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Toughening of poly(butylene terephthalate) with epoxidized ethylene propylene diene rubber

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In this paper, unepoxidized ethylene propylene diene rubber (uEPDM) was first epoxidized with formic acid and H_2O_2, and then the epoxidized ethylene propylene diene rubber (eEPDM) was melt-mixed with PBT resin in a Brabender-like apparatus. Toughening of PBT matrix was achieved by this method. The dispersion of rubber particles and phase structure of the blends were also observed by SEM. It has been suggested that the epoxy groups in the eEPDM could react with PBT end groups to form a graft copolymer which could act as an interfacial compatibilizer between the PBT matrix and eEPDM rubber dispersed phase. This is beneficial to the improvement of the impact performance of PBT. © 1997 Elsevier Science Ltd. All rights reserved.

INTRODUCTION

A large number of thermoplastic polymers exhibit strong limitations in their end use when both toughness and high impact resistance are required[1,2]. These shortcomings may be overcome by blending these materials with a suitable rubbery component[3-5]. The enhancement of toughness obtained is due to the presence of finely dispersed rubber particles which are thought to induce energy dissipation by both crazing and shear yielding of the matrix[1]. Poly(butylene terephthalate) (PBT), like some other polymers, is a brittle polymer with poor notched impact strength, especially at temperature below its glass transition and in the dry state. However, the impact performance of PBT may be improved by incorporating an appropriate rubber into the matrix[6,7].

In this paper, the toughening of PBT was achieved by adding to it an epoxidized ethylene propylene diene rubber (eEPDM). The unepoxidized EPDM rubber (uEPDM) was first epoxidized with formic acid and H_2O_2, and then melt-mixed with PBT resin in a Brabender-like apparatus. It was thought that the epoxy groups could react with PBT end groups to form a graft copolymer which could act as an interfacial agent between the PBT matrix and eEPDM rubber dispersed phase[8-10].

The aim of the present work was to investigate the influence of eEPDM on the impact performance of PBT/eEPDM blends, compared with the influence of uEPDM. The morphological features were also observed to show the dispersion of rubber particles and phase structure of the blends.

EXPERIMENTAL

Materials

PBT used in this paper was a commercial polymer, FR-PBT (made in Shanghai, China), which was dried in a vacuum oven at 120°C for 12 h before being used. The uEPDM was also a commercial polymer, EPT 4045 (made in Japan), 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.

Epoxidation procedure of EPDM rubber

The uEPDM was first dissolved in toluene under continuous stirring, then the solution was acidified stepwise with 88% formic acid to pH 2–3. When the expoxidation was performed at 50°C, the required amount of H_2O_2 (30%) was slowly dropped for about 30 min. The rapid introduction of this reagent is not recommended as 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 expoxidation, the rubber was coagulated in acetone, thoroughly washed with distilled water, soaked in 1% w/v Na_2CO_3 solution for 24 h, and finally 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 constant weight. The *FT*i.r. spectra of both uEPDM and eEPDM were recorded on BIO-RAD FTS-7 spectrometer using film cast directly on KBr plates.

Blend preparation

PBT/eEPDM and PET/uEPDM blends, having

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different rubber contents were processed at 245°C for 5 min at roller speeds of 40 rpm in a Brabender-like apparatus (Rheocoder XSS-300). The PBT/uEPDM blends were prepared for comparison purposes with PBT/eEPDM blends.

Material testing

PBT/eEPDM and PET/uEPDM blends, were further dried in a vacuum oven at 80°C for 24 h, then compression-moulded at 260°C to obtain specimens with thickness of 3.2 mm, which were cut into rectangular specimens of $63.5 \times 12.7 \times 3.2\,mm^3$ for performing Izod impact tests. The rectangular specimens were sharply notched with a fresh razor blade. The impact tests were performed by an Izod pendulum at room temperature.

Morphology observation

The test specimens were cold-fractured in liquid nitrogen. After coating with a thin layer of gold/palladium alloy, the fracture surfaces were observed by JXA-840 scanning electron microscope (SEM).

