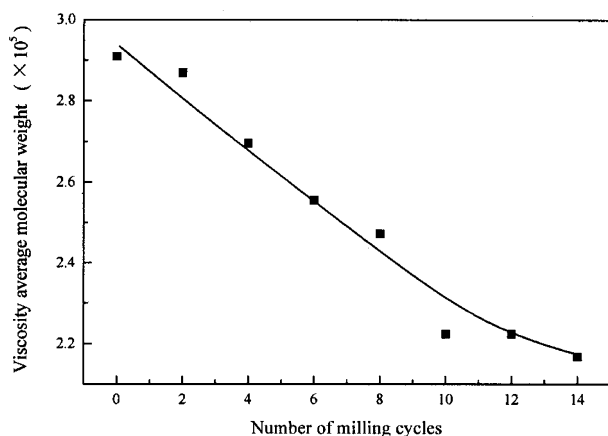


Figure 1. Variation of viscosity average molecular weight of PP during Pan-milling.

Table I. Effect of pan-milling on the melt index of PP

| n | 0 | 4 | 8 | 10 | 12 | 14 |
|--------------|-----|-----|-----|------|------|------|
| MI(g/10 min) | 3.4 | 4.7 | 9.2 | 11.1 | 13.5 | 14.0 |

value reduced from original 290900 to 216800. In accordance with the molecular weight reduction, the melt index of PP increased after pan-milling. As shown in Table I, the melt flow index of the sample pan-milled for 14 cycles is about 4.12 times of that of PP without being pan-milled. Obviously, the results were caused by chain scission of PP induced by the strong stress inside the pan-mill.

The macromolecular radicals formed by chain scission reaction will initiate graft polymerization reaction and result in PP graft copolymer if reactive low molecular monomers are present.

In our experiment, maleic anhydride (MAH) was used as the grafting monomer. The co-milled product was extracted by distilled water and acetone to remove the remnant MAH. Figure 2 shows the FT-IR spectra of PP and PP co-milled with MAH. In comparison with un-milled PP, the co-milled product has several new absorbance peaks. The peaks in 1775 cm^{-1} reflects the characteristic absorbance of -C=O group of anhydride, which is originated from the reaction between PP and MAH. The results show that by pan-milling PP with MAH, the macromolecular radicals of PP can induce graft copolymerization reaction and form PP-g-MAH copolymer. Because of its mechanochemical property, the reaction can be carried out without using initiators at ambient temperature.

Through adjusting processing conditions such as number of milling cycles, rotating speed of milling pan and temperature, PP-g-MAH with maximum graft rate of 1.03% can be obtained. Considering the economy of preparation, the graft rate of PP-g-MAH used in the following experiments is 0.76%.

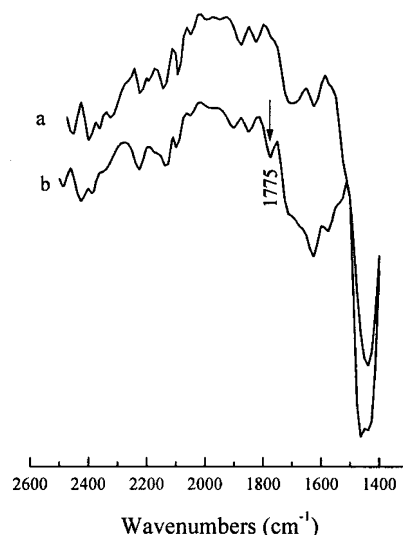


Figure 2. FT-IR spectra of a: PP and b: PP-g-MAH.

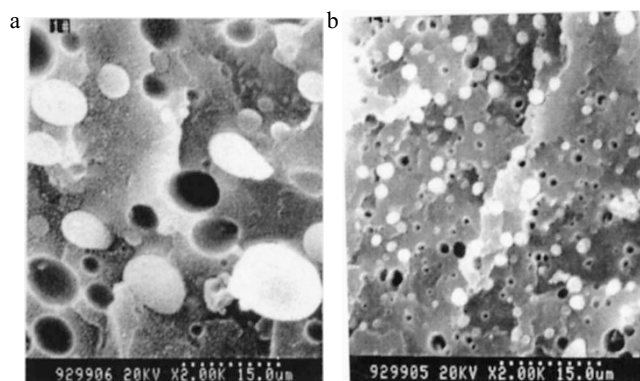


Figure 3. SEM photographs of a: PA6/PP (80/20, v/v) and b: PP-g-MAH (grafting rate: 1.45%) compatibilized PA6/PP/PP-g-MAH (80/9/11, v/v/v).

