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Use of PP-g-MA Prepared by Solution Process as Compatibilizer in Polypropylene/Polyamide 6 Blends

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Abstract

In this work, polypropylene grafted maleic anhydride (PP-g-MA) prepared by solution process was used as a compatibilizer for polypropylene (PP)/polyamide 6 (PA6) blends. PP with melt flow index (MFI) of 10 g/10 min was grafted with maleic anhydride (MA) using benzoyl peroxide (BPO) as an initiator and toluene as a solvent. The effects of BPO and MA concentration on the grafting degree of MA onto PP were studied. The grafting degree was determined by a back-titration procedure whereas the formation of graft copolymers was confirmed by FT-IR technique. It was found that the maximum extent of grafting achieved was 0.87%. Blend of PP (MFI of 25 g/10 min) and PA6 with weight ratio of 70/30 was prepared by twin screw extruder. The prepared PP-g-MA (0.87% grafting) was used as a compatibilizer at the amount of 5 and 10 parts per hundred of the blend. The testing specimens were prepared by injection molding machine. The results showed that the tensile strength of the compatibilized blends was substantially higher than that of the uncompatibilized blend whereas percent elongation and Young's modulus were comparable. Morphology of the blends investigated by SEM technique disclosed that the compatibilized blends exhibited a remarkable decrease in size of the dispersed domain. TGA and DSC were employed to investigate thermal behaviors of the blends. PP-g-MA had a slight influence on the thermal stability of the blends. The crystallization rate of PP in the blends was higher than that of the neat PP. On the contrary, the presence of PP reduced the crystallization rate of PA6 in the blends.

Key word : PP-g-MA, solution process, compatibilizer, polypropylene, polyamide 6

Introduction

In recent years, research into polymer blends of commodity plastics and engineering resins has increased significantly. This is a way of tailoring product properties to specific applications as an alternative to the direct synthesis of new materials. In general, melt mixing of two polymers leads to a two-phase system because polymers are often thermodynamically immiscible, and this situation leads to a high interfacial tension and poor interface adhesion.(8, 5) When commodity plastics (e.g. polypropylene, PP) and engineering resins (e.g. polyamide, PA) are mixed, they are incompatible owing to different polarities and crystalline structures. The weak interfacial adhesion of these two polymers results in inferior mechanical properties, poor dispersion of thecomponents and limited ability to develop materials.(7) The interphase was considered by many authors as the third phase in the blend, which has a thickness and properties different from those of the components. However, PP/PA blend still has received much attention because it combine the thermomechanical properties of PA with the insensitivity to humid environments and easy processing characteristics of PP. In order to obtain morphologies which give rise to good mechanical properties, the incompatible blends require a compatibilizer to achieve satisfactory interfacial adhesion and interfacial stress transfer between the phases. It was reported that graft copolymers can be used effectively as compatibilizer for polymer blends.(2, 6) PP-grafted-maleic anhydride (PP-g-MA) is the popular third component that is added to aid both adhesion and mixing in PP/PA system.(7, 3, 1) In PP/PA blend, the PP-g-MA compatibilizer preferentially resides at the interface of PP and PA and improves interfacial adhesion through the chemical linkage of the anhydride groups with the polyamide end groups.(9)

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Grafting of maleic anhydride onto PP has been prepared successfully by several researchers using various methods with the aim of achieving compatibility between polar and nonpolar polymers.(4) These processes are usually carried out in the presence of organic peroxide and can be conducted in the solid state, in the melt, or in the solution. Sathe, *et al.* (1994) synthesized PP-g-MA by solution process using benzoyl peroxide (BPO) as an initiator in toluene. They reported that the maximum extent of grafting achieved was 5.3%. Shi, *et al.* (2001) prepared PP-g-MA by melt reactive extrusion using dicumyl peroxide (DCP) as an initiator. It was found that the grafting degree of PP-g-MA increased with increasing the loading level of DCP, and that it was in the range of 0.6-5 wt%.

