Polymer Bulletin 58, 447–455 (2007)
DOI 10.1007/s00289-006-0682-4

Polymer Bulletin

Polymer Blends of PBT and PP Compatibilized by Epoxidized Ethylene Propylene Diene Rubber

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Received: 30 April 2006 / Revised version: 9 July 2006 / Accepted: 19 September 2006

Summary

In this paper, ethylene-propylene-diene-rubber (EPDM) was epoxidized with an *in situ* formed performic acid to prepare epoxided EPDM(eEPDM). The eEPDM were used to compatibilize poly(butylenes terephthalate)(PBT) and polypropylene(PP) blends in a haake mixer. FTIR results showed that the EPDM had been epoxidized. FTIR and torque test showed the epoxy functional groups in the eEPDM can react with the carboxylic acid or hydroxyl terminal groups in PBT at the interface to form PBT-g-EPDM copolymers. SEM observation showed that these *in situ* formed grafted copolymers tent to concentrate along the interface to reduce the interfacial tension at the melt and suppress coalescence by steric hindrance . higher quantity of eEPDM compatibilizer in the blend results in a better compatibilized blend in terms of finer phase domains. Notched Izod impact tests showed that both the adding of rubber and the formation of PBT-g-EPDM copolymer improved the toughness of PBT/PP blends.

Keywords

Polybutylene terephthalate- polypropylene- compatibilization-toughness- morphology

Introduction

Straight blends between polybutylene terephthalate (PBT) and polypropylene(PP) are considered to be immiscible or incompatible. In order to make polymer alloys from an incompatible polymer mixture, a compitibilizer must be used to improve the interfacial adhesion. Recently, there are considerable interests in this field. B.Boutevin et al. [1] investigated the compatibilization of PBT/PP blends by using a specially synthesized polyisoprene-b-PBT copolymer . The result showed that elongation at break of PBT/PP blends increased. Holsti-Miet-tinen and coworkers [2] used the epoxy functionalized polymer, ethylene-co-GMA. Tommi Vainio et al.[4] used functionalized PP by melting free radical grafting low volatile oxazoline to compatibilize PBT/PP blends. Yeong-Tarng Shieh et al.[5] studied that reactive compatibilization of PBT/PP blends by a mixture of PP-g-MA and epoxy resin. Ailing Zhang et al.[6] found that the addition of 1% liquid crystalline ionomer to the PBT/PP blends increased the ultimate tensile strength and the ultimate elongation. Riitta M et al.[7] used epoxy reactivity to compatibilize the PP/PBT blends, and founded that addition of 5 wt% of the compatibilizer improved the impact strength. In most of the above-mentioned literature, PBT/PP blends are relatively brittle,regardless of the interfacial strength or morphology. Since neither component is ductile.

In this paper, the EPDM was firstly epoxidized with *in situ* formed performic acid, which induced functional epoxy groups into the EPDM macromolecular backbone [8-11] and then the effect of eEPDM on the final morphology, impact strength and rheology of PBT/PP blends were investigated. Note that in addition to the eEPDM serves as impact modifiers,furthermore,the epoxy group in eEPDM reacts with carboxylic acid or hydroxyl terminal groups in PBT, thus a PBT-g-EPDM is formed and acts as a compatibilizer between PP and PBT.

Experimental

Materials

The PP used in this study is a commercial grade(T-H-022) of Qianguo Petrochemical Co, China; the melt flow index(MFI) is 2.60g/10min(230°C,2.16Kg). The PP was dried in a vacuum oven at 80°C for 24h before being used; the EPDM was also a commercial grade (4045) of JiLin Petrochemical Co. China, having diene component of 5-ethylidene-2-norbornene(ENB), propylene content(C_3) of 35.9mol%, and a glass transition temperature (Tg) of –60°C. The PBT used in this work is a commercial product of Yizheng Chemical Fiber Group, JiangSu. The MFI is 7.8g/10min(240°C, 5Kg). The hydroxyl and carboxyl end group concentrations are 44μeq/g and 20μeq/g, respectively. Prior to each processing step, PBT was dried in a vacuum oven for 24h at 120°C.

