

Effects of PP-g-MAH on the Mechanical, Morphological and Rheological Properties of Polypropylene and Poly(Acrylonitrile-Butadiene-Styrene) Blends

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Abstract: The effects of maleic anhydride-grafted polypropylene (PP-g-MAH) addition on polypropylene (PP) and poly(acrylonitrile-butadiene-styrene) (ABS) blends were studied. Blends of PP/ABS (70/30, wt%) with PP-g-MAH were prepared by a twin-screw extruder. From the results of mechanical testing, the impact, tensile and flexural strengths of the blends were maximized at a PP-g-MAH content 3 phr. The increased mechanical strength of the blends with the PP-g-MAH addition was attributed to the compatibilizing effect of the PP and ABS blends. In the morphological studies, the droplet size of ABS was minimized (6.6 μm) at a PP-g-MAH content of 3 phr. From the rheological examination, the complex viscosity was maximized at a PP-g-MAH content of 3 phr. These mechanical, morphological and rheological results indicated that the compatibility of the PP/ABS (70/30) blends is increased with PP-g-MAH addition to an optimum blend at a PP-g-MAH content of 3 phr.

Keywords: polymer blends, compatibilizer, mechanical properties, morphology, rheology.

Introduction

Polymer blending has been considered as an effective method for the development of new polymeric materials. The properties of the polymer blends are influenced by the properties of the each components and degree of the dispersion of the minor component. However, most of the polymer blends are found to be incompatible.¹⁻¹⁹ These incompatible polymer blends have poor mechanical and physical properties. In order to improve the mechanical properties of the polymer blends, the compatibilizer has been widely used.

The blending of various polymers with maleic anhydride grafted polymers as a compatibilizer has been a subject of recent years.²⁰⁻³⁷ In the melt blends, maleic anhydride groups can easily react with functional groups of polymers to form block or graft copolymers. These resulting copolymers efficiently reduce the interfacial tension between two polymers, thus, also improve physical and mechanical properties of the blends. In the literature, maleic anhydride (MAH) grafted polyethylene-octene elastomer has proven as an effective compatibilizer of nylon 6/poly(acrylonitrile-butadiene-sty-

rene) (ABS) blends.²⁰ Maleic anhydride grafted ABS have been used as both impact modifier and compatibilizer for polycarbonate (PC)/ABS blends.²⁶⁻³⁰ George *et al.*³¹⁻³³ and Nakason *et al.*³⁴ reported the effects of maleic modified polypropylene (PP) on the PP/nitrile rubber blends³¹⁻³³ and PP/maleated natural rubber blends as a compatibilizer.³⁴ In the studies of PP/clay nanocomposite, Park *et al.*³⁷ reported the effect of MAH-grafted PP (PP-g-MAH) on the thermal and rheological properties of the PP/clay nanocomposite.

PP has advantages of high heat distortion temperature, good processibility, and economic merits. However, PP has a disadvantage of low impact strength. In order to improve the ductile properties of the PP, ABS which is one of the most widely used rubber-toughened polymers could be used with a compatibilizer because of its poor compatibility between PP and ABS.³⁸⁻⁴¹ For the PP/ABS blends, Patal *et al.* have used compatibilizer such as acrylic acid grafted PP and hydroxyethyl methacrylate grafted PP.⁴⁰ From the study of Kum *et al.*, poly(styrene-co-acrylonitrile) grafted PP (PP-g-SAN) was used as a compatibilizer in the PP/ABS blends, in order to improve the compatibility of the PP/ABS blends.⁴¹

In this study, mechanical, morphological and rheological properties of the PP/ABS (70/30, wt%) blends with maleic

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anhydride grafted polypropylene (PP-g-MAH) are reported by the universal testing machine (UTM), Izod impact tester, scanning electron microscopy (SEM) and advanced rheometric expansion system (ARES). In particular, by the addition of compatibilizer such as PP-g-MAH, compatibilization effects of the PP/ABS blends have been investigated.