Roeder, *et al.* (2005) studied the effect of a commercial PP-g-MA at the interface of PP/PA6 blends by infrared spectroscopy, differential scanning calorimetry and transmission and scanning electron microscopy. The addition of small quantities of PP-g-MA to the blends increased the homogeneity of PA phase dispersion in the PP matrix with a reduction in the size of the domains and copolymer formation at the interface. Abacha and Fellahi (2005) prepared PP-g-MA compatibilizer by molten state in an internal mixer using DCP as an initiator. They also found that the incorporation of PP-g-MA enhanced the tensile and impact properties of the PP/PA6 blends. This was attributed to better interfacial adhesion as evidenced by scanning electron microscopy. The purpose of this research is to prepare PP and PA6 blends using PP-g-MA as a compatibilizer. PP-g-MA used in this work was synthesized by solution process in the presence of BPO initiator in toluene. The mechanical and thermal properties and morphology of the blends were investigated.

Experimental

Materials

Isotactic PPs with melt flow index (MFI) of 10 and 25 g/10 min (density of 0.91 g/cm^3) were supplied by Thai Polyethylene Co., Ltd. PA6 was provided by Thai Toray Synthetics Co., Ltd. MA (Fluka); BPO, toluene, acetone, methanol (Lab Scan); KOH (Carlo Erba); trichloroacetic (Riedel-de Haed); and cresol red (Asia Pacific Specialty Chemicals Limited) were all AR grades and used as received without further purification.

Synthesis and Analysis of PP-g-MA

The graft copolymer was synthesized in a four-necked round-bottom flask equipped with a stirrer, a condenser, a thermometer, and a nitrogen gas inlet. 2.5% w/v of isotactic PP with MFI of 10 g/10 min was dissolved in toluene (200 ml) at 110°C with stirring under nitrogen atmosphere throughout the reaction to remove dissolved oxygen. After complete dissolution of PP, BPO of 0.1, 0.15, and 0.3% w/v in toluene and MA of 1.25 and 2.5% w/v in toluene were added into the solution, and the reaction was allowed to proceed for 6 h. To avoid gelation, the obtained warm solution was poured out into 2000 ml of acetone under vigorous stirring for 5 minutes to precipitate the graft copolymer. The product was isolated, and washed with acetone several times, and subsequently dried in vacuum overnight at 60°C. The prepared PP-g-MA was then Soxhlet extracted with acetone for 16 h to remove traces of MA and toluene. Finally, the product was dried in vacuum at 60°C to constant weight.

The grafting degree was determined from the anhydride concentration presented in the graft copolymer by a non-aqueous back-titration procedure.(12) A small amount (1 g) of the purified product was dissolved in 100 ml of xylene at boiling temperature (136-140°C) in a conical flask, and a few drops of water were added to hydrolyze all anhydride functions into carboxylic acid functions. Afterwards, 10 ml of 0.05N potassium hydroxide solution in methanol was added into the flask. The formed solution was back titrated with 0.03N trichloroacetic solution in xylene using cresol red as the indicator.

The chemical structures of the graft copolymer were characterized using FT-IR spectrophotometer (Perkin-Elmer FT-IR System 2000). The purified product was mixed with KBr and the mixture was then compression molded into thin film with a thickness of about 0.05 mm.

Blend Preparation

The polymers used for the blends were PP (with MFI of 25 g/10 min) and PA6 (dried in an oven at 80°C for 24 h before blending to remove moisture). The prepared PP-g-MA with the highest maleic anhydride content was used as a compatibilizer. The effect of the compatibilizer was studied making use of the differing percentage of PP-g-MA, 5 and 10 phr in the PP/PA6 70/30 blend composition. The mixing of PP, PA6 and PP-g-MA was performed using a twin screw extruder (Thermo PRISM) at a screw speed of 50 rpm. The temperature of each zone was set at T_1 = 90°C, T_2 = 220°C, T_3 = 320°C, T_4 = 330°C, and T_5 (die) = 320°C. The extrudate was cooled in water and granulated.

