Compatibilization of PP/EPDM Blends by Grafting Acrylic Acid to Polypropylene and Epoxidizing the Diene in EPDM

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ABSTRACT: In this article, ethylene–propylene–diene-rubber (EPDM) was epoxidized with an *in situ* formed performic acid to prepare epoxed EPDM (eEPDM). The eEPDM together with the introduction of PP-*g*-AA was used to compatibilize PP/EPDM blends in a Haake mixer. FTIR results showed that the EPDM had been epoxidized. The reaction between epoxy groups in the eEPDM and carboxylic acid groups in PP-*g*-AA had taken place, and PP-*g*-EPDM copolymers were formed *in situ*. Torque test results showed that the actual temperature and torque values for the compatibilized blends were higher than that of the uncompatibilized blends. Scanning electron microscopy (SEM) observation showed that the dispersed phase domain size of compatibilized blends and the uncompatibilized blends were 0.5 and 1.5 μm, respectively. The eEPDM together with the introduction of PP-*g*-AA could compatibilize PP/EPDM blends effectively. Notched Izod impact tests showed that the formation of PP-*g*-EPDM copolymer improved the impact strength and yielded a tougher PP blend. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 3949–3954, 2006

Key words: elastomers; toughness; compatibilization; electron microscopy

INTRODUCTION

Polypropylene (PP) is a semicrystalline polymer with good mechanical and thermal properties, but its toughness, in particular its notched toughness, is not sufficient for application as an engineering plastics. Adding rubber phase is an efficient approach to increase the toughness of PP. The rubber phase in PP initially relieves the volume strain by cavitation, and therefore, acts as a stress concentrator. Cavitation of the rubber particles decreases the Von Mises yield stress and improves shear yielding of matrix.[1,2]

PP has been toughed by EPR and ethylene–propylene–diene (EPDM) rubber.[3–16] Satisfactory toughening is also obtained using SBS, SEBS, EBR, EVA, polybutadiene, and natural rubber.[17–25] However, these materials have unstable morphologies, since at low stress or quiescent conditions in the melt state the rubber domain can grow by coalescence, resulting in loss of mechanical properties. One may be able to achieve a stable morphology and enhanced properties with compatibilized blends.

To improve the mechanical properties of an immiscible polymer blend, there are generally two kinds of compatibilization, that is, physical compatibilization and chemical compatibilization. The former technique utilizes a premade block or graft copolymer whose constituent component is compatible (or miscible) with each component in the blend. In this method, compatibilizers such as block and graft copolymer are very effective in reducing the interfacial tension and improving interfacial adhesion by polymer chain entanglement or bridging at the interface.[26–33]

However, there are some limits to the use of a block or a graft copolymer as a compatibilizer in immiscible polymer blends. One is the difficulty in adequately dispersing a block copolymer near the interface between two phases due to its high viscosity. Another difficulty to be expected is that an added block copolymer can localize in the homopolymer phase in a micelle form rather than at the interface.[34–36]

To overcome these disadvantages, reactive blending techniques (chemical compatibilization), in which *in situ* block or graft copolymer as compatibilizer is produced because of the reaction between functional units in the polymer blends during melt blending, have been proposed and developed.[37–39] The functional units are easily introduced by a copolymerization reaction step or by the graft reaction during the extrusion process or batch mixing. Functional units on the polymer chain of an *in situ* compatibilizer can react very easily with other functional units in one of the constituent components in an immiscible polymer blend. The compatibilizer can effectively compatibi-

lize the blend. Baker and coworkers report that GMA grafted PP copolymer can effectively compatibilize the blends of PP homopolymer with acid-functionalized NBR rubber and improve impact energy eight times than those blends without the grafted copolymer.[40]

In this article, ester formation by carboxylic acid opening epoxide ring was selected and this reaction has been used in commercial blends.[41,42] However, to our knowledge, there are no papers using this reaction to deal with the PP/EPDM blend system. In our study, the EPDM was first epoxidized with *in situ* formed performic acid, which induced functional epoxy groups into the EPDM macromolecular backbone,[43–47] and then the effect of PP-*g*-AA on the final morphology, impact strength, and rheology of PP/EPDM blends were investigated. Note that the epoxy group in epoxided EPDM (eEPDM) reacts with carboxylic acid group in PP-*g*-AA; thus, PP-*g*-EPDM is formed and acts as a compatibilizer between PP and EPDM.