RESULTS AND DISCUSSION

FT i.r. spectra of eEPDM and uEPDM

Figure 1 shows typical FT i.r. spectra for uEPDM and eEPDM. It can be seen that the i.r. spectrum of eEPDM is different from that of uEPDM. The i.r. spectra of eEPDM are characterized by the presence of a specific epoxide band at $871\,cm^{-1}$ (asym. epoxide ring stretching), which does not appear in the i.r. spectra of uEPDM. Furthermore, the intensity of a specific C=C–H band at $808\,cm^{-1}$ decreases obviously after the epoxidation of uEPDM, which demonstrates the conversion of C=C double chemical bond in uEPDM to epoxy functional group in eEPDM[11].

Mechanical characterization

The notched impact strength I, obtained by Izod tests, as a function of rubber content for PBT/uEPDM blends and PBT/eEPDM blends, is shown in *Figure 2*. Up to 15 wt% rubber content, the toughness of PBT/uEPDM improved only a little and the blends still fractured in a brittle manner, while the toughness of PBT/eEPDM blends has evidently improved. As the rubber content approaches to 15 wt%, the PBT/eEPDM blend becomes super tough and its notched impact strength is about 23 times of that of pure PBT and about 10 times that
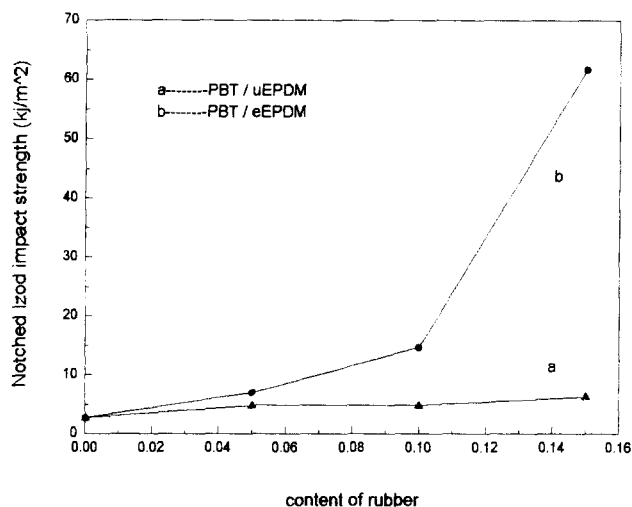
Figure 2 Plot of impact strength *versus* content of rubber for PBT/rubber blends

of PBT/uEPDM blends. This behaviour can be attributed to the fact that, going from the blends containing uEPDM to the blends containing eEPDM, a reduction of the size and an improved adhesion of the rubber domains into the matrix are achieved. This will be discussed in the next section.

Morphology

The morphological investigation was performed by SEM on cold-fractured surfaces of the PBT/uEPDM and PBT/eEPDM blends and the result is shown in *Figure 3*. It can be observed that with the increase of rubber content the average particle dimensions increase from about $1.0\,\mu m$ to $2.0\,\mu m$ in PBT/uEPDM blends and decrease from about $1.0\,\mu m$ to $0.4\,\mu m$ in PBT/eEPDM blends. When the rubber content is 15 wt%, the dispersed eEPDM particles are rather smaller than dispersed uEPDM particles. In PBT/uEPDM blends, there is hardly any rubber domain pulled away or deformed during the surface fracture, indicating that the uEPDM has poor adhesion to the PBT matrix. In the blends PBT/eEPDM, most of the rubber domain appears to be more irregular and more connected with the PBT matrix, suggesting an increase of the interfacial adhesion between the two phases. This phenomenon is in a good agreement with the impact properties.

Reactive blending

Because of epoxidation, eEPDM, bearing epoxy groups, provides the functionalized sites with which the terminal PBT hydroxide or carboxylic acid groups can react, as shown in *Scheme 1*.

When eEPDM is melt-mixed with PBT matrix, according to reactions shown in *Scheme 1*, a graft copolymer (eEPDM-g-PBT) is presumably formed in the interface between the rubber domains and PBT matrix, which can act as an effective compatibilizer, decreasing the interfacial tension, resulting in a finer dispersion of the rubber phase and ultimately improving the toughness of PBT resin[10].