Dumbbell shape tensile specimens (ASTM D 638 Type I) of the materials were prepared using injection molding machine (Battenfield BA 250CDC) with a screw rotational speed of 65 rpm. The temperature for each zone was set at T_1 = 248°C, T_2 = 255°C, T_3 = 250°C, and T_4 = 240°C, and the mold temperature was set at 80°C.

Characterization, Morphology Analysis and Property Measurements of the Blends

The chemical structures of the blends were characterized using a FT-IR spectrophotometer (Perkin-Elmer FT-IR System 2000). A scanning electron microscope (Jeol JSM-6400) was used to observe the morphology of the blends. The accelerated voltage was 15 kV. The polymer blends were fractured in liquid nitrogen and the fracture surfaces were sputter coated with a thin layer of gold before observation.

Tensile testing of the blends was determined using a Universal Testing Machine (LLOYD LR 10K) with a 10 kN load cell at a crosshead speed of 50 mm/min. The tensile strength, elongation at break and modulus for each blend were determined using the average value from five specimens.

The thermal properties of the blends were analyzed using DSC and TGA techniques. For DSC analysis, the blend samples were tested with a differential scanning calorimeter (Perkin Elmer DSC Diamond) at the temperature range from 60 to 240°C under nitrogen atmosphere. The samples were heated to 240°C at a rate of 10oC/min and held at this temperature for 3 min. Then, the samples were cooled to 100°C at 40°C/min and kept at this temperature for 1 min to erase the previous thermal history. After that, the samples were reheated to 240°C at a heating rate of 10°C/min. Melting and crystallization temperatures were determined from this DSC experiments. For TGA of the blend, a thermogravimetric analyzer (Mettler Toledo TGA/SDTA 851e) was used at the temperature range from 60 to 1000°C with the heating rate of 20°C/min under nitrogen atmosphere.

Results and Discussion

Percent Grafting

Percent grafting of PP-g-MA as a function of concentration of BPO initiator and MA monomer is shown in Figure 1. The maximum percent grafting at 0.87% was obtained by the application of 1.25% of MA and 0.15% of BPO. The initial increase in the percent grafting is caused by an increase in concentration of radicals formed through the decomposition of initiator. Thus, the higher the concentration of BPO radicals, the higher the chain transfer to PP backbone and the higher the percent grafting. Furthermore, an increase in BPO concentration decreases the percent grafting because of the termination reactions between the PP radicals. Thus, the lower the concentration of radicals, the lower the percent grafting of PP-g-MA. In addition, it can be seen that the percent grafting of PP-g-MA prepared from 2.5% of MA was lower than that from 1.25% of MA at each BPO concentration. At higher monomer concentration, many reactions may compete with the grafting reaction in the solution. This means that the higher monomer concentration causes side reactions (such as chain transfer to monomer). The percent grafting at a monomer concentration of 2.5% is therefore lower than that of 1.25%. In this work, PP-g-MA with 0.87% grafting was used as a compatibilizer for PP/PA6 blends.

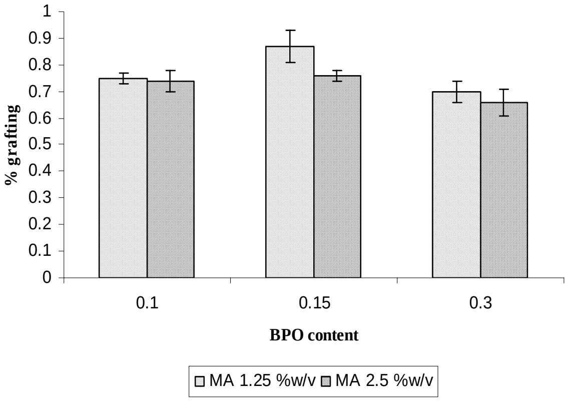


Figure 1. Percent grafting of PP-*g*-MA as a function of BPO and MA concentration**.**

FT-IR Analysis of PP-g-MA

The graft copolymer was confirmed using FT-IR spectroscopy. The FT-IR spectra of PP and PP-g-MA (0.87% grafting) are shown in Figures 2 and 3, respectively. The spectra of graft copolymer showed peaks at 1780 and 1720 cm^{-1}, characteristics of cyclic anhydride groups. Also in grafted sample, the intensity (at 1460, 1380 and 1170 cm^{-1}) diminishes, showing that MA has been introduced as a graft onto PP.