Experimental

Materials. The materials used in this study were PP, ABS and PP-g-MAH. The polymers used in this study were obtained from commercial sources. The PP was supplied by Samsung Total Petrochemicals Co. The ABS was supplied by LG Chem. Ltd. The graft polymer PP-g-MAH (Polybond 3150) was supplied by Crompton Corp., and maleic anhydride content of PP-g-MAH was 0.5 wt%. The characteristics of the PP, ABS and PP-g-MAH are summarized in Table I.

Blend Preparations. The blends of PP, ABS and PP-g-MAH were prepared using a 11 mm diameter twin screw extruder with a screw ratio of 40:1 length to diameter (Bau Tech. Co.). Prior to extrusion, PP, ABS and PP-g-MAH were dried in a vacuum oven at 80 °C for 24 h. For the PP/ABS blends, the ABS with the weight fractions ranged from 0.0 to 1.0 with increment of 0.1 were mixed with the PP using the extruder. Also, PP-g-MAH was added in the PP/ABS blends with 0, 1, 3, and 5 phr as a compatibilizer. The temperature of the extruder was set at 180 to 220 °C in feeding and barrel zones, respectively. The screw speed of the extruder was set at 100 rpm. Samples were compression molded using a hot press at 220 °C for 5 min. Before preparation of the samples, all the samples were dried under vacuum (< 1 mmHg) at 80 °C for 24 h.

Mechanical Properties. The impact strength of the PP/ABS/PP-g-MAH blends was investigated under the ambient condition by notched Izod impact strength method (McVan Instruments ITR-2000). The impact tester was performed according to the ASTM D-256 and 7 specimens were measured and averaged. Tensile and flexural strength of PP/ABS/PP-g-MAH blends were investigated under the ambient condition using a universal testing machine (Instron 4467). Tensile test was performed according to the ASTM D-638. The speed of cross-head movement was 5.0 mm/min. Flexural test was performed according to the ASTM D-790. The span length and the speed of cross-head movement were 40

mm and 2.8 mm/min, respectively. For the measurements of tensile and flexural strength, 7 specimens were measured and averaged.

Scanning and Transmission Electron Microscopy. The morphology of the PP/ABS/PP-g-MAH blends was obtained by scanning electron microscopy (SEM) (Hitachi S-4300) after Pt coating. The samples were fractured at the cryogenic condition. Also, the morphology of the PP/ABS/PP-g-MAH blends was obtained by transmission electron microscopy (TEM) (FEI Tecnai 20, Eindhoven, Netherlands) after microtoming of the sample using diamond knife (Power-Tome PC Ultramicrotome, Boeckeler Instruments, Inc.).

Rheology. Rheological properties of the PP/ABS/PP-g-MAH blends were measured using advanced rheometric expansion system in oscillatory shear at 8% strain in the parallel-plate arrangement with 25 mm plate. The frequency sweep from 0.1 to 100 rad/s was performed at 220 °C under dry nitrogen condition. For the measurements, the samples were tested within the linear viscoelastic strain range.

Results and Discussion

Figure 1 shows the impact strength of the PP/ABS blends with the PP-g-MAH content (0, 1, 3, and 5 phr). From Figure 1, it is observed that the impact strength of the PP and ABS shows 81.0 and 283.0 J/m, respectively. From Figure 1, it is observed that the value of the impact strength follow the additive rule with the negative deviation, which may be due to the immiscibility between the PP and ABS. From Figure 1, it is observed that the impact strength of the blend is increased especially in the PP/ABS (70/30 wt%) blend which is the PP-rich composition when the PP-g-MAH is added in the amount of 3 phr. Particularly, impact strength of PP/ABS (70/30) blend is increased from 100.2 to 128.1 J/m, when the PP-g-MAH is added in the amount of 3 phr. The

