Impact Modification of Polypropylene by Ethylene Propylene Copolymer-Grafted Maleic Anhydride

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ABSTRACT: Blends of polypropylene (PP) and ethylene propylene rubber (EPR) were studied. The effect of the level of rubber addition and the ethylene content is described. The results show that the viscosity of the PP, rubber content, ethylene content, and grafted EPR by maleic anhydride (MA) are important factors in controlling the blend properties. The miscibility and dynamic properties of the blends were studied by DMTA. Impact and tensile properties were also studied. SEM was used for the investigation of the phase morphology and rubber particle size and particle-size distribution. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 1257–1265, 1999

Key words: polymer blends; impact modification; ethylene propylene copolymer; polypropylene; maleic anhydride

INTRODUCTION

In recent years, polymer blending has been widely used for the toughening of thermoplastics. A great deal of work has been carried out on binary blends containing polypropylene (PP) and elastomers.[1–5] The rubber modification of PP with the ethylene propylene copolymer (EPR) can lead to a material with improved impact strength and environmental stress-cracking resistance.[6]

The relationships between the structure and properties of rubber-modified polymers are complex because of the number of structural variables involved.[7,8] The important factors in rubber toughening are the (a) rubber content, (b) rubber particle size and particle-size distribution, (c) degree of crosslinking of the rubber, and (e) degree of interfacial adhesion.[9] For each type of material, there appears to exist an optimum particle size for toughening.

The rubber particles dispersed in the rigid matrix stop craze growth, which can lead to the formation and development of failure cracks during impact, and at the same time, the particles act as stress concentrators, forming a barrier to the extension of crazing.

Generally, the properties of the PP/EPR blends depend on the copolymer composition. Decrease of the propylene content in the copolymer lowers all the parameters in the blends.[10]

For modification of the miscibility and interfacial adhesion in polymer blends, copolymers can be used. In comparison with the traditional copolymerization process, modification of the existing polymers by reactive melt processing offers not only flexibility in tailoring polymer properties or specific applications but also reductions in equipment investment.[11]

In the present article, we attempted to improve the impact properties of PP by EPR with various contents of ethylene, and the effect of propylene viscosity [PP with different melt flow indexes (MFIs)], EPR modified by maleic anhydride (MA), and particle size on the impact properties of PP were studied.

Table I   Composition and Characterization of Materials

Polymer	Code	Viscosity ML (1 + 4) 125°C	MFI (g/10 min)	Ethylene Content (wt %)	Tg (°C)
EPR	504	26	—	52	−55
EPR	808	46	—	75	−38
EPR	805	35	—	75	−36
PP	S30S	—	1.8	—	10
PP	C30S	—	7	—	9

EXPERIMENTAL

Polypropylene (IPP, Arak Petrochemical of Iran) and ethylene propylene rubber (Vistalon, Exxon Chemical, Brussels Belgium) were used in this study. All other chemicals and solvents including dicumyl peroxide (DCP, 97%), (the initiator), and MA (the reactive monomer) were of reagent grade and were used without further purification. The characterization of the materials is given in Table I.

Blend Preparation

PP/EPR blends containing 0, 5, 10, 20, 40, 60, and 80 wt % of EPR were prepared by melt-mixing in a Haake Buchler Rheomix 750 internal mixer at 200°C, 60 rpm for 8 min. For grafting MA onto EPR, the components were mixed in a Haake internal mixer. The amounts of MA were 0.5, 1, 1.5, and 2 phr and the amount of DCP was constant at 0.25 phr. The optimum amount of MA was 1 phr in the blends and the total mixing time was 30 min. The rotor speed was 10 rpm for the first 1 min and then increased to 40 rpm thereafter. The temperature of the mixing chamber was set at 140°C for the first 1 min and then was increased to 160°C.

Gel Content

The gel content of the samples [EPR–grafted MA (g-MA)] were determined by an extraction proce-

dure in cyclohexane at room temperature for 60 h. The solution was subsequently filtered and the insoluble materials were combined and dried under a vacuum at 140°C to a constant weight.

Fourier Transform Infrared Spectroscopy

After extraction of the nonreacted MA by water and acetone, the samples (EPR–g-MA) were pressed at about 170°C to prepare films, which had been dried in a vacuum oven (1 day at 110°C). The IR spectra were taken using a Bruker IFS 48 FTIR spectrometer. The relative peak height of the anhydride absorption band of 1785 cm^{-1}, asymmetric of carboxyl stretching, to the C—H stretching peak (715 cm^{-1}) was taken as an approximate indicator of the extent of MA grafting.

Specimen Preparation

The tensile bars conformed to ASTM D-638 and were strained using an crosshead speed of 50 mm/min in an Instron 6025 testing machine.

Impact bars according to ASTM D-256 were used to measure the notched Izod impact strength using a Zwick 5102 pendulum impact testing machine in the temperature range of −140 to 20°C. The average values of at least five tests are reported.

