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Preparation of Polypropylene Compatibilizer by Radiation Grafting and Its Effect on PP/Nylon 6 Blend

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Summary: The polypropylene-based compatibilizers, polypropylene-g-maleic anhydride (PP-MAH), polypropylene-g-maleic anhydride/styrene (PP-St/MAH), and polypropylene-g-acrylic acid (PP-AA), were prepared by a high energy irradiation method. The compatibilizing effect of newly prepared graft copolymers on immiscible PP/Nylon6 blends has been studied by means of UTM, SEM and DSC techniques. The results indicate that PP-MAH and PP- St/MAH are more effective compatibilizers for PP/Nylon6 blends than PP-AA, and the compatibilizing effect on PP/Nylon6 blends depends on molecular structure of the compatibilizers and the composition of the blends.

Keywords: blend; compatibilizer; nylon 6; polypropylene

Introduction

Although blending two or more polymers offers an economic way to produce new materials with a desired property combination,[1] most of polymer blends are immiscible or incompatible and both. Reasons for an incompatibility are a high tension and therefore leading to poor adhesion. Recently, much attention has been paid to the study of using graft or block copolymers as compatibilizers for immiscible polymer blends because they are one of the simplest and most efficient methods for development of new high-performance polymer materials. Usually, suitably chosen graft or block copolymers, whose segment may be chemically identical with those in the respective phases or miscible with one of the phases, can act as ‘‘interfacial agents’’ to reduce the interfacial tension and improve the interfacial adhesion of the immiscible components.[2–4]

Blends of polypropylene (PP) and nylon have received a considerable attention due to the combination of the thermo-mechanical property of nylon with an easy processability of polypropylene.[5] However, PP and nylon are immiscible due to the differences in the polarity and crystalline structure between two polymers.[6] The compatibilizers for immiscible PP/Nylon blends such as PP grafted with maleic anhydride (MAH), acrylic acid (AA), and glycidyl methaccrylate[7–10] have been prepared by solution grafting,[11,12] melt grafting,[13–15] and solid state grafting[16–18] in the presence of peroxide initiator. However, these methods have several shortcomings. First, an initiator must be used, which leads to a more complicated compatibilization chemistry. Second, polymerization is usually not complete under the available thermal conditions. Residual monomers from thermal polymerization may thus adversely influence the thermal and mechanical properties of the blends. On the other hand, graft polymerization induced by high energy irradiation method is a well-established and does not require any initiators. This technique thus has advantages, such as the fact that the

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polymerization proceeds mildly and thoroughly, the chemistry of the reaction system is free of contamination, and the energy consumption is relatively low.[19]

In this paper, the PP-based graft copolymers, polypropylene-g-maleic anhydride (PP-MAH), polypropylene-g-styrene/maleic anhydride (PP-St/MAH), and polypropylene-g-acrylic acid (PP-AA), were prepared by high energy irradiation method. The compatibilizing effect of newly prepared graft copolymers on immiscible PP/Nylon6 blends has been studied by means of UTM, SEM and DSC techniques.

Experimental Part

Materials

Nylon 6 (Ny6) (d: 1.084 g/ml, T_g: 62.5 °C, T_m: 228.5 °C) was purchased from Aldrich Chemical Company. Polypropylene (PP) (B310, MW: 523,000) used in PP/Ny6 blends and atactic PP (MW: 43,000) for the preparation of compatibilizers was donated from Honam Pertochemical Co. Maleic anhydride (MAH) (Showa chemical) was purified by recrystallization from diethyl ether. Acrylic acid (AA) and styrene (St) were purchased from Junsei Chemical and used as received.

