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Effect of γ-irradiation on brittle–tough transition of PBT/EPDM blends

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Irradiation can be applied to crosslink the dispersed elastomer phase to increase the modulus and decrease the voiding ability of the elastomer, which results in increasing critical brittle–tough transition elastomer content at constant temperature. The experimental results show that at 25°C the critical elastomer content of EPDM shifts to higher composition (shift of about 4 wt%) for PBT/EPDM blends after 100 kGy γ-irradiation. © 1997 Elsevier Science Ltd.

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Introduction

Irradiation induces crosslinks in ethylene-propylene-diene monomer rubber (EPDM) resulting in an increment of the plateau modulus. The plateau modulus G_2 can be correlated with the average molecular weight between crosslinks (M_c) using classical rubber elasticity theory[1]

$$M_c = \frac{\rho RT}{G_2} \quad (1)$$

where ρ is the rubber density, R is the gas constant and T is the reference temperature.

Another effect of irradiation on the property of EPDM is to increase the break stress. According to Bucknall *et al.*[2,3], Gent *et al.*[4] and Liang *et al.*[5], increasing either the modulus or the break stress of rubber phase will result in decreasing its voiding ability, which certainly influences the brittle–tough transition (BTT) temperature at constant elastomer content or critical BTT elastomer content at constant temperature of polymer blends only if the irradiation effect on the properties of the matrix can be neglected within the range of irradiation doses.

Van der Sanden *et al.*[6] found that for polycarbonate (PC)/EPDM blends the BTT temperature shifted to a higher temperature (shift of about 15°C) with increasing irradiation doses from 0 to 200 kGy, within which the properties of PC were not influenced by the irradiation.

In order to provide a further understanding of the influence of the properties of dispersed rubber phase on the critical BTT elastomer content at constant temperature of polymer blends, irradiation was applied to poly(butylene terephthalate) (PBT)/EPDM blends in our study.

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 EPDM 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 of −60°C.

Sample preparation. In general, it is hard to improve the toughness of PBT by blending it with EPDM directly because of the poor compatibility between these two polymers. In order to observe the phenomenon of brittle–tough transition for PBT/EPDM blends at room temperature, EPDM was first epoxidized by performic acid *in situ* formed with formic acid and H_2O_2 to introduce the polar epoxy groups into EPDM macromolecule backbone, which can improve the compatibility between PBT matrix and the dispersed EPDM phase. The details of the epoxidation procedure will be published in another paper[7]. The blends of PBT and epoxidized EPDM in weight ratios of 100/0, 96/4, 92/8, 90/10, 88/12, 86/14, 84/16 and 80/20 were prepared in the melt using a Brabender-like apparatus (Rheocoder XSS-300, made in Shanghai, China) at 245°C for 4 min at roller speeds of 40 rpm. The PBT/EPDM blends were further dried in a vacuum oven at 80°C for 24 h and at 110°C for at least 4 h, then compression-moulded at 250°C to obtain specimens with thickness of 3.2 mm, which were cut into rectangular specimens of 63.5 × 12.7 × 3.2 mm^3. The rectangular specimens were sharply notched with a fresh razor blade for performing notched Izod impact testing. In addition, the PBT/EPDM (100/0) sample was compression-moulded at 250°C to obtain specimens with thickness of 1 mm, which was cut into dumbbell-shaped specimens of 20 × 3.4 × 1 mm^3 for performing tensile test.

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Table 1 Effect of γ-irradiation (100 kGy) on mechanical properties of PBT and EPDM

Properties of PBT and EPDM	Impact strength ($kJ\,m^{-2}$) of PBT	Young's modulus (MPa) of PBT	Fracture energy ($kJ\,m^{-2}$) of PBT	Fracture stress (MPa) of PBT	Fracture stress (MPa) of EPDM
Unirradiated	1.3 ± 0.1	1836 ± 60	25 ± 1	56 ± 2	5.3 ± 0.2
Irradiated	1.2 ± 0.1	1796 ± 60	26 ± 1	55 ± 2	10.6 ± 0.2

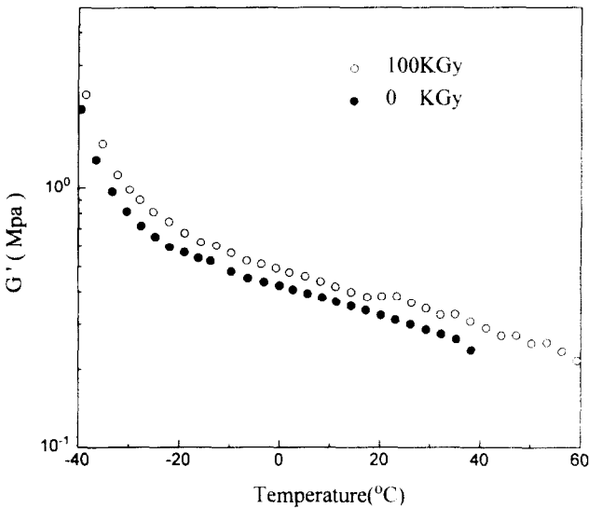

Figure 1 Dynamic shear modulus vs. temperature of EPDM rubber (system error ~2%)

γ-Irradiation of the specimens. One half of the notched impact specimens of the blends and the dumbbell-shaped specimens of PBT were irradiated with a dose of 100 kGy carried out with $^{60}C_0$ γ-rays in air at room temperature. In order to investigate the influence of γ-irradiation on the mechanical properties of the EPDM elastomer, cast plates of the epoxidized EPDM rubber from toluene solution (thickness 0.5 mm) were also irradiated with the same dose.