Compatibilizing Effect of PP-g-MAH on PA6/PP Blend

Morphological Analysis. The simple blend of PA6/PP and PP-g-MAH compatibilized PA6/PP blend was prepared by twin screw extruding and injection molding. The morphology of their fracture surface was observed by SEM. As shown in Figure 3, the PP separate phase in PA6 matrix is very coarse and irregular, the size of which ranged widely from several microns to larger than $10\text{ }\mu\text{m}$ (Figure 3a). In contrast, the morphology of PA6/PP compatibilized by PP-g-MAH was obviously improved (Figure 3b). The PP phase dimension reduced to around $1.5\text{ }\mu\text{m}$ and the distribution of PP also becomes more uniform. The morphology improvement is caused by the enhanced polarity of PP, which resulted in increased affinity with PA6. Of course, such morphology will contribute to the improvement of mechanical properties of the blend.

Rheological Analysis. The torque at equilibrium of PA6/PP and PP-g-MAH compatibilized PA6/PP blends was investigated at 230°C with a Hakke torque rheome-

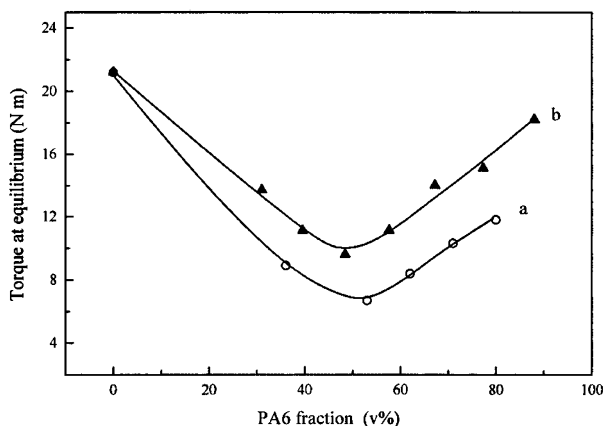


Figure 4. Torque at equilibrium of a: PA6/PP blend without compatibilizer and b: PP-g-MAH (grafting rate: 0.76%) compatibilized PA6/PP blend. Volume percentage of PP-g-MAH: 11%.

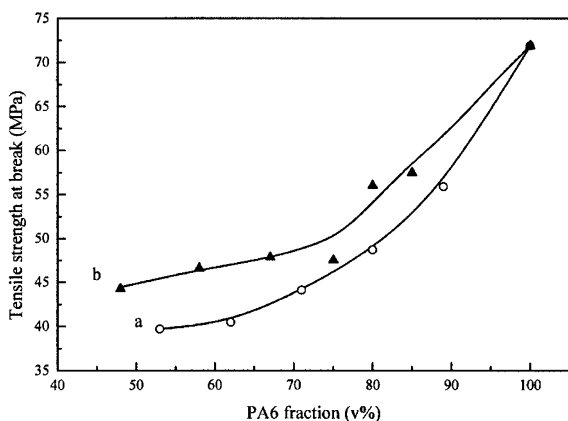


Figure 5. Tensile strength of a: PA6/PP blend without compatibilizer and b: PP-g-MAH (grafting rate: 1.45%) compatibilized PA6/PP blend. Volume percentage of PP-g-MAH: 11%.

ter. As shown in Figure 4, the torque at equilibrium of compatibilized system is much higher than that of simple blend. The reason is that the end groups of PA6, *i.e.*, amine groups, can react with the anhydride groups contained in PP-g-MAH. The physical interaction between PA6 and PP will also be enhanced owing to the increased compatibility. As a result, there exists more intimate penetration and entanglement of the two polymer chains. During melting process, the melt viscosity of the compatibilized system is higher than simple blend and thus results in larger torque at equilibrium.