Preparation of Graft Copolymers and PP/Nylon6 Blends

PP was dry blended with MAH (3 phr), St (1 phr)/MAH (3 phr), or AA (3 phr) in a lab-scale Brabender at 130°C and 65 rpm rotor speed for 6 min. The prepared samples were γ-irradiated under various irradiation doses ranging from 25 to 100 kGy at a dose rate of 20 kGy/h and at room temperature. The crude products, PP-MAH, PP-St/MAH, and PP-AA, were purified by refluxing in xylene at 130 °C for 2 h and poured into a large excess of acetone. The products were filtered, washed with acetone, and then dried at 80 °C.

PP was stabilized with Irganox 1010 and all polymers were dried in a vacuum oven at 80 °C overnight before blending. PP/Ny6 blending was carried out in the same lab-scale Brabender at 240 °C and 65 rpm rotor speed for 6 min.

Characterization

The grafting degree (DOG) was measured by an acid-base titration method.[4] A known weight of graft copolymer was dissolved in hot xylene, and titrated with alcoholic potassium hydroxide (0.01 N), which had been standardized against potassium phthalate using 1% thymol blue as an indicator. The FT-IR spectrum of graft copolymers was recorded by a Bruker Tensor 37 FT-IR spectrometer. The tensile properties and impact properties were measured according to ASTM D638 and ASTM D256 respectively. Thermal analysis was performed with a DSC Q100 differential scanning calorimeter. The test was conducted in a nitrogen atmosphere with the heating rate of 10 °C/min between 30 and 250 °C. The melting temperatures (T_m) values were taken from the second heating curve. Crystallinities were calculated by using an extrapolated value of the enthalpy corresponding to the melting of 100% crystalline samples: $\Delta H_{PP} = 137.9$ J/g and $\Delta H_{Nylon6} = 190$ J/g.[20] The fractured surfaces of the various blends were examined under a Philips XL30S FEG.

Results and Discussion

Synthesis of Compatibilizers

An acid-base titration was performed to measure the degree of grafting and the results are shown in Figure 1. The grafting degrees of MAH, St/MAH and AA onto PP increased with the total absorbed doses. The grafting degree of AA is higher than that of MAH due to higher polymerizability of AA. The highest grafting degrees of PP-St/MAH and PP-AA are 1.01 and 2.87 wt% respectively. The grafting degree of PP-St/MAH was higher than that of PP-MAH. This is due to the fact that the presence of styrene capable of donating electrons could activate MAH by rendering

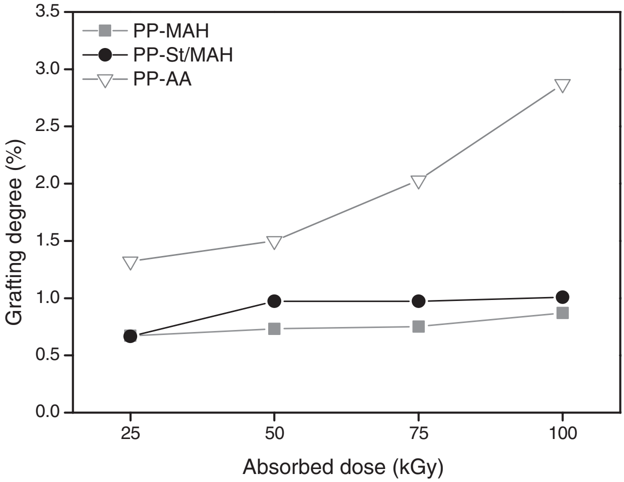

Figure 1.
The effect of absorbed dose on the grafting degree.

its structure unsymmetrical and its π bond of radical-anion characters.[14]

The FT-IR spectra of pure PP and compatibilizers are shown in Figure 2. After the graft copolymerization of MAH and St/MAH onto PP, the peaks of the carbonyl group of MAH at 1855 and 1782 cm^{-1} were observed. And also the peaks of the aliphatic CH group of PP and the out-of-plane bending peaks of benzene ring in styrene appeared at 2725 and 705 cm^{-1}. In case of PP-AA, the peak of the carbonyl group of the acrylic acid appeared at 1712 cm^{-1}. These indicate that the MAH, St/MAH, and AA were successfully grafted onto PP.