Dynamic mechanical analysis. Dynamic shear moduli of the irradiated EPDM and unirradiated EPDM plates were measured using rectangular shaped specimens (37 mm × 4.8 mm × 0.5 mm) in the temperature range from −70°C up to 60°C. A Rheovibron DDVII spectrometer (made in Japan) was used at a constant frequency of 3.5 Hz and a heating rate of $3°C\,min^{-1}$.

Mechanical properties testing. The impact tests of the specimens of irradiated and unirradiated PBT/EPDM blends were performed on an Izod pendulum at 25°C. The tensile test were performed by using an Instron (model 1121) with an elongational rate of $5\,mm\,min^{-1}$.

Characterization of the blend morphology. Scanning electron microscope (SEM) (JEOL model JXA-840, made in Japan) with an accelerating voltage of 15 kV was used to investigate the impact fracture surfaces of the PBT/EPDM blends. The fracture surfaces were sputter-coated with gold (to provide the electrical conductivity) in a vacuum chamber. In order to observe the undeformed phase morphologies developed in the moulded specimens, they were immersed in liquid nitrogen for about 20 min, then cold-fractured, which surfaces were also observed.

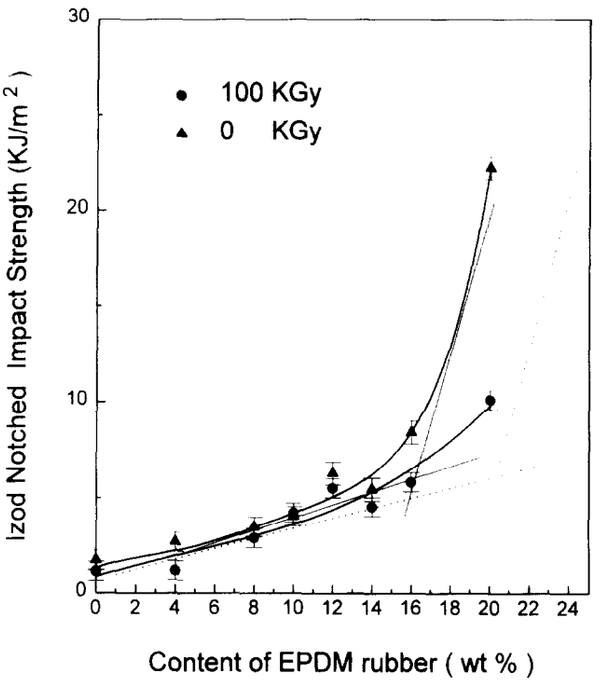

Figure 2 Notched impact strength of PBT/EPDM blends vs. EPDM rubber content

Results and discussion

γ-Irradiation includes crosslinks in EPDM rubber and the fracture stress of EPDM after 100 kGy irradiation is much higher than that of unirradiated EPDM (*Table 1*). As shown in the dynamic shear modulus of EPDM rubber (*Figure 1*), EPDM rubber has a rubbery plateau above the glass transition temperature T_g about −42°C. For the irradiated EPDM rubber, the height of plateau modulus G_2 is larger than that of the unirradiated EPDM rubber. The influence of γ-irradiation on PBT has been observed via tensile test and notched Izod impact test. Clearly, within the range of irradiation doses we used (0–100 kGy), the mechanical properties of PBT have no obvious changes after irradiation, which can be seen from *Table 1*.

In *Figure 2* the notched impact strength of the irradiated PBT/EPDM blends and unirradiated PBT/EPDM blends are shown as a function of EPDM rubber content, from which it can be seen that the critical BTT EPDM rubber content shifts to higher content (shift of about 4 wt%) after 100 kGy γ-irradiation. The critical BTT elastomer content is defined as the rubber content at cross point of two tangents, as is shown in *Figure 2*. One of the two dotted tangents for irradiated PBT/EPDM is presumed according to the tendency in the curve. Here we must note that the properties of PBT and the undeformed phase morphologies, such as the dispersed particle dimensions and the phase interface