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 PH2-3.The epoxidation was performed at 50°C, and the required amount of H_2O_2(30%)was slowly dropped in 30min. 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 8h 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 PBT/PP/eEPDM blends, having different PBT/PP compositions and rubber contents were prepared at 240°C for 10 min in a Haake apparatus. The rollers speed is 60 rpm. The blends then hot-pressed in the same hydraulic press 240Kg/cm^2, at 240°C. The compression-moulded sheets were cut into rectangular specimens with the dimension of 63.5×12.7×3.0mm^3 for Izod impact tests, and a notch of 2.5 mm depth with an angle of 45° was milled 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 coated with gold in vacuum before being examed.

FTIR. spectra

The phenol /Chloroform(2/3) as the solvent was used to dissolve pure PBT and PBT/eEPDM blend ,it is founded that the PBT and PBT-g-EPDM are dissolved ,but the EPDM don't. After filtering, the filter liquor is evaporated to form films .The films and the FTIR.spectra using the hot pressed films of EPDM and eEPDM were recorded on BIO-RAD FTS-7.

Torque rheology

The torque measurements of PP blends were performed on a Thermo Haake mixer. The rotating speed was set at 60rpm and the temperature was set at 240°C.

Results and Discussion

FTIR. spectra

Figure1(1,2) showed typical FTIR.spectra of EPDM and eEPDM. It can be seen that the i.r. spectrum of eEPDM is different from EPDM. The i.r.spectra of eEPDM is characterized by the presence of a specific epoxide band at 871cm^{-1} (asym.epoxide ring stretching).But it does not appear in the i.r. 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 convert to the epoxy functional group in eEPDM. To use an excess of trichloroacetic acid with epoxy groups reaction. Then introduing sodium hydroxide titrates surplus trichloroacetic acid. According to this method, the amount of epoxy groups is 0.8wt%. Figure1(3) showed FTIR.spectra of pure PBT. Figure1(4) showed FTIR.spectra of PBT/eEPDM blend. Before examanation, the phenol /Chloroform(2/3) as the solvent was sed to dissolve PBT/eEPDM blend..The soluble fraction in the blend should include pure PBT and PBT-g-EPDM. The insoluble fraction in the blend was EPDM. To select soluble fraction and remove the solvent to form a film. As shown in Figure1(3,4), 1460cm^{-1} urepresents characteristic band of CH_2 on the EPDM. The intensity of bands at 1460cm^{-1} of the PBT/eEPDM blend in the FT-IR spectra is obviously higher than that of pure PBT .This indicates that a reaction takes place between PBT and eEPDM during the mixing process, and results in the formation of the PBT-g-EPDM.