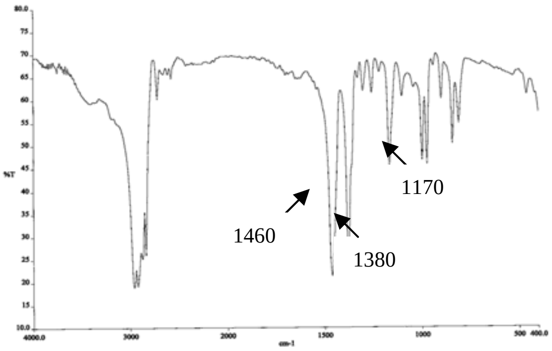


Figure 2. FT-IR spectrum of polypropylene with MFI of 10 g/10 min.

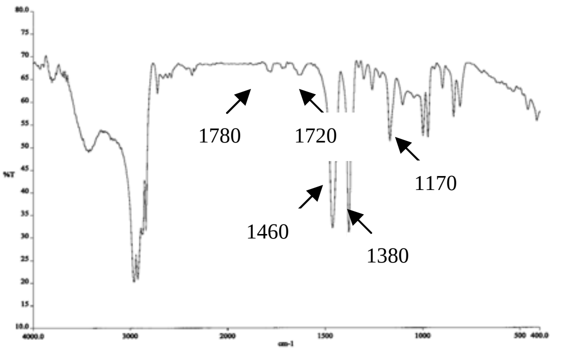


Figure 3. FT-IR spectrum of PP-*g*-MA (0.87% grafting) prepared from PP with MFI of 10 g/10 min.

FT-IR Analysis of the Blends

Figure 4 shows the infrared spectrum of the PP/PA6 uncompatibilized blend at weight ratio of 70/30 with the characteristic peaks of PP at 1460, 1380 and 1170 cm^{-1} and the characteristic peaks of PA6 at 3310, 1640 and 1540 cm^{-1}. Figures 5 and 6 show infrared spectra of the PP/PA6 70/30 blend with the incorporation of 5 and 10 phr of PP-g-MA compatibilizer, respectively. The spectrum of the compatibilized blend displays two other peaks due to the formation of imide linkage. The peak at 1770 cm^{-1} was assigned to the carbonyl vibration of the imide group and the peaks at 1360 and 715 cm^{-1} to the -C-N- in the cyclic imide. The result indicates the formation of the imide linkage by reaction at the interface. Compatibilization is considered to occur through chemical linkage of the anhydride on the compatibilizer chain and the PA end groups as shown in Scheme 1. This can be further confirmed by the SEM observation.

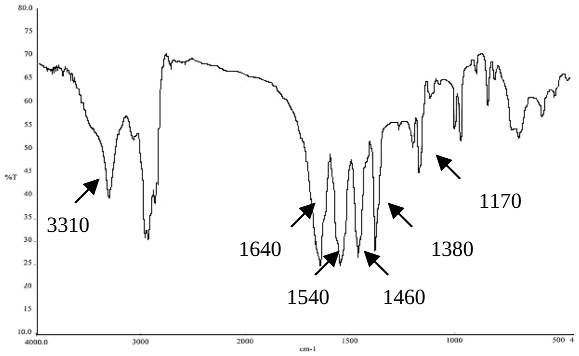


Figure 4. FT-IR spectrum of PP/PA6 uncompatibilized blend at weight ratio of 70/30.