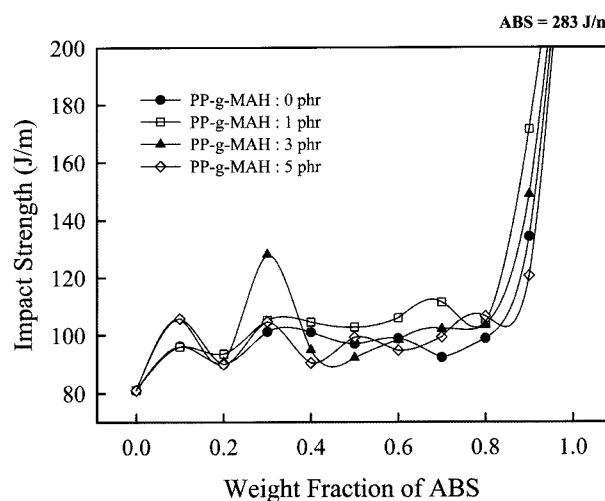


Figure 1. Impact strength of the PP/ABS blends with PP-g-MAH content: (●) PP/ABS; (□) PP/ABS/PP-g-MAH (1 phr); (▲) PP/ABS/PP-g-MAH (3 phr); (◇) PP/ABS/PP-g-MAH (5 phr).

Table I. Characteristics of Polymers Used in This Study

Samples	\bar{M}_w	T_g (°C)	T_m (°C)
PP ^a	230,000	5	164
ABS ^b	160,000	118	-
PP-g-MAH ^c	330,000	-	157

^aSupplied by Samsung Total Petrochemicals Co. ^bSupplied by LG Chemical Ltd. (acrylonitrile: 22, butadiene:15, styrene: 63 wt%). ^cSupplied by Crompton Corp. (maleic anhydride content: 0.5 wt%).

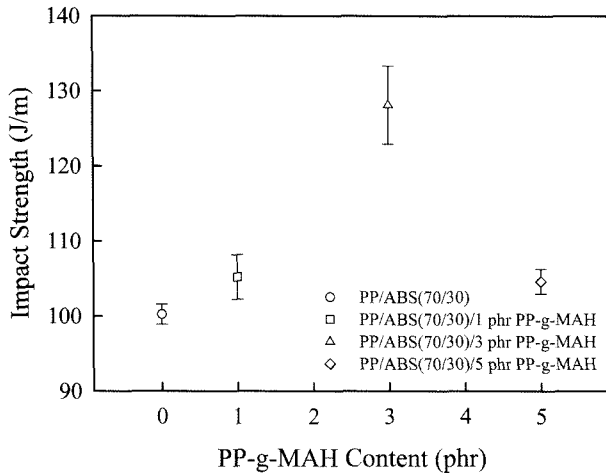


Figure 2. Impact strength of PP/ABS (70/30) blends with PP-g-MAH content: (○) 0 phr; (□) 1 phr; (△) 3 phr; (◇) 5 phr.

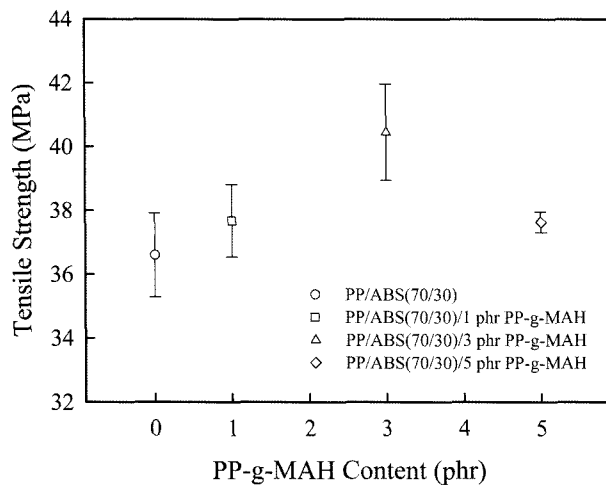


Figure 3. Tensile strength of PP/ABS (70/30) blends with PP-g-MAH content: (○) 0 phr; (□) 1 phr; (△) 3 phr; (◇) 5 phr.

increase of the impact strength in the PP-rich composition (PP/ABS=70/30) is maybe due to the fact that the small amount of the ABS as well as the addition of the PP-g-MAH was effectively affected to increase of the mechanical properties of the PP by the rubber toughening effect in the PP/ABS blends.