Properties of PP/Ny6 Blends

PP, Ny6, and compatibilizers were blended in a lab-scale Brabender according to the composition in Table 1.

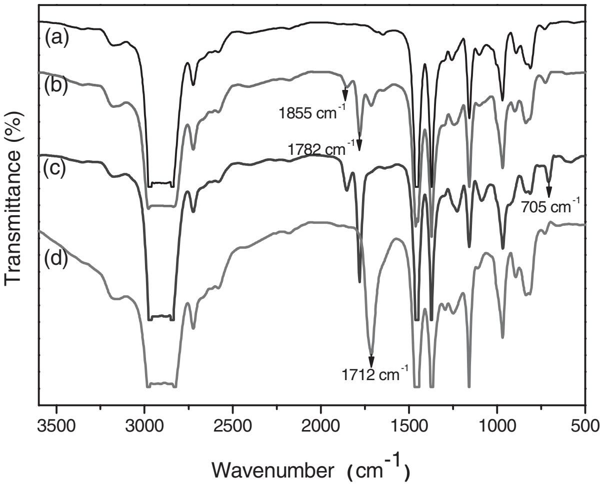

Figure 2.
FT-IR spectra: (a) atactic PP, (b) PP-MAH (c) PP-St/MAH, and (d) PP-AA after the extraction.

Table 1.
Formulations used in this study.

Formulation	PP wt%	Ny6 wt%	Compatibilizer wt%
Neat Polymers			
PP	100	0	0
Nylon6	0	100	0
Blends			
PP/Ny6 (70:30)	70	30	0
PP-MAH toughened Blends			
PP/Ny6 (65:30) PP-MAH[a] (5)	65	30	5
PP/Ny6 (50:30) PP-MAH[a] (10)	60	30	10
PP-St/MAH toughened Blends			
PP/Ny6 (65:30) PP-St/MAH[b] (5)	65	30	5
PP/Ny6 (60:30) PP-St/MAH[b] (10)	60	30	10
PP-AA toughened Blends			
PP/Ny6 (65:30) PP-AA-1[c] (5)	65	30	5
PP/Ny6 (60:30) PP-AA-1[c] (10)	60	30	10
PP-AA toughened Blends			
PP/Ny6 (65:30) PP-AA-2[d] (5)	65	30	5
PP/Ny6 (60:30) PP-AA-2[d] (10)	60	30	10

[a] PP-MAH (DOG: 0.87).
[b] PP-St/MAH (DOG: 1.01).
[c] PP-AA-1 (DOG: 2.02).
[d] PP-AA-2 (DOG: 2.87).

The tensile properties and impact strength of the blend (PP/Ny6) are summarized in Table 2. The tensile strength (TS) and elongation at break (%El) of PP-AA toughened blends increased when compared to the uncompatibilized blends. However, these properties were lower than those of PP-MAH and PP-St/MAH toughened blends. The PP-AA with higher DOG may show better compatibilizing effect for the PP/Ny6 blend

Incorporation of PP-MAH and PP-St/MAH into PP/Ny6 blend improved the mechanical properties such as TS, %El, and

Table 2.
Mechanical properties of PP/Ny6 blends.

Formulation	Tensile strength kgf/mm^2	Elongation at break %	Impact strength kgf/cm
Neat Polymers			
PP	2.73	220	–
Ny6	5.24	386	–
Blends			
PP/Ny6 (70:30)	1.63	15	6.23
PP-MAH toughened Blends			
PP/Ny6 (65:30) PP-MAH (5)	1.73	255	7.08
PP/Ny6 (60:30) PP-MAH (10)	1.85	294	7.74
PP-St/MAH toughened Blends			
PP/Ny6 (65:30) PP-St/MAH (5)	1.95	290	8.05
PP/Ny6 (60:30) PP-St/MAH (10)	1.96	300	7.82
PP-AA toughened Blends			
PP/Ny6 (65:30) PP-AA-1 (5)	1.72	80	5.00
PP/Ny6 (60:30) PP-AA-1 (10)	1.73	73	4.30
PP-AA toughened Blends			
PP/Ny6 (65:30) PP-AA-2 (5)	1.77	140	6.32
PP/Ny6 (60:30) PP-AA-2 (10)	1.66	145	5.72