The reaction product, eEPDM-g-PBT, is made from an eEPDM backbone and some PBT branches during melt-mixing. Although only a small quantity of graft copolymer can be formed, these small quantities of
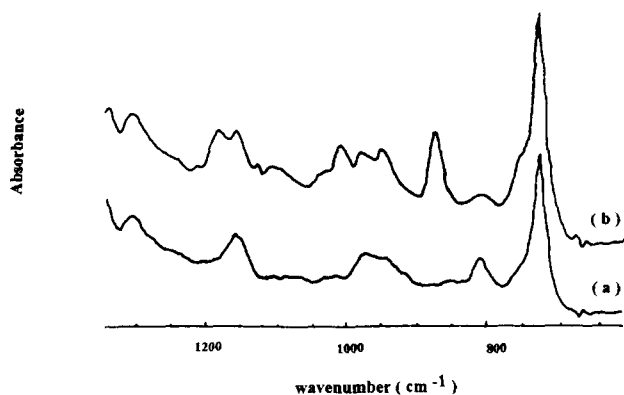
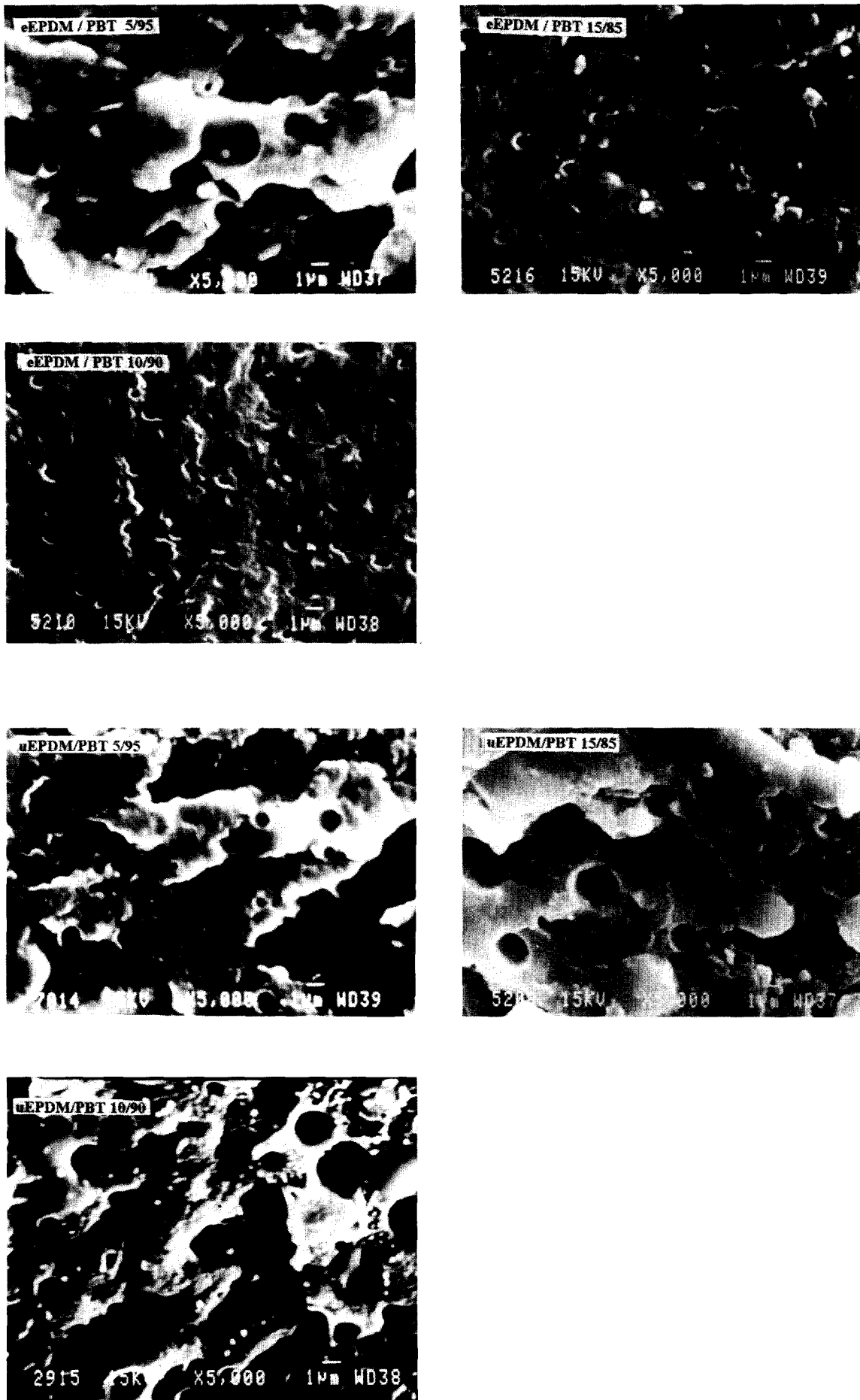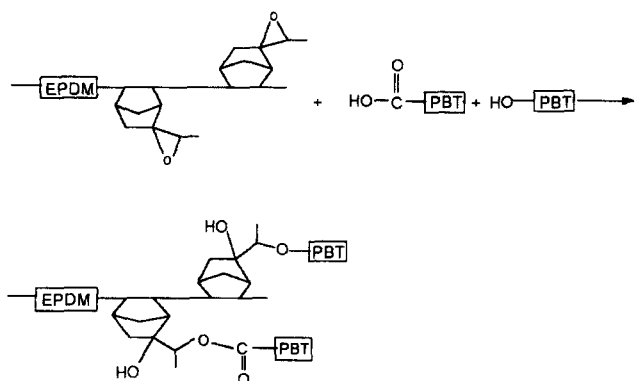**Figure 1** FT i.r. spectra for uEPDM (a) and eEPDM (b)