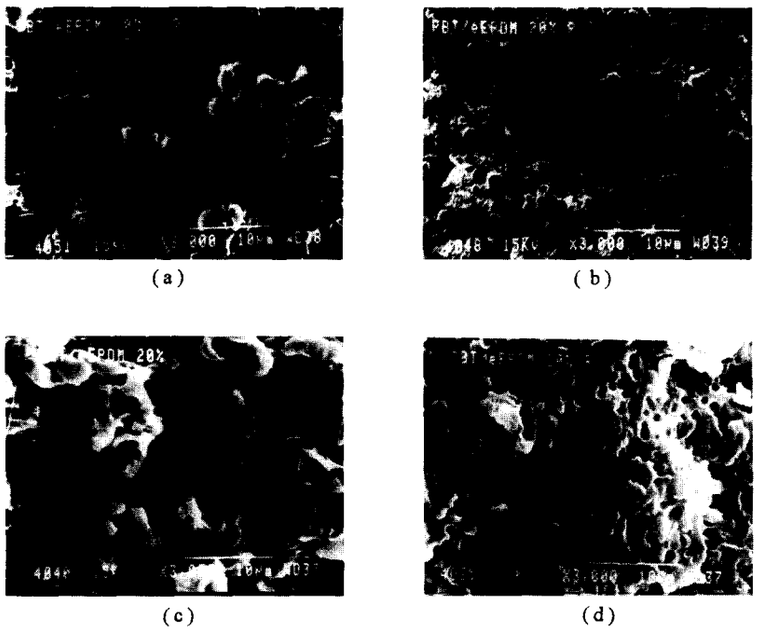

Figure 3 SEM micrographs of the fracture surfaces of PBT/EPDM (80/20) blends. (a) The cold-fractured surface without irradiation; (b) the cold-fractured surface with irradiation; (c) the impact fracture surface without irradiation; (d) the impact fracture surface with irradiation

between the matrix and the rubber particles deduced approximately by the agreement of the vagueness, coarseness and irregularity at edges of the voids, developed in the moulded specimens of PBT/EPDM blends, are not influenced by irradiation, as are shown in SEM photographs of the cold-fractured surfaces of the PBT/EPDM (80/20) blends in *Figures 3a* and *b*, so the shift of critical rubber content can just result from the changes of the properties of EPDM. For PC/EPDM blends, van der Sanden *et al.*[6] found that BTT temperature shifted to higher temperature (shift of about 15°C) with increasing irradiation doses from 0 to 200 kGy for a certain rubber content. In our experiment, we found that the critical rubber content shifts to a higher content (about 4 wt%) with increasing irradiation dose from 0 kGy to 100 kGy at a constant temperature (25°C). Therefore, it is thought that increasing temperature and increasing rubber content (if the rubber size remains unchanged) is equivalent for the brittle–tough transition behaviour of polymer blends.

A large number of experimental results[8–10] show that matrix shear yielding is the most effective way to dissipate impact or tensile energies, which means the critical point of BTT for polymer blends is corresponding to the point of matrix shear yielding. This can be clearly seen from *Figures 3c* and *d*, where the matrix with a ductile fracture was much more deformed for unirradiated PBT/EPDM blends (80/20) while the matrix with a brittle fracture was relatively smooth for the irradiated PBT/EPDM blends (80/20).

Conclusions

For PBT/EPDM blends, irradiation just changes the properties of the dispersed EPDM phase and has no influence on the properties of PBT matrix and the morphology of the blends within the range of irradiation doses from 0 to 100 kGy. The shift of critical rubber content at a constant temperature must result from the changes of the properties of dispersed phase (modulus and fracture stress). The experimental results show that the critical elastomer content shifts to higher content (shift of about 4 wt%) at 25°C for PBT/EPDM blends after 100 kGy γ-irradiation.

Acknowledgement

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References

1. Ferry, J. D., *Viscoelastic Properties of Polymers*. Wiley, New York, 1980.
2. Lazzeri, A. and Bucknall, C. B., *J. Mater. Sci.*, 1993, **28**, 6799.
3. Bucknall, C. B., Karpodinis, A. and Zhang, X. C., *J. Mater. Sci.*, 1994, **29**, 3377.
4. Gent, A. N. and Tompkins, D. A., *J. Polym. Sci. A2*, 1969, **7**, 1483.
5. Haojun Liang, Wei Jiang, Jilin Zhang and Bingzheng Jiang, *J. Appl. Polym. Sci.*, 1996, **59**, 505.
6. van der Sanden, M. C. M., de Kok, J. M. M. and Meijer, H. E. H., *Polymer*, 1994, **35**, 2995.
7. Wang, X. H. and Wang, Z., *Polymer*, in press.
8. Wu, S., *J. Polym. Sci. Polym. Phys. Edn.*, 1983, **21**, 699.
9. Li Qiang, Zheng Wenge, Qi Zongneng, Wu Xuanzheng and Cai Zhonglong, *Science in China B*, 1993, **23**, 469.
10. Margolina, A. and Wu, S., *Polymer*, 1988, **29**, 2170.