EXPERIMENTAL

Materials

The PP used in this study was commercial grade (T-H-022) of Qianguo Petrochemical, China; the melt flow index (MFI) is 2.60 g/10 min (230°C, 21.6N). The PP was dried in a vacuum oven at 80°C for 24 h before being used; the EPDM was also commercial grade (4045) of JiLin Petrochemical. China, having diene component of 5-ethylidene-2-norbornene (ENB), propylene content (C_3) of 35.9 mol %, and a glass transition temperature (T_g) of −60°C. The PP-*g*-AA was kindly offered by Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, and it was prepared by melt extrusion. The MFI (230°C, 21.6N) and graft degree of PP-*g*-AA are 3.80 g/10 min and 0.8%, respectively.

Epoxidation procedure of ethylene–propylene–diene-rubber

The EPDM was first dissolved in toluene under continuous stirring; then the solution was acidified stepwise with 88% formic acid to pH 2–3.When the epoxidation was performed at 50°C, the required amount of H_2O_2 (30%) was slowly dropped in 30 min. A rapid introduction of this reagent is not recommended, because it causes excessive development of oxygen due to the decomposition of hydrogen peroxide at high temperature. The reaction duration was about 8 h at 50°C. After epoxidation, the rubber was coagulated in acetone, thoroughly washed with distilled water, and rinsed with distilled water again to ensure that any remaining acid has been removed. The rubber prepared was dried in a vacuum oven at 40°C to a constant weight.

Blending and sample preparation

The PP/EPDM, PP/eEPDM, PP/PP-*g*-AA/EPDM, and PP/PP-*g*-AA/eEPDM blends, having different rubber contents, were prepared at 200°C for 5 min at rollers speeds of 70 rpm in a Haake apparatus and then hot-pressed in the same hydraulic press 240 kg/cm^2 at 190°C. The content of PP-*g*-AA in the blends was set at 7 wt %. The compression-molded sheets were cut into rectangular specimens of 63.5 × 12.7 × 3.0 mm^3 for Izod impact tests, and a notch of 2.5-mm depth with an angle of 45° was made on the specimens.

Izod impact testing

The notched Izod impact strength was measured with an XJU-22 impact testing machine, according to ASTM D256. The temperature was 23°C.The average values of at least five tests are reported.

Blend morphology

The morphological structure of the blends was characterized by scanning electron microscopy (SEM; molded Japan JSM5600). Samples were fractured under liquid nitrogen, and then vacuum coated with gold before examining.

FTIR spectra

The FTIR spectra using the hot pressed films of EPDM, eEPDM, PP-*g*-AA, and PP/PP-*g*-AA/eEPDM blends were recorded on BIO-RAD FTS-7.

Torque rheometer

The torque measurements of PP blends were performed on a thermo Haake mixer. The rotating speed was set at 70 rpm and the temperature was set at 200°C.