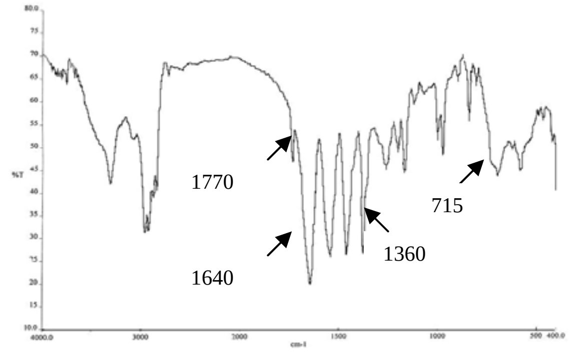


Figure 5. FT-IR spectrum of 70 PP/30 PA6 blend with the incorporation of 5 phr of PP-*g*-MA compatibilizer.

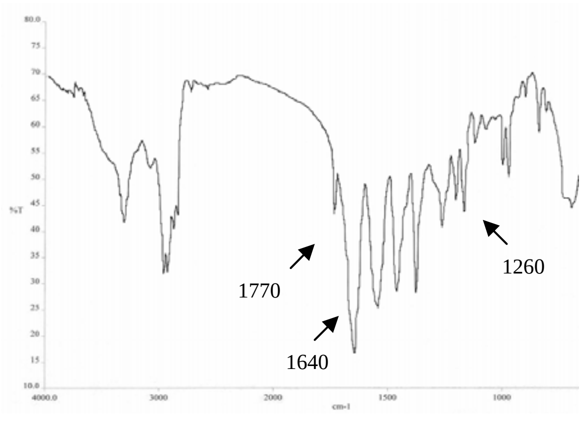
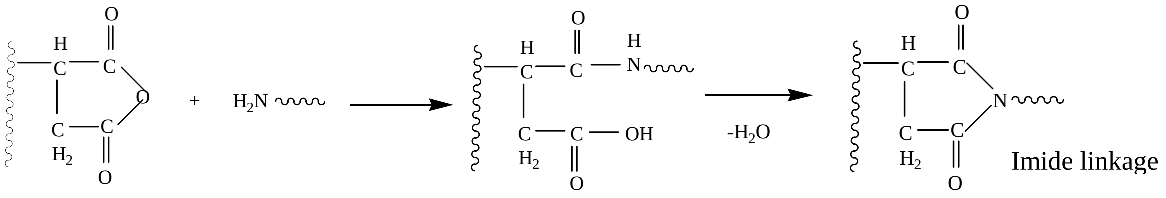


Figure 6. FT-IR spectrum of 70 PP/30 PA6 blend with the incorporation of 10 phr of PP-g-MA compatibilizer.



Scheme 1. Reaction of amine with anhydride-grafted polypropylene proceeds to imide linkage.

Morphology Analysis

Blending of PP and PA6 to improve mechanical properties can result in some difficulties to obtain a homogeneous system. Large PA6 spherical domains surrounded by the continuous PP phase were observed in the PP/PA6 blend (Figure 7a), contrasting to the homogeneous morphology of the compatibilized blend of PP/PA6/PP-g-MA (Figures 7b and 7c). The addition of PP-g-MA leads to a decrease in the diameter of PA6 domains. This homogeneous dispersion is related with the compatibilizing effect, due to the interfacial adhesion of PP and PA6. On the other hand, the addition of the compatibilizer in polymer blends improved interfacial adhesion between domains and matrix and reduced the size of the dispersed domain.

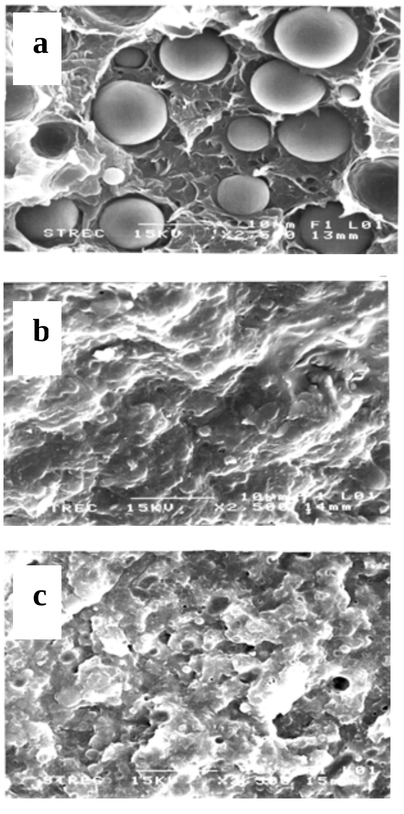


Figure 7. SEM micrographs of PP/PA6/PP-g-MA: (a) 70/30/0, (b) 70/30/5 and (c) 70/30/10