Figure 3 SEM micrographs of the fracture surface of the uEPDM/PBT and eEPDM/PBT blends

Scheme 1

eEPDM-g-PBT could act as an interfacial compatibilizer between the PBT matrix and eEPDM rubber and result in improvement of the toughness.

CONCLUSIONS

In PBT/EPDM blends, the size of rubber domains is large and the adhesion between the rubber and plastic phase is poor. Therefore, its toughness is improved only a little. However, when epoxidized EPDM is used, its epoxy-containing groups can react with PBT matrix, forming a graft copolymer EPDM-g-PBT. A better homogeneity and finer dispersion of the rubber phase in the matrix are obtained. This will induce local yielding of PBT around the rubber particles, dissipate the impact energy and improve its impact-resistance performance.

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REFERENCES

1   Bucknall, C. B. 'Toughened Plastics', Applied Science Publ., London, 1977
2   Paul, D. R. and Newman, S. 'Polymer Blends', Academic Press, New York, 1978
3   Cimmino, S., D'Orazio, L., Greco, R., Maglio, G., Malinconico, M., Mancarella, C., Martuscelli, E., Musto, P., Palumbo, R. and Ragosta, G. *Polym. Eng. Sci.* 1985, **25**, 193
4   Coppola, F., Greco, R. and Ragosta, G. *J. Mater. Sci.* 1986, **21**, 1775
5   Karger-Kocsis, J., Kallo, A., Szafner, A., Bodor, G. and Senger, Z. *Polymer* 1979, **20**, 37
6   Wilfong, D. L., Hiltner, A. and Baer, E. *J. Mater. Sci.* 1986, **21**, 2014
7   Pilati, F. *Polym. Eng. Sci.* 1983, **23**, 750
8   Moffett, A. J. and Dekkers, M. E. J. *Polym. Eng. Sci.* 1992, **32**, 1
9   Greco, R., Musto, P., Ragosta, G. and Scarinzi, G. *Makromol. Chem., Rapid Commun.* 1988, **9**, 129
10 Cecere, A., Greco, R., Ragosta, G., Scarinzi, G. and Taglialatela, A. *Polymer* 1990, **31**, 1239
11 Roux, C., Pautrat, R., Cheritat, R. and Ledran, L. *J. Polym. Sci., Part C: Polym. Symp.* 1969, **16**, 4687