The dynamic mechanical properties of the blends were determined using $35 \times 12 \times 0.8$ mm compression-molded test pieces using a Polymer Lab DMTA. The DMTA system possessed liquid nitrogen cooling facilities, which allowed testing to be completed over the whole temperature range.

The fracture surface of the impact specimens, phase morphology, particle size, and particle-size distribution of the blends were studied using scanning electron microscopy (SEM, S-360 Cambridge).

Table II   Gel and Graft Content

EPR (phr)	DCP (phr)	MA (phr)	Gel Content (%)	Relative Peak Height
100	0.25	0.5	0.20	0.30
100	0.25	1	0.47	0.65
100	0.25	1.5	0.54	0.58
100	0.25	2	0.58	0.56

Figure 1 FTIR spectra of (a) EPR and (b) EPR with 1 phr MA.

The rheological behavior of the PP, EPR, and the blends were investigated using a rheometer (Instron capillary Model 3211).

RESULTS AND DISCUSSION

Gel and Graft Content

Table II shows the effect of MA on the crosslinking of EPR at a constant initiator (DCP) and relative peak height of the anhydride absorption band of 1785 cm^{-1} to the C—H stretching peak (715 cm^{-1}). It can be seen that by increasing the amount of MA the gel content increases rapidly up to 1 phr MA and then slows down and the relative peak height increases up to 1 phr and then decreases. Therefore, the optimum amount of MA was 1 phr.

Figure 1 shows the FTIR spectra of EPR and EPR–g–MA with 1 phr MA. The carboxyl group peak (1785 cm^{-1}) of MA can be seen in spectrum

Figure 2 Capillary rheology of starting polymers at 200°C.

Figure 3 Capillary rheology of the PP, EPR, and the blends at 200°C.

Figure 4   Effect of rubber content on modulus of PP/ EPR blends.

(b) (EPR–g-MA), which is absent in the EPR spectrum (a).

Rheological Behavior

The rheological characterization of the PP, EPR, and the blends are shown in Figures 2 and 3. The monotonic dependence of the blends' melt viscosity on the composition and the reduction in the melt viscosity with decrease of the rubber content in the blends can be seen. The melt viscosities of the polymers (PP, EPR) and the blends decrease with increasing shear rate, showing a pseudoplastic behavior. The n as defined in the power law equation $\tau = K(\gamma)^n$ for PP, EPR, and the blends is

Figure 6   Notched Izod impact strength of PP, (S30S)/ EPR(504) 80/20, and PP(S30S)/ EPR(504)g-MA 80/20 blends versus temperature: (a) -140 to $0°C$; (b) -80 to $20°C$.

Figure 5   Effect of PP content on yield stress of PP/ EPR blends.

less than 0.5. The melt viscosity ratio of the matrix and the dispersed phase (η_m/η_d) strongly affect the rubber particle size and the blend properties. According to Wu,[12] the smallest power particle size can be obtained when the viscosity ratio η_m/η_d is about unity.

Mechanical Characterization

The mechanical characterization shows a clear influence of the composition on the properties considered (Figs. 4 and 5). Both the yield stress and modulus increase with an increasing amount of PP in the blends. An abrupt change in the slope of the yield stress (or modulus) composition curves occurs in the composition of more than 60% of EPR.

Figure 7 SEM micrograph of crack branching of PP/EPR 80/20 blends at temperatures below −100°C.

The results show that in the blends of PP/EPR the yield stress, tensile strength, and modulus is increased by increasing the PP content, which is attributed to the crystallinity of the PP; such blends are known as impact-modified thermoplastics (toughened plastics). With a high EPR content (more than 60%), the yield stress point, tensile strength, and modulus decrease dramatically and the blends are known as thermoplastic elastomers.

The notched Izod impact strength of EPR-modified PP blends versus a wide range of temperature is plotted in Figure 6(a,b). It can be seen that the curves can be divided into four regions as follows:

Figure 8 SEM micrograph of crack branching of PP/EPR 80/20 blends at temperatures below −100°C at high magnification.

Table III   EPR Particle Size and Impact Strength of PP/EPR Blends

PP/EPR	Rubber Content	Average Diameter of Rubber Particles (μm)	Impact Strength (J/m)
C30S	0	—	40
C30S/808	5	1.0	59
C30S/808	10	1.3	74
C30S/808	20	2.0	78
C30S/808	40	2.8	102
C30S/805	5	0.9	51
C30S/805	10	1.2	62
C30S/805	20	2.0	70
C30S/805	40	2.4	96
C30S/504	5	0.8	57
C30S/504	10	1.2	80
C30S/504	20	2.1	148
S30S	0	—	60
S30S/504	5	0.7	90
S30S/504	10	0.9	250
S30S/504	20	1.0	>720
S30S/808	20	1.3	507
S30S/805	20	1.3	770
S30S/504-g-MA	5	0.3	130
S30S/504-g-MA	10	0.3	420
S30S/504-g-MA	20	0.3	>1350
S30S/808-g-MA	20	0.9	>800

(a) Extremely low temperature region (−140 to −100°C): The impact strength increases with decreasing temperature (below −100°C). Figures 7 and 8 show the crack propagation. It is clear that, initially, the crack grows in a certain plane and then zigzags to an area not in line with the previous plane.