Tensile Testing

Figure 8 shows the tensile strength of the polymer blends. The results indicated that the blend of PP/PA6 70/30 incorporated with 5 and 10 phr of PP-g-MA exhibited much higher tensile strength than uncompatibilized samples. This reflected that PP-g-MA increased the compatibility between PP and PA6. Moreover, tensile strength of the blends slightly increased as the amount of PP-g-MA increased from 5 to 10 phr. However, there are insignificant differences in the elongation behavior and Young’s modulus between the uncompatibilized and compatibilized samples, as can be seen in Figures 9 and 10, respectively.

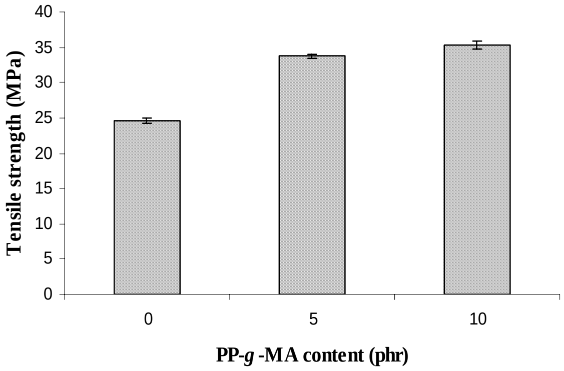


Figure 8. Tensile strength of PP/PA6 70/30 blends with various amount of PP-*g*-MA.

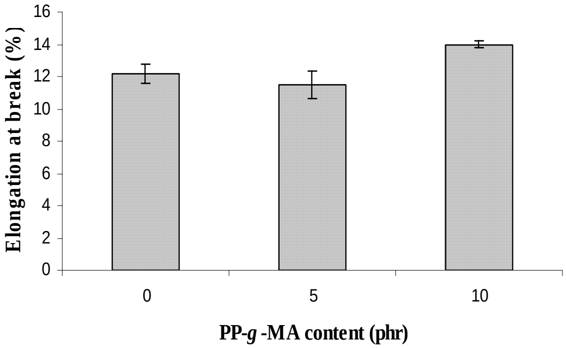


Figure 9. Elongation at break of PP/PA6 70/30 blends with various amount of PP-*g*-MA.

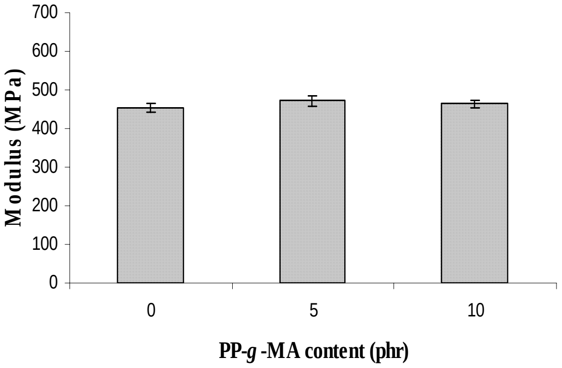


Figure 10. Young's modulus of PP/PA6 70/30 blends with various amount of PP-*g*-MA.

Thermal Behaviors

DSC results are summarized in Table 1 and Figures 11-14. Figure 11 shows the DSC cooling curves of PP and the PP/PA6 70/30 blends compatibilized with 0, 5 and 10 phr of PP-g-MA. The cooling crystallization temperatures (T_c) of the PP component in these blends are higher than that of the neat PP (9-11°C), an indication of fast nucleation due to the crystalline PA6 as nucleating agent across PP-PA interface to promote PP crystallization in these compatibilized PP/PA6 blends. Whereas, Figure 12 shows that the T_cs of the PA6 component in these compatibilized blends are about 2-3°C lower than that of the neat PA6, an indication of slower nucleation. The presence of PP and PP-g-MA tends to interfere with the PA6 crystallization. This is in good agreement with earlier works reported by Campoy, Tseng and their coworkers. The glass transition temperature of PP and PA6 can not be detected in these heating thermograms.