RESULTS AND DISCUSSION

FTIR.spectra

Figure 1 shows typical FTIR spectra of EPDM (1) and eEPDM (2). It can be seen that the IR spectrum of eEPDM is different from that of EPDM. The IR spectra of eEPDM are characterized by the presence of a specific epoxide band at 870 cm^{-1} (asym epoxide ring stretching). But it does not appear in the IR spectra of EPDM. Furthermore, the intensity of the specific C=C—H band at 808 cm^{-1} decreases because of the epoxidation of EPDM, which demonstrates that the C=C double chemical bond in EPDM converts to the epoxy functional group in eEPDM. Figure 1 shows the IR spectrum of PP-*g*-AA (3). It can be seen that the
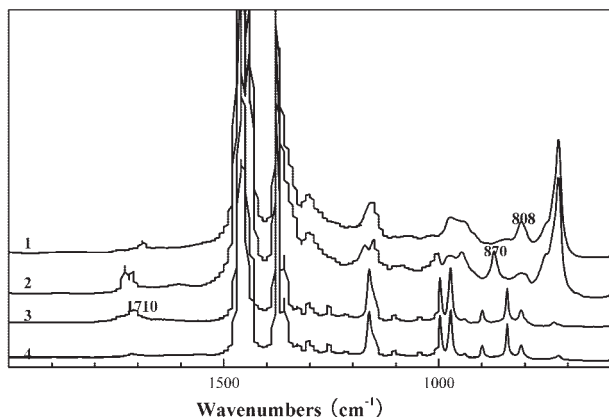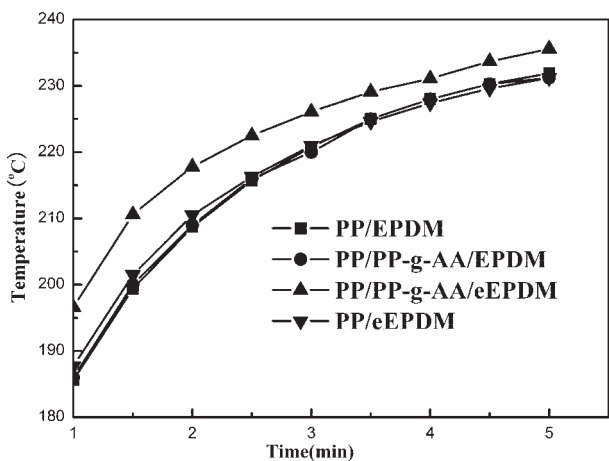
Figure 1 FTIR of (1) EPDM, (2) eEPDM, (3) PP-*g*-AA, and (4) PP/PP-*g*-AA/eEPDM.
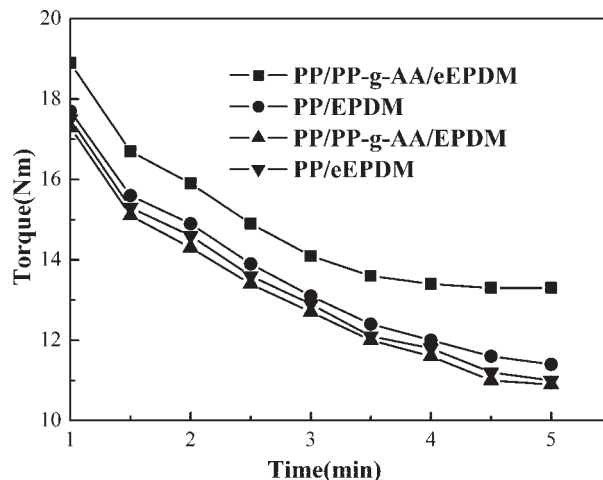

Figure 3 Evolution of torque with time for PP blends in Haake mixer.

wave number of 1710 cm^{-1}, representing C=O, is the characterization of carboxylic acid group in PP-*g*-AA. Figure 1 shows that the specific band of carboxylic acid group in PP-*g*-AA (4) becomes weaker, and the epoxide band at 870 cm^{-1} disappears. It can be concluded that the reaction between AA in PP-*g*-AA and epoxy group in eEPDM has taken place.

Torque tests

Plots of actual temperature and torque value in the internal mixer versus mixing time at the setting temperature of 200°C for PP blends are given in Figures 2 and 3, respectively. For PP/EPDM, PP/eEPDM, and PP/PP-*g*-AA/EPDM blends, it can be seen from Figure 2 that the actual temperature in the mixer increased rapidly during a short time and it reached 227°C after 5 min, which is higher than the setting temperature. This is due to viscous heating of polymer even if there are no reactions. For the PP/PP-*g*-AA/

eEPDM blend, it is noted that the actual temperature in the mixer reaches 235°C. This is due to both viscous heating of highly viscous PP-*g*-EPDM copolymer formed during the reaction and the exothermic heat of chemical reaction. When the reaction between the epoxy group in eEPDM and carboxylic acid group in PP-*g*-AA occurs, the torque value for the PP/PP-*g*-AA/eEPDM blend is higher than that of the PP/EPDM, PP/PP-*g*-AA/EPDM, and PP/eEPDM blends (Fig. 3). Thus, it can be concluded that the reaction occurs between the AA in PP-*g*-AA and the epoxy group in eEPDM.