impact strength (IS). This can be attributed to the fact that PP-MAH and PP-St/MAH have good interfacial interactions with PP and also Ny6 because MAH unit could interact with functional groups of Ny6.

Therefore, the compatibilizing effect of PP-MAH and PP-St/MAH is more effective than that of PP-AA. And the PP-AA with higher DOG can improve the mechanical properties of PP/Ny6 blend.

The thermal properties of the blends were characterized by DSC. The results of crystallization temperature (T_c), melting temperature (T_m), and the crystallinity (W_c) of PP and Ny6, of the pure components and of the blends, are shown in Table 3.

When compared to the T_c of pure PP, the T_c of PP component in the blend was slightly increased by the nucleating agent-like behavior of the already crystallized Ny6 component.[4] The T_m of PP and Ny6 component in the blend was similar to that of pure PP and Ny6. The W_c of PP and Ny6 component in the blend decreased with comparison to those of pure PP and Ny6. The W_c of PP-MAH and PP-St/MAH toughened blend was lower than that of PP-AA toughened blend, indicating that PP-MAH and PP-St/MAH disturb much more the crystalline structure of the blend components than PP-AA dose. This decrease in crystallinity was caused by the difficulty in polymer chain arrangement, restricting movement by branched chains.[21]

Figure 3(a) shows the cooling thermograms of the investigated samples. PP-AA did not interfere in the crystallization peak of Ny6, but the incorporation of PP-MAH and PP-St/MAH caused its disappearance. The crystallization process of Ny6 in the blends may happen in two steps, one at the usual T_c of nylon and the other at that of PP. The disappearance of the crystallization peak at the usual T_c for Ny6 suggests that the whole Ny6 crystallization coincidentally took place at the usual T_c for PP. This crystallization behavior did not mean that Ny6 co-crystallized with PP, since each component showed a separated melting endotherm (Figure 3(b)). Hence, the coincident crystallization of Ny6 with PP is a concurrent crystallization and it is due to the reduction of the particle sizes of Ny 6 in the PP/PP-MAH/Ny6 and PP/PP-St/MAH/Ny6 blend.[4]

The morphological effect of compatibilizers in the blend was characterized by a scanning electron microscope. Figure 4 shows the fractured surface morphology of the blends with and without the compatibilizers. The images of the PP/Ny6 blend with PP-AA seen in Figure 3(d) and 3(e) reveal that PP-AA is not as effective as PP-MAH or PP-St/MAH. On the other hand, PP-MAH and PP-St/MAH showed almost continuous phases as shown in

Table 3.
Thermal properties of pure PP, Ny6 and their blends.

Formulation	T_c (°C)		T_m (°C)		W_c (%)	
	PP	Ny6	PP	Ny6	PP	Ny6
Neat Polymers						
PP	121	–	166	–	58.5	–
Ny6	–	175	–	223	–	27.2
Blends						
PP/Ny6 (70:30)	123	193	166	219	41.8	10.9
PP-MAH toughened Blends						
PP/Ny6 (60:30) PP-MAH (10)	122	–[a)]	165	219	33.0	8.1
PP-St/MAH toughened Blends						
PP/Ny6 (60:30) PP-St/MAH (10)	122	–[a)]	165	220	33.8	8.2
PP-AA toughened Blends						
PP/Ny6 (60:30) PP-AA-1 (10)	123	190	164	219	34.5	10.5
PP-AA toughened Blends						
PP/Ny6 (60:30) PP-AA-2 (10)	123	191	165	219	35.5	10.1

[a)] Not detected.