Table 1. DSC data of PP, PA6 and PP/PA6 blends

Blends	Composition	PP		PA6	
		Tc(°C)	*Tm*(°C)	*Tc*(°C)	*Tm*(°C)
PP		107	161,166	-	-
PA6		-	-	156	220
PP/PA6	70/30	111	158,168	179	220
PP/PA6/PP-g-MA	70/30/5	116	161	172	216
PP/PA6/PP-g-MA	70/30/10	118	161	-	219

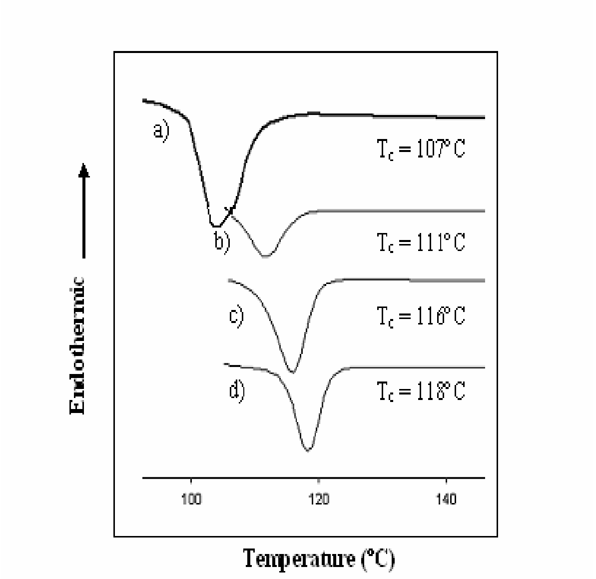


Figure 11. DSC cooling curves showing the crystallization temperature of a) PP, b) PP in PP/PA6 70/30 blend, c) PP in PP/PA6/ PP-*g*-MA 70/30/5 blend, and d) PP in PP/ PA6/PP-*g*-MA 70/30/10 blend.

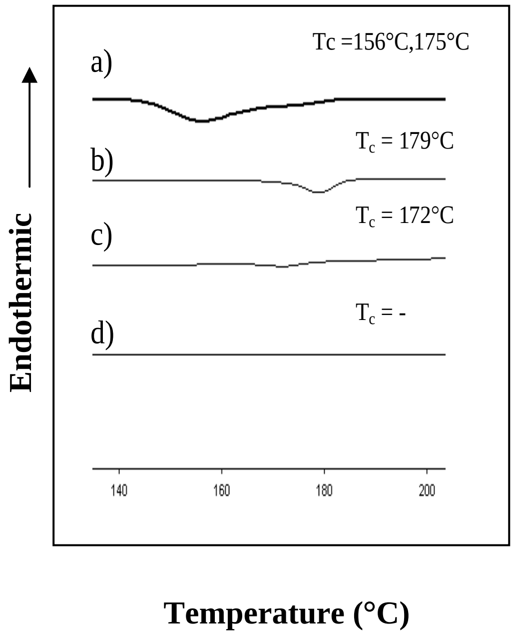


Figure 12. DSC cooling curves showing the crystallization temperature of (a) PA6, (b) PA6 in PP/PA6 70/30 blend, (c) PA6 in PP/PA6/PP-*g*-MA 70/30/5 blend, and (d) PA6 in PP/PA6/PP-*g*-MA 70/30/10 blend.