Figures 2-4 show the impact strength, tensile strength and flexural strength of the PP/ABS (70/30) blends with the amount of PP-g-MAH content (0, 1, 3, and 5 phr), respectively. From Figures 2-4, it is observed that impact, tensile and flexural

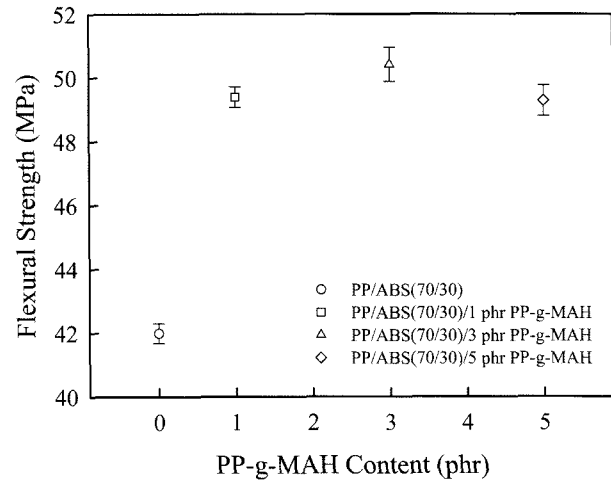


Figure 4. Flexural strength of PP/ABS (70/30) blends with PP-g-MAH content: (○) 0 phr; (□) 1 phr; (△) 3 phr; (◇) 5 phr.

strength of the PP/ABS (70/30) blends show maximum values of 128.1 J/m, 40.5 and 50.4 MPa, respectively, at the PP-g-MAH of 3 phr. Impact, tensile and flexural strength, then, decrease with the increases of the PP-g-MAH. The decreases of the mechanical properties after 3 phr of the PP-g-MAH are maybe due to the solubilizing effect of the PP-g-MAH in the PP/ABS blends since the impact, tensile and flexural strength of the PP-g-MAH are not as high as those of the PP and ABS. From the results of the Figures 1-4, it is suggested that optimum quantity of the PP-g-MAH is 3 phr in order to increase the compatibility of the PP/ABS (70/30) blends.

The values of mechanical strength and domain size of the PP/ABS (70/30) blends with the PP-g-MAH content are summarized in Table II. From Table II, the impact, tensile and flexural strength of the PP/ABS (70/30) blends is increased when the PP-g-MAH is added up to 3 phr. When the PP-g-MAH is added in the amount of 5 phr, the mechanical strength is decreased. From the results of the impact, tensile and flexural strength of the PP/ABS (70/30) blends with the PP-g-MAH, it is suggested that the increase of mechanical properties of the blend is due to the toughening effect of ABS in the PP/ABS blend because of the increase of compatibility by adding the PP-g-MAH. The relation between mechanical strength and droplet size of ABS in the PP/ABS (70/30) blends will be discussed in next section.

To see the compatibilization effects of PP-g-MAH on the

Table II. Mechanical Strength and Diameter of Domain of the PP/ABS (70/30 wt%) Blends with PP-g-MAH Content

PP-g-MAH (phr)	Impact Strength (J/m)	Tensile Strength (MPa)	Flexural Strength (MPa)	Diameter (μm)
0	100.2	36.6	42.0	18.2
1	105.2	37.7	49.4	10.6
3	128.1	40.5	50.4	6.6
5	104.6	37.6	49.3	7.5