Morphology

The morphological investigation is performed by SEM on cold-fractured surface of the PP/EPDM, PP/eEPDM, PP/PP-*g*-AA/EPDM, and PP/PP-*g*-AA/eEPDM. The results are shown in Figure 4. The rubber and PP-*g*-AA contents are set at 14 wt % and 7 wt %, respectively. It can be seen that when there is no PP-*g*-AA in the blend, the average domain size of the dispersed phase is 1.5 μm, and the interfacial adhesion between the dispersed and matrix phase is poor [Figs. 4(a) and 4(b)]. For the PP/PP-*g*-AA/EPDM blend, since there are no compatibilization reactions existing, the average domain size does not vary [Fig. 4(c)]. However, in Figure 4(d), the dispersed phase domain size decreases significantly and is 0.5 μm. This indicates that the PP-*g*-AA molecules at the interface react with the epoxy group in eEPDM by ring opening to form ester linkages. PP-*g*-EPDM molecules formed on the interface between the PP and EPDM phases. Meanwhile, the PP-*g*-AA molecules remain entangled with other PP molecules in the matrix phase. Therefore, the formation of PP-*g*-EPDM reduces average particle size of dispersed phase. It has been recently
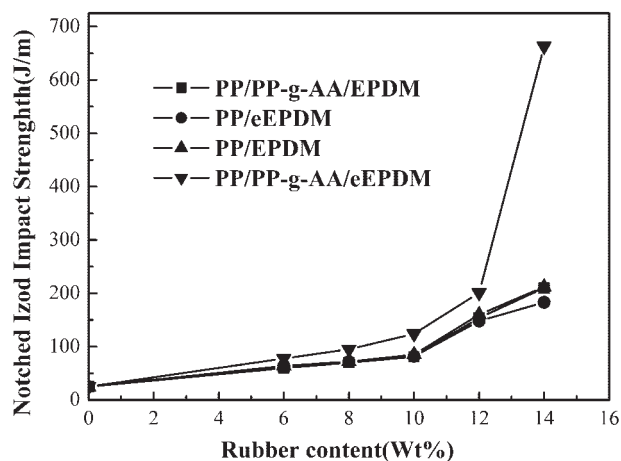

Figure 2 Evolution of temperature with time for PP blends in Haake mixer.

(a)

(b)

(c)