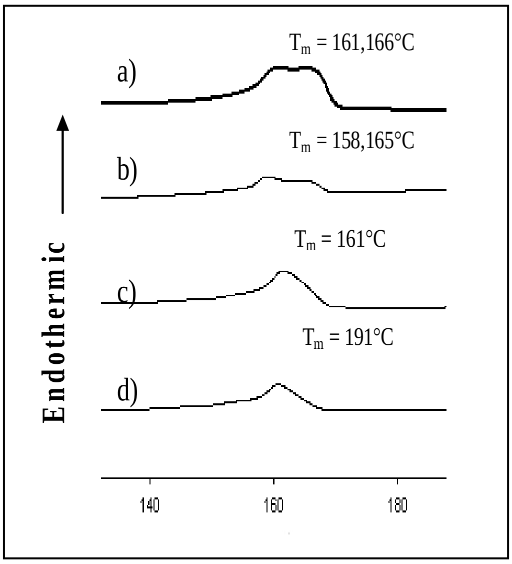


Figure 13. DSC heating curves showing the melting temperature of (a) PP, (b) PP in PP/PA6 70/30 blend, (c) PP in PP/PA6/PP-*g*-MA 70/30/5 blend, and (d) PPin PP/PA6/PP-*g*-MA 70/30/10 blend.

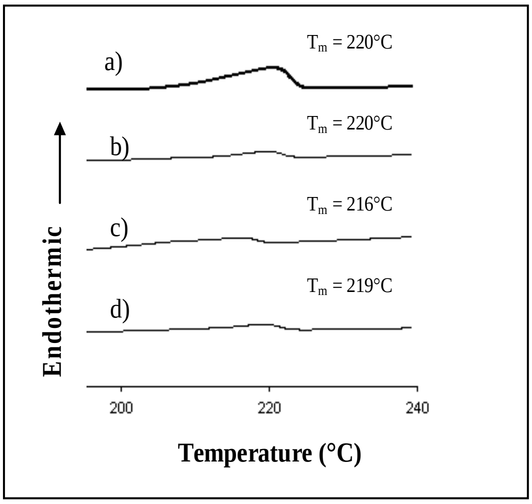


Figure 14. DSC heating curves showing the melting temperature of (a) PA6, (b) PA6 in PP/PA6 70/30 blend, (c) PA6 in PP/PA6/PP-*g*-MA 70/30/5 blend, and (d) PA6 in PP/PA6/PP-*g*-MA 70/30/10 blend.

PP and PA6 are semicrystalline polymers with melting temperature (T_m) at about 161 and 220 °C, respectively (as shown in Figures 13 and 14). No marked change is observed for the melting points of the two phases in these uncompatibilized and compatibilized blends except for that of the PP/PA6/ PP-g-MA 70/30/10 blend.

TGA results are summarized in Table 2. The onset temperature and the 50% decomposition temperature of PP, PA6, PP-g-MA, and PP/PA6 70/30 blends compatibilized with 0, 5 and 10 phr of PP-g-MA were investigated. It can be seen that the compatibilizer had a slight influence on the thermal stability of the blends. The decomposition temperatures are in the range of 418-461°C.

Table 2. TGA data of PP, PA6, PP-*g*-MA and PP/PA6 blends.

Blends	Composition	Onset temperature (°C)	50% Decomposition temperature (°C)
PP		442	459
PA6		418	440
PP-*g*-MA		439	461
PP/PA6	70/30	418	453
PP/PA6/PP-*g*-MA	70/30/5	435	453
PP/PA6/PP-*g*-MA	70/30/10	439	458

Conclusions

In this study, PP-g-MA compatibilizer synthesized by solution process has been shown to improve the dispersion, interfacial adhesion and tensile strength in PP/PA6 blends. The better interfacial adhesion was evidenced by scanning electron microscopy. The addition of PP-g-MA to this incompatible blends increased the homogeneity of PA6 phase dispersion in the PP matrix with a reduction in the size of the domains. The tensile strength of the uncompatibilized blend was lower than that of the compatibilized blends due to poor adhesion between the phases. With improved adhesion by PP-g-MA, the tensile strength of the PP/PA6 blends was increased remarkably. The crystallization of these blends has been investigated. It is found that the crystallization rate of PP in the blends is higher than the pure PP. This behavior is related to the nucleating activity by the PA6 component. On the contrary, the presence of PP and PP-g-MA interferes with the crystallization of PA6 in the blends.

Acknowledgments

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