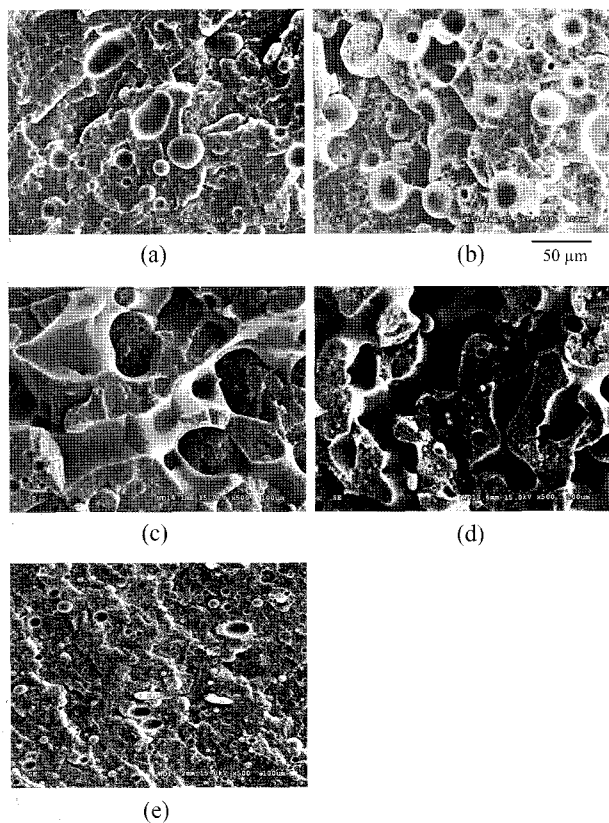


Figure 5. Scanning electron micrographs of the cryogenically fractured surfaces of PP/ABS blends: (a) 90/10; (b) 70/30; (c) 50/50; (d) 30/70; (e) 10/90.

PP/ABS (70/30) blend, morphological studies were performed using scanning electron microscopy (SEM). Figures 5 and 6 show the SEM images of cryogenically fractured surface of the PP/ABS (90/10, 70/30, 50/50, 30/70, 10/90) blends without and with PP-g-MAH, respectively. From Figures 5 and 6, it is observed that the droplet size of the PP/ABS blends is decreased for all the blend compositions when the PP-g-MAH (3 phr) is added. Especially for the PP/ABS (70/30) blend, it is observed that the droplet size is decreased from 18.2 to 6.6 μm when the PP-g-MAH (3 phr) is added in the blend. From the results of Figures 5 and 6, it is suggested that the PP-g-MAH is an effective compatibilizer of the PP/ABS blends when the PP-g-MAH is added in the amount of 3 phr.

Figure 7(a-d) shows SEM images of the cryogenically fractured surfaces of the PP/ABS (70/30) blends with the PP-g-MAH in the amount of 0, 1, 3, and 5 phr, respectively. From Figure 7, it is observed that the droplet size is decreased from 18.2 to 10.6, 6.6 and 7.5 μm when the PP-g-MAH is added in the amount of 0, 1, 3 and 5 phr, respectively. In order to avoid large error due to the observation of the fractured surface by cryogenic fracturing, the extrudate of PP/ABS (70/30) blends was microtomed using diamond knife (PowerTome PC Ultramicrotome, Boeckler Instruments, Inc.).

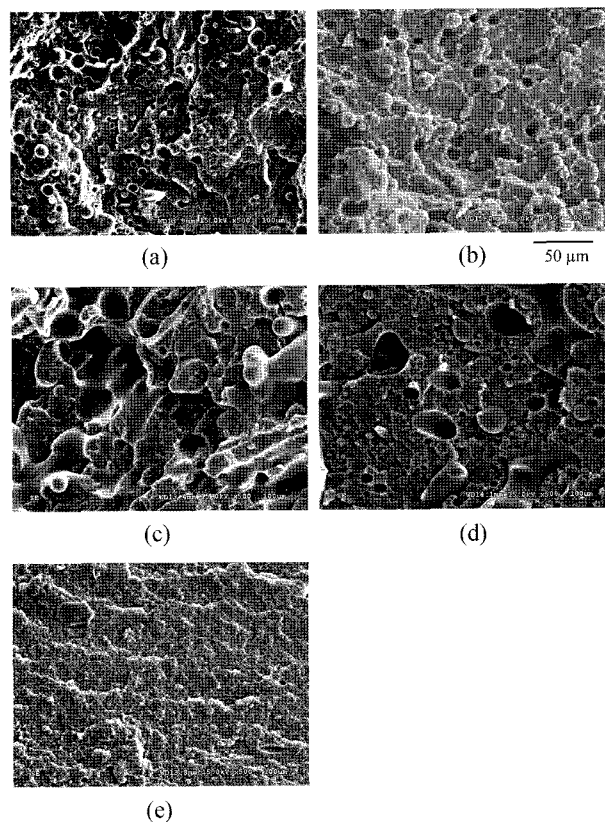


Figure 6. Scanning electron micrographs of the cryogenically fractured surfaces of PP/ABS blends with PP-g-MAH (3 phr): (a) 90/10; (b) 70/30; (c) 50/50; (d) 30/70; (e) 10/90.