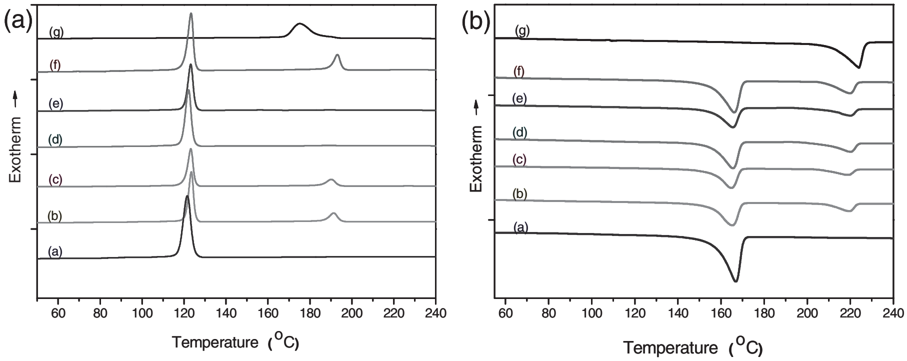

Figure 3.
DSC curves: (a) cooling and (b) heating; for (a) pure PP, (b) PP/PP-AA-2/Ny6, (c) PP/PP-AA-1/Ny6, (d) PP/PP-St/MAH/Ny6, (e) PP/PP-MAH/Ny6, (f)PP/Ny6, and (g) pure Ny6.

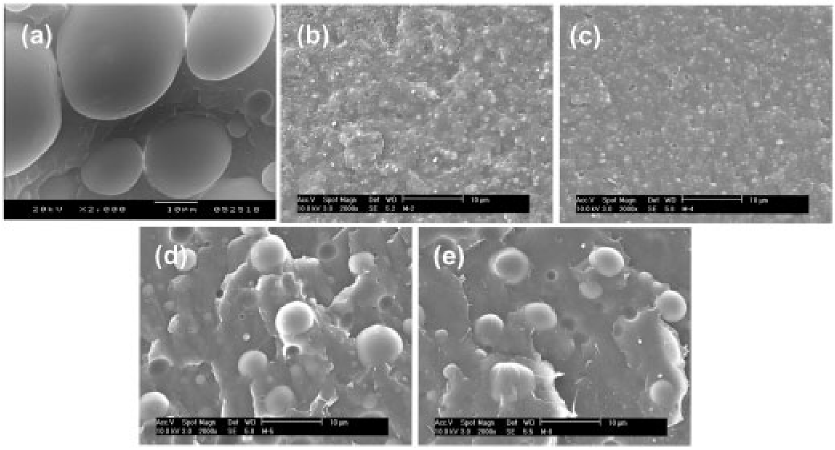

Figure 4.
Scanning electron micrographs of PP/Ny6 blends: (a) without any compatibilizers; (b) with 10 wt% of PP-MAH; (c) with 10 wt% of PP-St/MAH; (d) with 10 wt% of PP-AA-1; (e) with 10 wt% of PP-AA-2.

Figure 3(b) and 3(c). These results are in line with those of the thermal analysis and mechanical properties.

Conclusion

The effective compatibilizers, PP-MAH, PP-St/MAH, and PP-AA, for PP/Nylon6 blends were prepared by radiation-induced graft polymerization of functional monomers onto PP. The compatibilizing effect of graft copolymers depends on the molecular structure of the compatibilizers and the composition of the blends. PP-MAH and PP-St/MAH showed better compatibilizing effect than PP-AA due to the better interaction of MAH unit with amide, amine, or carboxylic acid groups in Nylon6. PP-AA with higher DOG may also show better compatiblizing effect. The blends with PP-MAH or PP-St/MAH also showed fine dispersion and improved interfacial adhesion in the morphology.

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