(d)
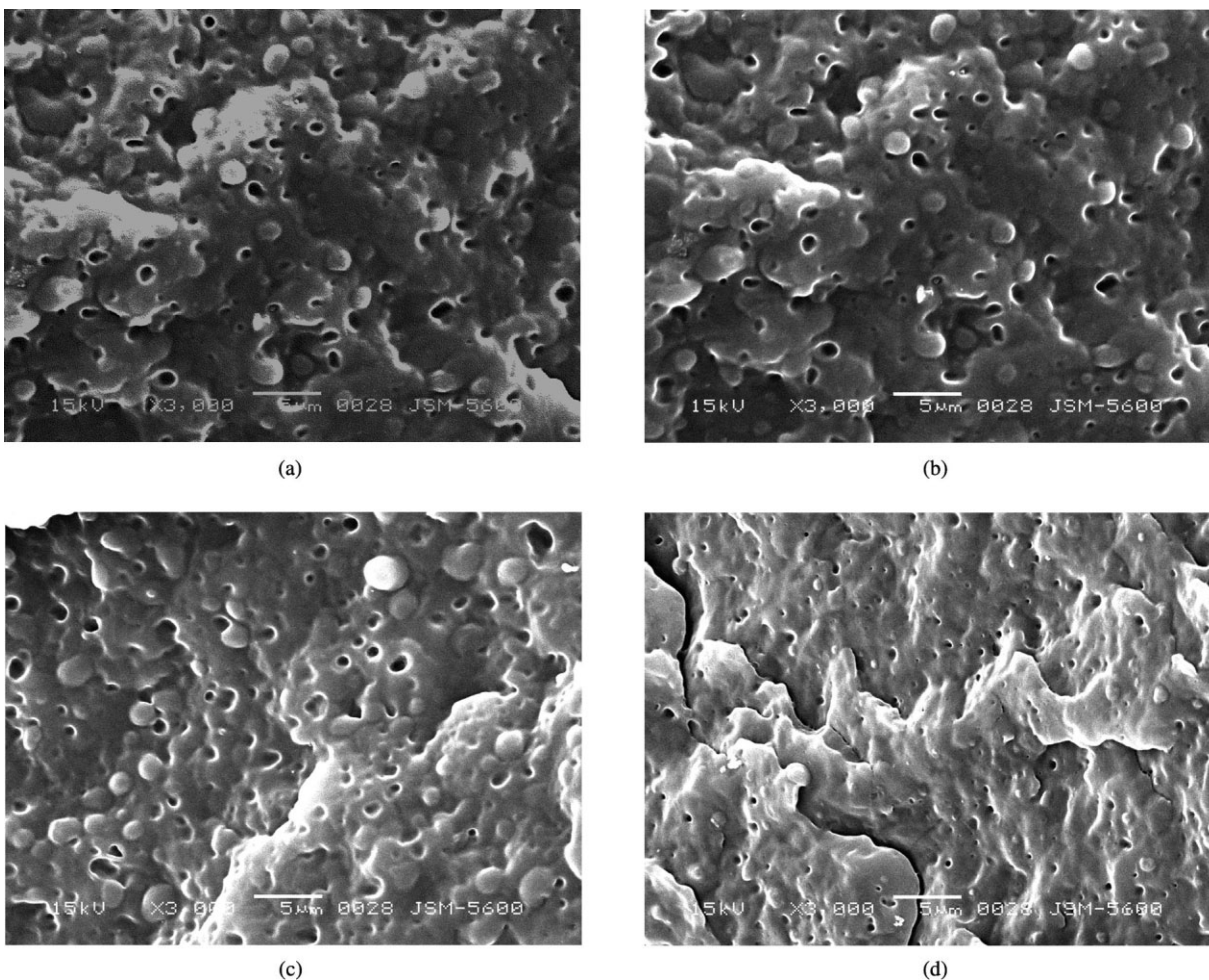
Figure 4 SEM images of (a) PP/EPDM, (b) PP/eEPDM, (c) PP/PP-*g*-AA/EPDM, and (d) PP/PP-*g*-AA/eEPDM. Rubber content 14 wt %; PP-*g*-AA 7 wt %.

reported by O'Shaughnessy and Sawhney[48] and Fredrickson and Milner[49] that the suppression of drop-let–droplet coalescence, through steric hindrance by the form of the copolymer at the interface, is a dominant mechanism.
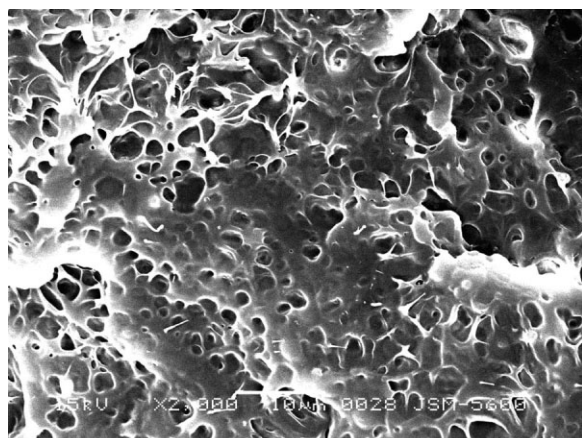
Impact properties