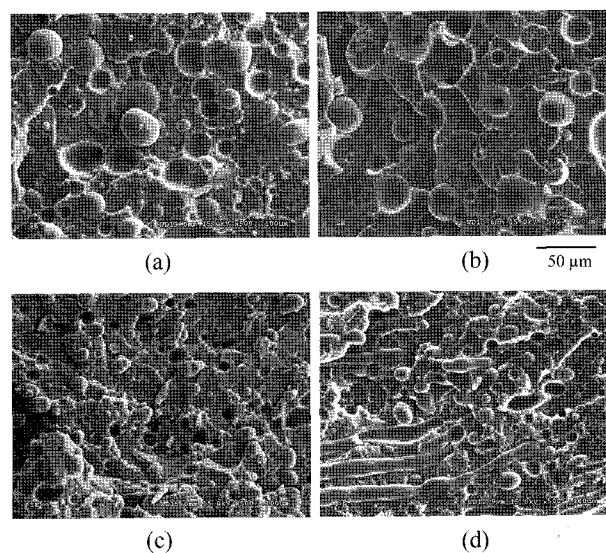


Figure 7. Scanning electron micrographs of the cryogenically fractured surfaces of PP/ABS (70/30) blends with PP-g-MAH: (a) 0 phr; (b) 1 phr; (c) 3 phr; (d) 5 phr.

The ABS phase was dissolved selectively using tetrahydrofuran. Figure 8(a-d) shows SEM images of the microtomed surfaces of the PP/ABS (70/30) blends with the PP-g-MAH

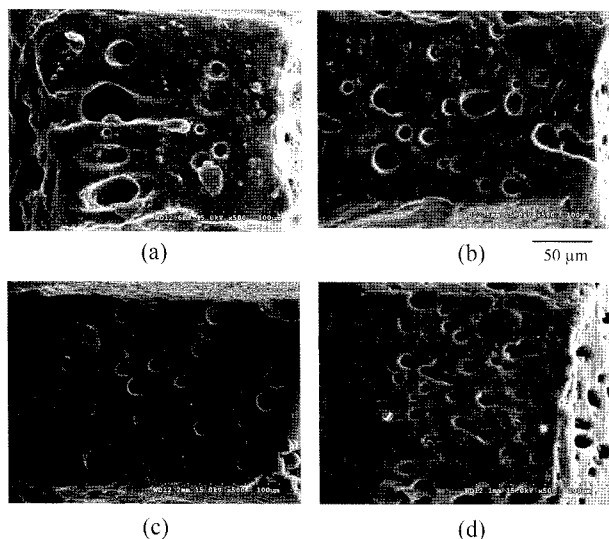


Figure 8. Scanning electron micrographs of the microtomed surfaces of PP/ABS (70/30) blends with PP-g-MAH: (a) 0 phr; (b) 1 phr; (c) 3 phr; (d) 5 phr. The ABS phase was dissolved using tetrahydrofuran.

in the amount of 0, 1, 3, and 5 phr, respectively. From Figure 8, it is observed that the droplet size of the ABS is observed to be from 18.9, 12.4, 7.2 and 8.0 μm when the PP-g-MAH is added in the amount of 0, 1, 3 and 5 phr, respectively. The droplet size of the ABS phase in the PP/ABS blend does not change significantly and shows similar behavior with the fracturing method for the SEM of the blends.

In Table II, the droplet size obtained from Figure 7 showed minimum value when the PP-g-MAH was added in the amount of 3 phr. From Table II, it is also shown that maximum values of the mechanical properties such as impact, tensile and flexural strength are observed when the droplet size of the PP/ABS (70/30) blend shows minimum value such that the PP-g-MAH is added in the amount of 3 phr. The decrease in droplet size suggests the increase of the compatibility between the PP and ABS since the decrease of the droplet size in the polymer blend is related with the decrease of the interfacial tension between the two polymers.³⁵ In the study of PP/nitrile rubber (NBR) blends with PP-g-MAH by George *et al.*,³³ the size of the dispersed phase NBR decreased as the addition of MAH. They say that this is due to the dipolar interactions between the maleic anhydride group and polar NBR. In this study of the PP/ABS blend with MAH, there may be dipolar interactions between the maleic anhydride group and polar nitrile group in the ABS. Therefore, the size of the dispersed phase (ABS) decreased with the addition of MAH which may act as a compatibilizer in the PP/ABS blends.