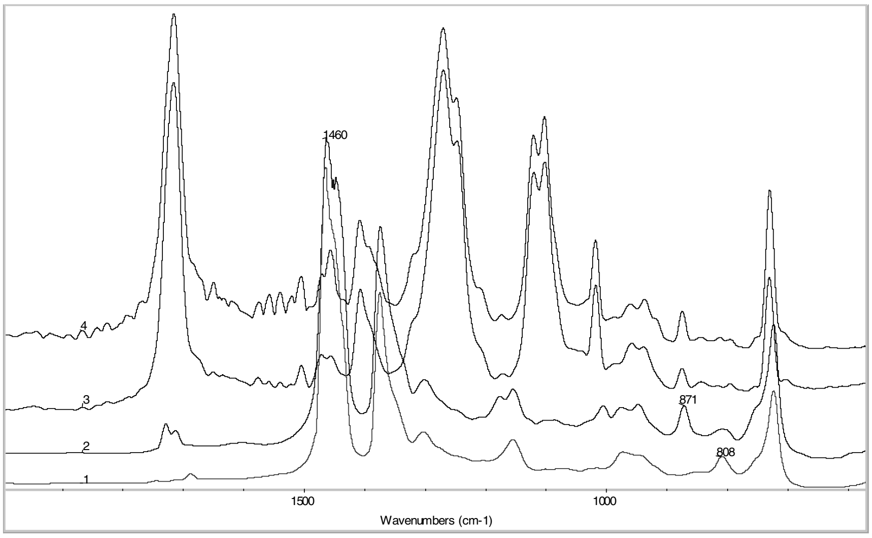


Figure 1 FTIR spectra of (1)EPDM, (2)eEPDM, (3)PBT and (4)PBT/eEPDM

Torque tests

Plots of actual temperature and torque value in the internal mixer *versus* mixing time at the setting temperature of 240°C for PBT/PP (50/50) blends are given in Figure2 and Figure3, respectively. For PBT/PP blend, it can be seen from Figure2 that the actual temperature in the mixer increases rapidly during a short time and it reached 250°C after 10 minutes, which is higher than the setting temperature. This is due to viscous heating of polymer even if there is no reaction. For the PBT/PP /eEPDM blends, it is noted that the actual temperature in the mixer reaches 258°C. This is due

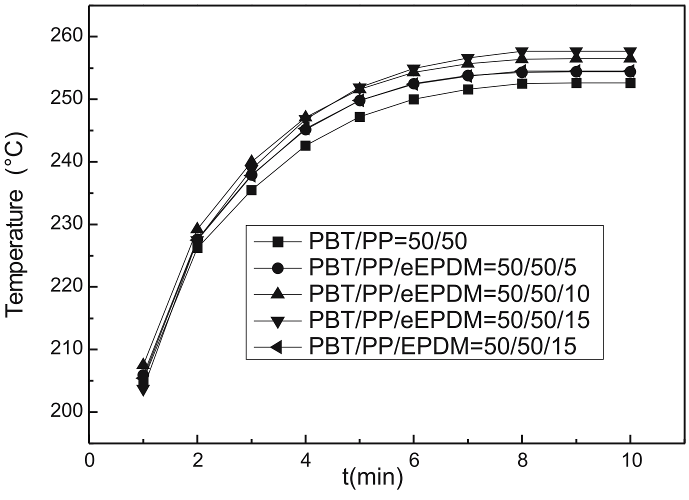


Figure 2 Evolution of temperature with time for PBT blends in Haake mixer

to both viscous heating of highly viscous PBT-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 or hydroxyl terminal groups in PBT occur (see Figure3), the torque values of the PBT/PP blends raises with the increase of the eEPDM content.Furthermore,for reactive PP/PBT/eEPDM (50/50/15)blend,its actual temperature in the mixer and torque values are higher than non- reactive PP/PBT/EPDM (50/50/15)blend.These raise can be attributed to the increase of molecular weight from the anticipated epoxy coupling reactions to form PBT-g-EPDM copolymers.

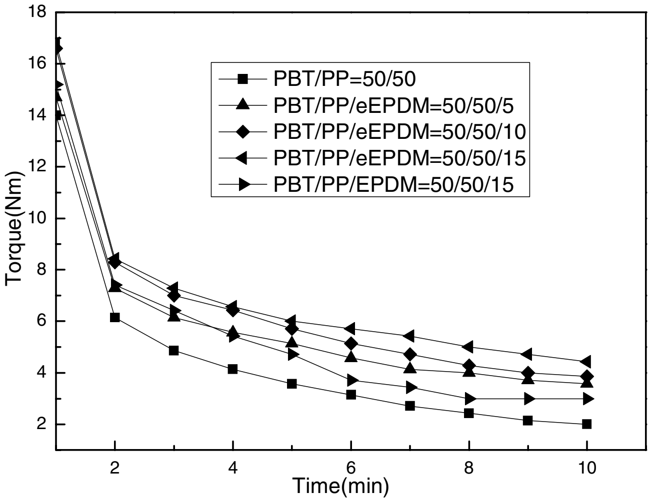
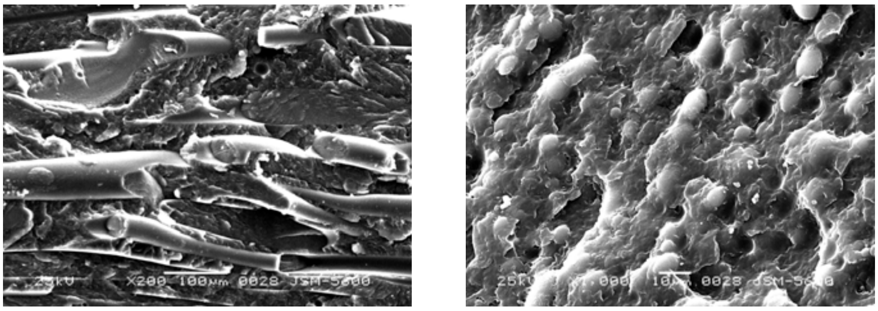