The notched impact strength, obtained by Izod testing, as a function of rubber content for PP/EPDM, PP/eEPDM, PP/PP-*g*-AA/EPDM, and PP/PP-*g*-AA/eE-PDM blends, is shown in Figure 5. Up to 14 wt % rubber content, the toughness of PP/EPDM, PP/eE-PDM, and PP/PP-*g*-AA/EPDM improves only a little, and the blends still break in a brittle manner, whereas the toughness of PP/PP-*g*-AA/eEPDM blend has been improved evidently. As the rubber content is 14 wt %, the PP/PP-*g*-AA/eEPDM blend becomes tougher and the notched impact strength is about 25 times that of pure PP. Figure 6 presents the fracture surfaces of PP/PP-*g*-AA/EPDM and PP/PP-*g*-AA/eEPDM blends, which have the same compositions with 7 wt % PP-*g*-AA
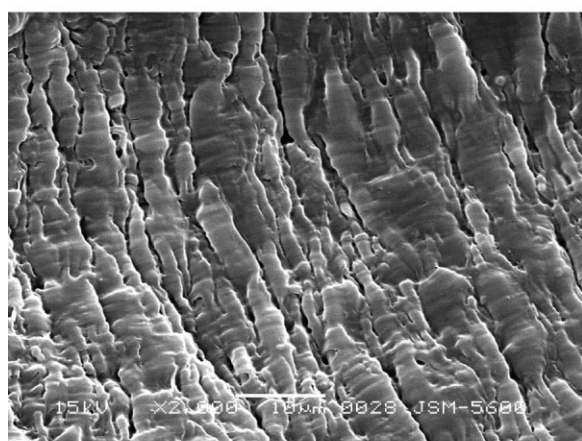
and 14 wt % rubber. The SEM micrographs are taken directly behind the notch. The lower impact strength of the PP/PP-*g*-AA/EPDM blend is clearly reflected by its

Figure 5 Notched impact strength of PP blends with different EPDM content.

been epoxidized. The absorption peak of carboxylic acid group in PP-*g*-AA became weaker, and the epoxide absorption peak in eEPDM disappeared after blending. Torque test shows that the actual temperature torque value for the compatibilized blends is higher than that of the uncompatibilized blends. These results show that the reaction between epoxy groups in the eEPDM and carboxylic acid groups in PP-*g*-AA had taken place. And PP-*g*-EPDM copolymers were formed *in situ*.

SEM images showed that the domain size for the unreactive blends, including PP/EPDM, PP/eEPDM, and PP/PP-*g*-AA/EPDM, was almost the same; while for the reactive blends, the domain size was smaller. This is because the formation of PP-*g*-EPDM leads to reduced dispersed phase particle size. The compatibilizer could compatibilize PP/EPDM blends effectively and improve the degree of dispersion and morphology stability. This will induce local yielding of PP around the rubber particle. Notched Izod impact tests showed that the formation of PP-*g*-EPDM copolymer induced a further improvement of impact property and a tougher PP blend is obtained.

Figure 6 Morphology of the fracture surface (a) PP/PP-*g*-AA/EPDM and (b) PP/PP-*g*-AA/eEPDM.

fracture surface [Fig. 6(a)]. The fracture surface has a small hemispherical zone behind the notch, consisting of stretched matrix material. The presence of voids is due to the cavitation of the rubber particles, but no matrix shear yielding takes place. It displays a brittle fracture mode at 23°C. Figure 6(b) displays the fracture in a ductile manner on which rumpled surface can be seen. The rumples lie parallel to the notch and give rise to tufts of highly drawn material. The rumples have been explained as being due to considerable drawing ahead of the crack tip before unstable fracture sets in. The extensive deformation of the cavitation ahead of the crack tip gives rise to these structures.[50]

CONCLUSION

In this study, ethylene–propylene–diene-rubber (EPDM) was epoxidized with an *in situ* formed performic acid. The eEPDM together with the introduction of PP-*g*-AA was used to compatibilize PP/EPDM blends. FTIR results showed that the epoxide absorption peak appeared on the spectra of eEPDM. The EPDM had

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