We have also observed the droplet size of the PP/ABS (70/30) blends using TEM shown in Figure 9. Figure 9(a-d) shows TEM images of the PP/ABS (70/30) blends with the

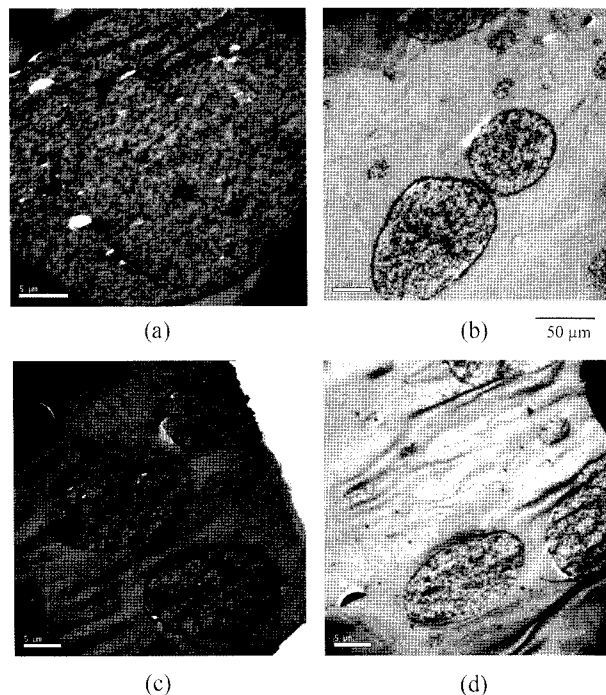


Figure 9. Transmission electron micrographs of PP/ABS (70/30) blends with PP-g-MAH: (a) 0 phr; (b) 1 phr; (c) 3 phr; (d) 5 phr.

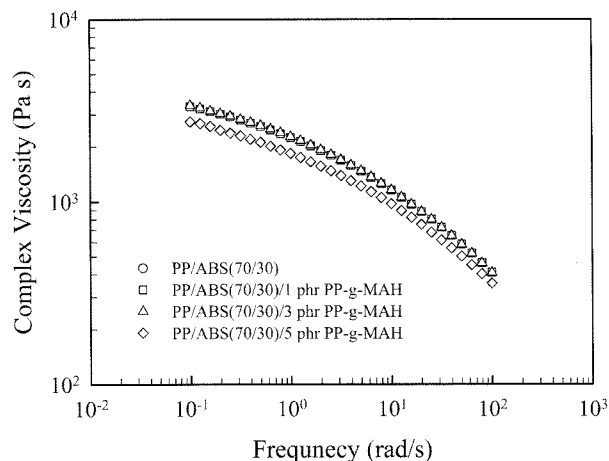


Figure 10. Complex viscosity of PP/ABS (70/30) blends with PP-g-MAH: (○) 0 phr; (□) 1 phr; (△) 3 phr; (◇) 5 phr.

PP-g-MAH in the amount of 0, 1, 3, and 5 phr, respectively. Since the droplet size of the ABS was too large in the PP/ABS (70/30) blends, it was somewhat difficult to measure the droplet size of the ABS using TEM as can be seen from Figure 9.

Figure 10 shows the complex viscosity of the PP/ABS (70/30) blends with the PP-g-MAH in the amount of 0, 1, 3, and 5 phr, respectively. From Figure 10, it is observed that the complex viscosity of the PP/ABS (70/30) blends shows the highest value when the PP-g-MAH is added in the amount of 3 phr. The increase of the complex viscosity in the PP/