Figure 9 Effect of rubber content on impact strength and BTT of PP(S30S)/EPR(504) g-MA blends.

Figure 10 Storage modulus traces of PP/EPR blends with different rubber content.

(b) Low-temperature region (-100 to $-60°C$): Impact strengths were low and did not change with the temperature. The fracture

surfaces were rough and exhibited no stress-whitening zone and no crack branching. It should be noted that the T_g of

Figure 11 Tan δ traces of PP/EPR blends with different rubber content.

Figure 12 Tan δ traces of PP/EPR and PP/EPR-g-MA 80/20 blends.

the EPR elastomer is in the neighborhood of $-60°C$.

(c) Intermediate-temperature region (-60 to $0°C$): Above the glass transition temperature of the EPR, the impact strength begins to increase with increasing temperature. The stress-whitening zone can be seen in this region and these zones increase with increasing temperature.

(d) High-temperature region ($0–20°C$): Impact strength increases dramatically with increasing temperature.

The results show that the average particle size of modified systems depends largely on the relative viscosity between the minor phase (EPR) and the major phase (PP). When the viscosity of EPR is low (e.g., EPR 504), the resulting rubber particle sizes in the PP/EPR blends are low for both PP S30S (high viscosity) and PP C30S (medium or low viscosity). When the viscosity of EPR is high (e.g., EPR 808), it becomes more difficult to obtain blends with smaller rubber particles (Table III).

Figures 9 and 6(b) show the effect of the rubber content and rubber particle size on the impact strength, respectively. It can be seen that by increasing the rubber content and decreasing the rubber particle size the impact strength increases at all temperatures and the brittle tough transition (BTT) decreases to a lower temperature.

Thermal Behavior

The DMTA curves show that PP/EPR blends are immiscible. Figures 10 and 11 show the storage modulus and tan δ of the PP/EPR blends with different rubber content. It can be seen (Fig. 10) that by increasing the rubber content the storage modulus decreases, which is correlated with impact strength improvement. At high rubber content ($>60\%$ wt), the storage modulus dramatically decreases, which is attributed to the phase-inversion phenomenon. The same trends are also seen in increasing the height of the T_g peaks of the rubber in tan δ traces (Fig. 11).

Figure 12 shows the tan δ traces of the PP/EPR 80/20 and PP/EPR-g-MA 80/20 blends. It can be seem that by grafting MA onto EPR the height of the tan δ trace of the PP/EPR-g-MA blend increases, which is correlated to the impact

Figure 13 SEM micrograph of notched Izod impact fracture surface of PP/EPR 80/20 blends, at 0°C, further away from notch tip.

Figure 14 SEM micrograph of notched Izod impact fracture surface of PP/EPR 40/60 blends at low temperature.

strength improvement of the PP/EPR-g-MA blends.

Morphological Observation

The notched Izod fracture surface of the blends was studied by using SEM from close to the notch tip toward the end of the fracture. Figure 13 shows an SEM micrograph of the fracture surface of the PP/EPR 80/20 blend. It can be seen that the dispersion of the rubber particles is uniform and Figure 14 shows that even at 60% EPR no phase inversion occurs and still the PP phase is dominated as a continuous phase. At high rubber content (>60%), phase inversion occurs.

Figures 15 and 16 and show the differences

Figure 15 SEM micrograph of notched Izod impact fracture surface of PP/EPR 80/20 blends, at 0°C, at notch tip.

Figure 16 SEM micrograph of notched Izod impact fracture surface of PP/EPR-g-MA 80/20 blends, at 0°C, at notch tip.

between the fracture surface morphology of the PP/EPR 80/20 and PP/EPR-g-MA 80/20 blends at the notch tip at the same magnification. As one can see, the PP/EPR GMA blend had a tough fracture surface compared with the PP/EPR blend and the mechanisms of toughening are multiple crazing, shear yielding, and cavitation. The results also show that the rubber particle size is decreased by grafting EPR with MA.

CONCLUSIONS

The melt viscosities of the polymers (PP, EPR) and the blends decrease with increasing shear rate, showing pseudoplastic behavior.

Both yield stress and modulus increase with an increasing amount of PP in the blends. The toughening of PP with EPR is possible. The impact strength of the PP/EPR blends increases by increasing the rubber content and decreasing the rubber particle size at both low and high temperatures. The grafting of EPR with MA in the blends decreases the rubber particle size from 1.05 to 0.34 μm and improves the impact strength.

SEM studies showed that the dispersion of the rubber particles is uniform. In the blends with rubber content up to 60% wt, the PP is continuous and then phase inversion occurs.

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