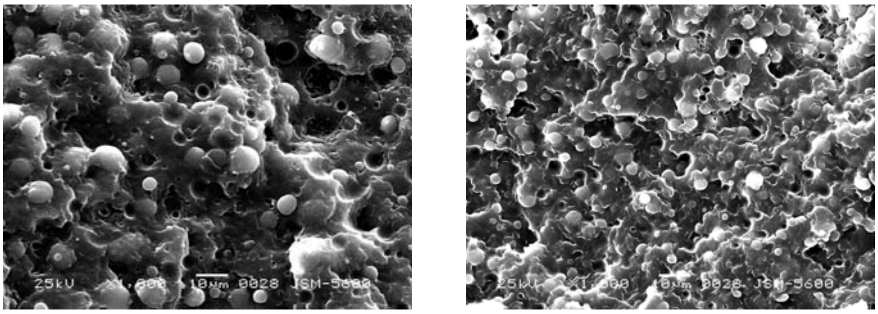
Figure 3 Evolution of torque with time for PBT blends in Haake mixer

Morphology

Figure4 shows the SEM micrographs of the uncompatibilized and compatibilized 50/50 PBT/PP blends. Figure4a shows that the co-continuous structure of the uncompatibilized 50/50 PBT/PP blend. Figure4(b-d) show the morphologies of the blends containing various amounts of eEPDM compatibilizer, from 5 to 15 phrs. The domain size decreases with the increase of compatibilizer quantity as expected from any efficient compatibilizer. Figure5 shows the SEM micrographs of the uncompatibilized and compatibilized 30/70 PBT/PP blends. It can be seen the same result as Figure4. This result may be caused by the formation of PBT-g-EPDM as compatibilizer at the interface reducing the interfacial tension and result in finer phase domains. A.Gonzalez-Montiel et al. [12] investigated the compatibilization of nylon6/PP blends by using SEBS-g-MA. By TEM observation, they think that the MA grafted to the rubber reacts with the amine end-groups of the polyamide, forming a rubber-nylon6 graft copolymer that locates at the interface between nylon6 and PP. It has been recently reported by Shaughnessy[13] that the suppression of droplet-droplet coalescence through steric hindrance by the form of the copolymer at the interface is the dominant mechanism.