Mechanical Properties. Figures 5 and 6 show the tensile strength and Izod impact strength of PA6/PP and PP-g-MAH compatibilized PA6/PP blends. The data of Young's modulus and break strain of the two systems were shown in Figures 7 and 8. For uncompatibilized blend, the tensile strength, modulus and break strain reduced sharply with the fraction of PP increases. Impact strength of PA6/PP has slight increase when PP fraction is around 20% (as shown in Figure 6). However, the addition of PP-g-MAH has significant improv-

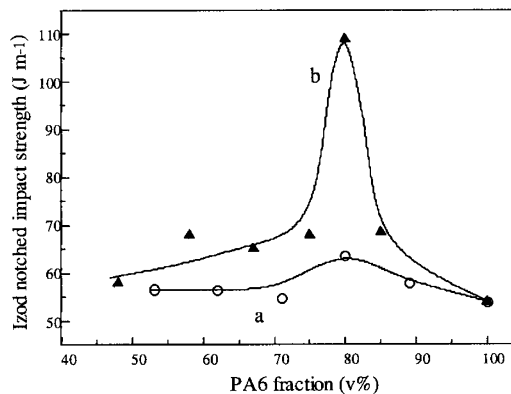


Figure 6. Impact strength of a: PA6/PP blend without compatibilizer and b: PP-g-MAH (grafting rate: 1.45%) compatibilized PA6/PP blend. Volume percentage of PP-g-MAH: 11%.

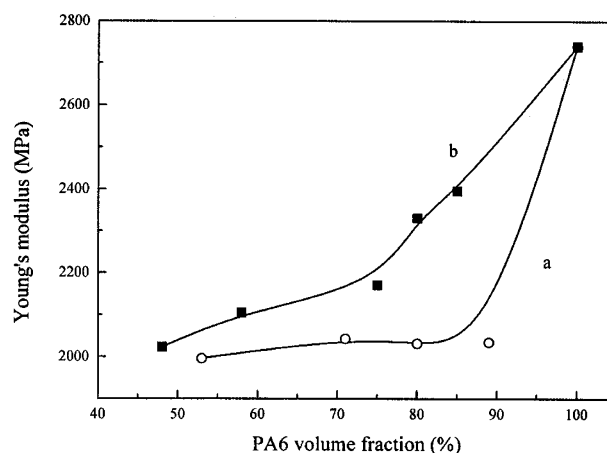


Figure 7. Young's modulus of a: PA6/PP blend without compatibilizer and b: PP-g-MAH (grafting rate: 1.45%) compatibilized PA6/PP blend. Volume percentage of PP-g-MAH: 11%.

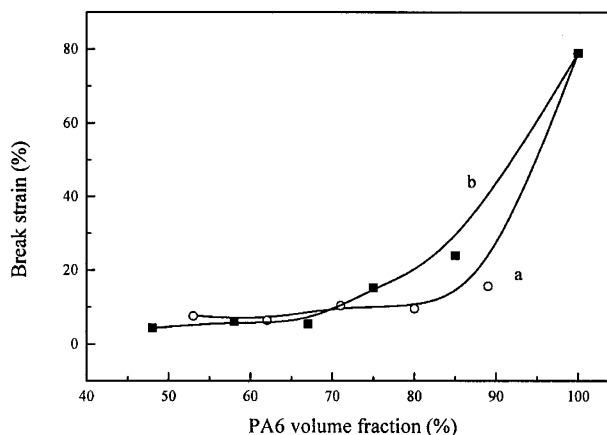


Figure 8. Break strain of a: PA6/PP blend without compatibilizer and b: PP-g-MAH (grafting rate: 1.45%) compatibilized PA6/PP blend. Volume percentage of PP-g-MAH: 11%.

ing effect on mechanical properties of the blend. As mentioned above, because of the much-modified microstructure, PP has smaller phase dimension and more uniform dispersion in PA6 matrix and the interfacial adhesion was also strengthened. As a result, in compari-

Table II. Effect of compatibilizer content on mechanical properties of PA6/PP blends^a

| Compatibilizer content V% | Tensile strength MPa | Young's modulus MPa | Break strain % | Notched Izod impact strength J m ⁻¹ |
|------------------------------|-------------------------|------------------------|-------------------|---|
| 0 | 48.69 | 2032 | 10 | 63.5 |
| 5.5 | 54.47 | 2304 | 20 | 70.1 |
| 11 | 56.02 | 2330 | 26 | 108.9 |

^aGraft rate of PP-g-MAH: 0.75%, volume ratio of PA6 in the blend: 20%.

son with PA6/PP (80/20) blend, the tensile strength and impact strength of PP-g-MAH compatibilized blend increased from 48.69 MPa and 63.5 J m⁻¹ to 57.56 MPa and 108.9 J m⁻¹ respectively. Young's modulus and break strain also increased from 2030 MPa and 8.7% to 2330 MPa and 20.5%, exhibiting the excellent compatibilizing effect of mechanochemically prepared PP-g-MAH compatibilizer.