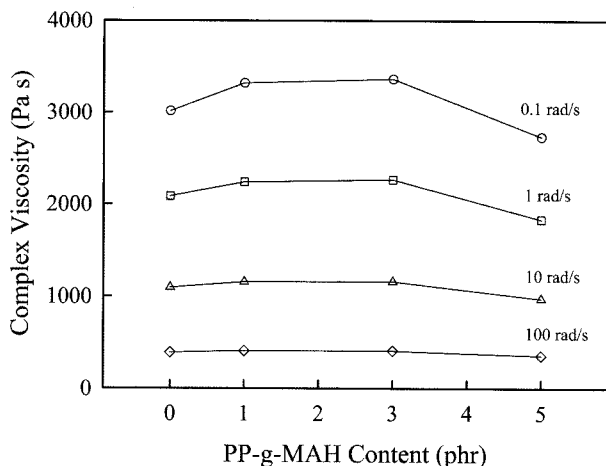


Figure 11. Complex viscosity of PP/ABS (70/30) blends with PP-g-MAH at different frequencies: (○) 0.1 rad/s; (□) 1 rad/s; (△) 10 rad/s; (◇) 100 rad/s.

ABS (70/30) blends with the PP-g-MAH (3 phr) may be due to the compatibilizing effect of the PP-g-MAH. The result of the complex viscosity is consistent with the results of the mechanical properties and morphology, which is that the impact, tensile and flexural strength are increased and the droplet size is decreased when the PP-g-MAH is added in the amount of 3 phr. When the concentration of the PP-g-MAH is 5 phr, the decrease of complex viscosity of the PP/ABS (70/30) blend is maybe due to the solubilizing effect of PP-g-MAH or the formation of the separate phase of the PP-g-MAH because of the high amount of the PP-g-MAH. Also, the decrease of complex viscosity in the concentration of 5 phr (PP-g-MAH) of the PP/ABS (70/30) blend can be considered by the elongated morphology which is shown in Figure 7(d).

Figure 11 shows the complex viscosity of the PP/ABS (70/30, wt%) blends with the PP-g-MAH content at different frequencies. From Figure 11, it is observed that the complex viscosity at the frequency of 0.1 rad/s shows the highest value when the PP-g-MAH is added in the amount of 3 phr. Similar result was reported by Nakasan *et al.*,³⁴ Hong *et al.*,⁹ and Sung *et al.*³⁵ for maleated natural rubber/PP blends, ABS/PC/polycaprolactone ternary blend and PP/poly(styrene-co-acrylonitrile) blend containing compatibilizer, respectively. From Figure 10, the increase of the complex viscosity is more significant at low frequencies (0.1 and 1.0 rad/s). This is because that the rheological properties of the complex viscosity at long time relaxation region (low frequencies) reflects the interfacial properties of the polymer blends.^{9,36,41} From the results of mechanical properties, morphology and complex viscosity of the PP/ABS (70/30) blends, it is suggested that the compatibility of the two polymer is increased when the PP-g-MAH is added in the optimum amount of 3 phr as a compatibilizer.

Conclusions

In this study, the effects of PP-g-MAH on the PP/ABS blends were investigated using impact tester, universal testing machine, scanning electron microscopy and rheometer. From the results of mechanical strength of the PP/ABS (70/30 wt%) blends, mechanical strength such as impact, tensile and flexural strength was increased with the addition of PP-g-MAH (3 phr). From the results of the impact, tensile and flexural strength of the PP/ABS (70/30) blends, it is concluded that the increase of mechanical properties of the blend is due to the toughening effect of ABS in the PP/ABS blend because of the increase of compatibility by adding the PP-g-MAH.

From the morphological studies of the PP/ABS (70/30) blends with the PP-g-MAH, droplet size of the ABS showed minimum value when the PP-g-MAH was added in the amount of 3 phr. When the droplet size of the PP/ABS (70/30) blend was minimum value, the mechanical properties such as impact, tensile and flexural strength showed maximum values when the PP-g-MAH was added in the amount of 3 phr. The decrease in droplet size suggests the increase of the compatibility between the PP and ABS. In the study of the rheological properties of the PP/ABS (70/30) blends with PP-g-MAH, it was observed that complex viscosity of the PP/ABS (70/30) blends showed the highest values when the PP-g-MAH was added in the amount of 3 phr.

From the above results of the mechanical properties, morphology and complex viscosity of the PP/ABS (70/30) blends with the PP-g-MAH, it is concluded that compatibility of the blend is increased when the PP-g-MAH is added and the optimum concentration of the PP-g-MAH is 3 phr.

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