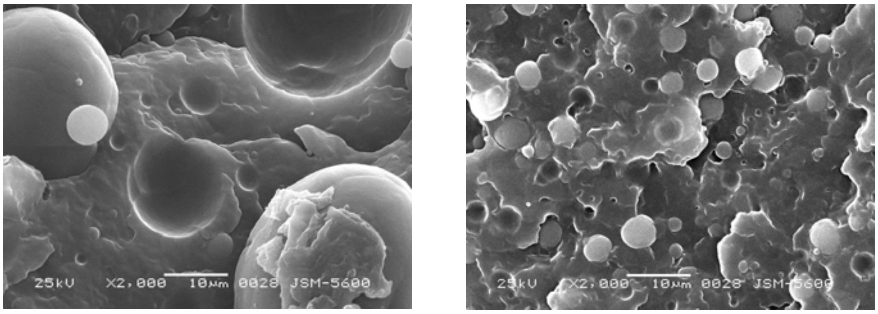


(a) PP/PBT=50/50 (b) PP/PBT/eEPDM=50/50/5

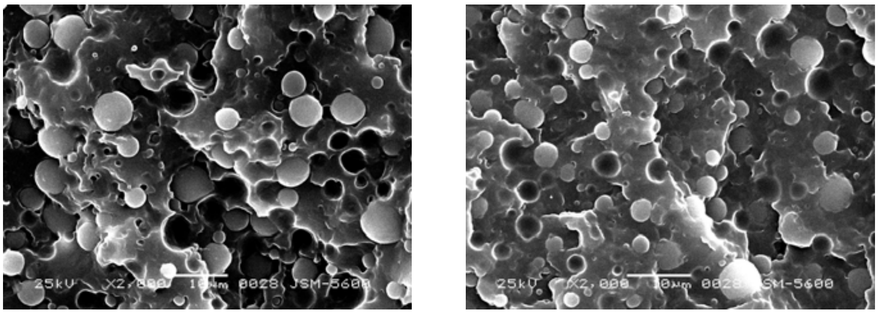


(c) PP/PBT/eEPDM=50/50/10 (d) PP/PBT/eEPDM=50/50/15

Figure 4 SEM images of PBT/PP (50/50) blends with different eEPDM



(a) PBT/PP=30/70 (b) PBT/PP/eEPDM=30/70/5



(c) PBT/PP=30/70/10 (d) PBT/PP/eEPDM=30/70/15

Figure 5 SEM images of PBT/PP (30/70) blends with different eEPDM

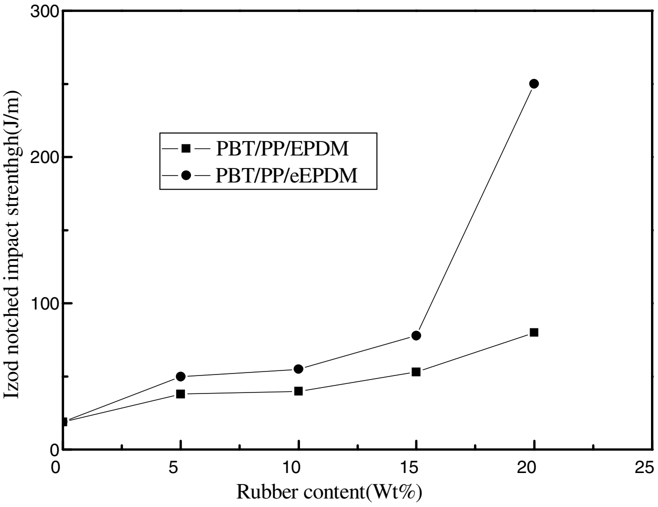


Figure 6 Notched impact strength of PP blends with different EPDM content. PBT/PP=30/70

Mechanism Properties

The notched impact strength, as a function of rubber content for PBT/PP/EPDM, PBT/PP/eEPDM blends is shown in Figure6. PBT/PP ratio is 30/70. Up to 20Wt% rubber content, the toughness of PBT/PP/EPDM improves a little .This is because the adding of EPDM, which can decrease the yield stress of PBT/PP blends. But the blends still fracture in a brittle manner. Whereas the toughness of PBT/PP/eEPDM blend has evidently improved. As the rubber content is 20Wt%,the PBT/PP/eEPDM blend becomes tougher and its notched impact strength is about 4 times that of PBT/PP/EPDM. This is because both the adding of rubber and the formation of PBT-g-EPDM at the interface between PBT and PP, which decrease the disperse phase domain size. Figure7 showed the relation of tensile strength and rubber content for