The influence of compatibilizer content on mechanical properties of PA6/PP blend was listed in Table II. With the increase of PP-g-MAH content, all the mechanical properties including tensile strength, young's modulus, break strain and impact strength were enhanced. For at high compatibilizer content, there are more PP-PA6 copolymer formed during thermal blending process, which favors the dispersion of PP in PA6 matrix.

Compatibilizing Mechanism. The compatibilizing effect of PP-g-MAH on PA6/PP was also confirmed by co-solvent experiment.¹⁹ Uncompatibilized PA6/PP blend and PP-g-MAH compatibilized PA6/PP blends were added into formic acid solvent. For the uncompatibilized system, PA6 will dissolve thoroughly in the solvent and remained PP will float on the solution. However, for the PP-g-MAH compatibilized PA6/PP blend, only cloudy solution can be obtained. The result was caused by the formation of PA6-PP copolymer, which functions to reduce surface tension between PP and formic acid and prevent PP from floating to the surface, just like surfactant in emulsion system.

PA6 in PP-g-MAH compatibilized PA6/PP blend was extracted by formic acid. The remnant insoluble substances was dried and characterized by FT-IR. The results were showed in Figure 9. In comparison with PP-g-MAH, the remnant substances have absorption peak in 1725 cm⁻¹, which might be the characteristic absorption of imide group and have no absorption in 1775 cm⁻¹, which is the characteristic absorption of anhydride group. The variation could be interpreted by the formation of PP-PA6 copolymer according to the following reaction:

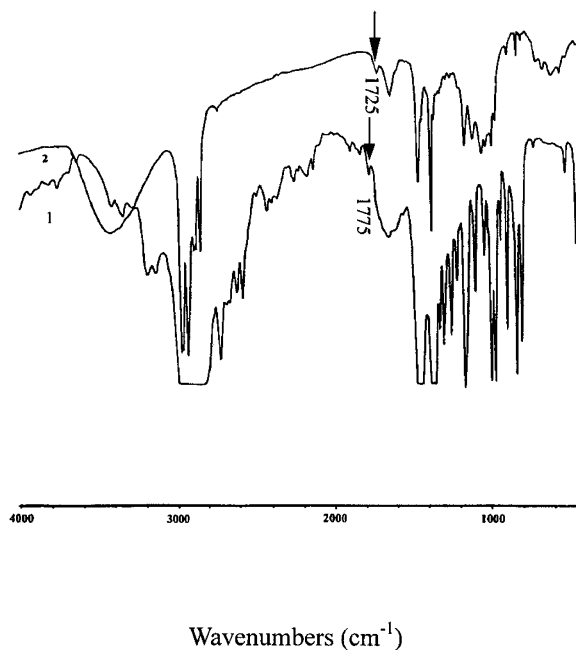
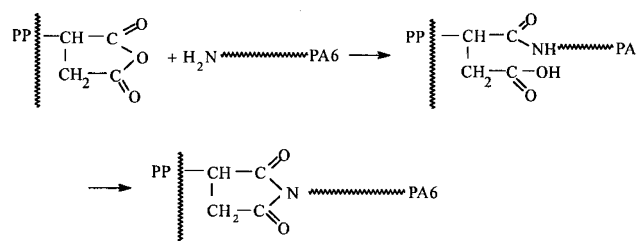


Figure 9. FT-IR spectra of PP-g-MAH and remnant substances of blend extracted with formic acid. 1: PP-g-MAH, 2: remnant substances.



Scheme 1.

CONCLUSIONS

Through pan-milling PP and MAH in solid state, PP-g-MAH copolymer was mechanochemically prepared. In comparison with common grafting methods, pan-milling can be conducted at ambient temperature and without using any initiators or solvents. The obtained PP-g-MAH can be used as compatibilizer for PA6/PP blend. Morphological study shows that the mechanochemically prepared PP-g-MAH significantly improved the microstructure of PA6/PP, resulting in much reduced PP dimension and more uni-

form dispersion in PA6 matrix. The mechanical properties were thus greatly enhanced. Especially, the impact strength almost doubled compared to uncompatibilized one. The remarkable compatibilizing effect of PP-g-MAH on PP/PA6 blend may owe to its strong interaction with PA6. Solid phase mechanochemical processing is a novel way to get PP/PA6 blend with higher performances and hopeful to be applied in even larger scale.

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