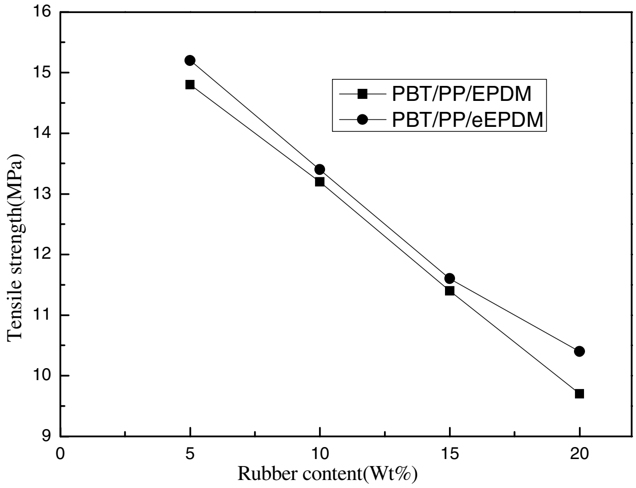
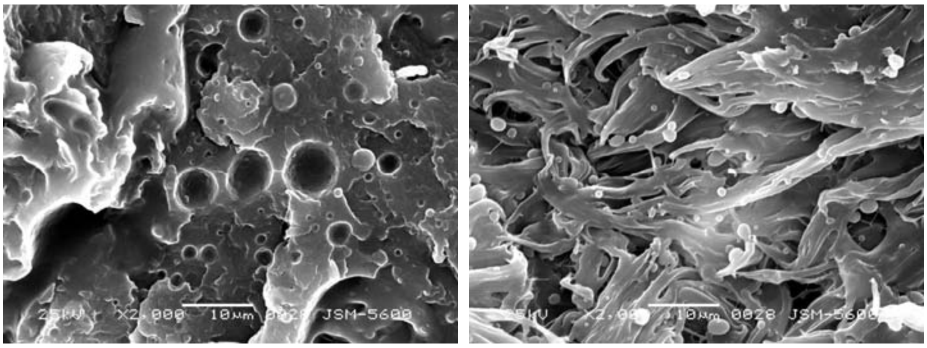


Figure 7 Tensile strength of PP blends with different EPDM content. PBT/PP=30/70



a b

Figure 8 Morphology of the fracture surface (a) PBT/PP/EPDM, (b) PBT/PP/eEPDM

PBT/PP/EPDM, PBT/PP/eEPDM blends.The result showed that tensile strength of compatibilized blends is higher than incompatibilized blends.It due to the formation of PBT-g-EPDM , which increased the interfacial adhension and led to improve the tensile strength. Figure8 present the fracture surfaces of PBT/PP/EPDM and PBT/PP/eEPDM blends and they have the same compositions. The SEM micrographs are taken directly behind the notch. The lower impact strength of the PBT/PP/EPDM blend is clearly reflected by its fracture surface(Figure8a). It can be seen many naked and pulled particles.It displays a brittle fracture mode at 23°C. Figure8b displays the fracture in a ductile manner on which fibre surface can be seen. This may be relieved the volume strain by debonding between PBT and PP phasesand leaded to decrease of von Mises yield stress. It improvesd shear yielding of matrix and further improve its impact-resistance performance.

Conclusions

In this study, ethylene-propylene-diene-rubber (EPDM) was epoxidized with an *in situ* formed performic acid. The eEPDM was used to compatibilize PBT/PP blends. FTIR results showed that the epoxide absorption peak appeared on the spectra of eEPDM. The EPDM had been epoxidized. Torque test showed that the actual temperature and torques value for the compatibilized blends were higher than that of the uncompatibilized blends. These results showed that the reaction between epoxy groups in the eEPDM and carboxylic acid groups or hydroxyl terminal groups in PBT had taken place and PBT-g-PP copolymers were formed in situ. SEM images showed the disperse phase domain size decreased with the increase of eEPDM quantity. This is because the formation of PBT-g-EPDM which leads to reduce dispersed phase particle size and improves morphology stability. Notched Izod impact tests showed that both the adding of rubber and the formation of PBT-g-EPDM copolymer induced local yielding of matrix and improved the toughness of PBT/PP blends.

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