Impact behaviour of polystyene/EPDM-rubber blends : influence of electron beam irradiation

polymer communications

Impact behaviour of polystyrene/EPDM-rubber blends: influence of electron beam irradiation

J. G. M. van Gisbergen, C. P. J. H. Borgmans, M. C. M. van der Sanden and P. J. Lemstra
Department of Polymer Technology, Eindhoven University of Technology, PO Box 513, 5600 MB Eindhoven, The Netherlands
(*Received 18 September 1989*)

Electron beam irradiation of polystyrene/ethylene propylene diene monomer (PS/EPDM) blends, using polystyrene/polybutadiene block copolymers as compatibilizers, resulted in a two to three fold increase in Izod impact value. This greatly increased impact resistance is probably related to radiation-induced grafting of the butadiene part of the block copolymer, located at the interface, onto the dispersed EPDM particles.

(Keywords: polystyrene/EPDM-rubber blends; impact strength; electron beam irradiation; grafting)

Introduction

Toughening of brittle polymers by dispersing rubbery particles is a subject of widespread interest[1–4]. The importance of morphology, i.e. the particle size and distribution, has been analysed for various systems. The adhesion between the dispersed rubbery particles and the matrix has been considered to be an important parameter, at least in matrices which craze upon loading, for example polystyrene[2].

In previous papers[5,6], we have reported upon the use of electron beam irradiation as a tool to control the morphology of immiscible polymer blends. The principle is as follows: blends are prepared using a well-tuned kneader (extruder) inducing an optimum morphology, for example in pelletized form. Before subsequent processing into a moulded product, via injection moulding, the pellets are irradiated. In the case of rubbery particles dispersed in a high(er) T_g matrix, electron beam irradiation usually results in crosslinking of the dispersed phase whereas the matrix is not affected. Consequently during subsequent processing steps the morphology is fixated. The beam response of a material is dependent on the chemical structure. Polyamides, polyesters and in particular polystyrene are relatively inert in contrast to easily crosslinkable rubbers such as EPDM[7,8]. However, in the special case of polystyrene/rubber blends it is rather difficult to induce crosslinking in the dispersed rubbery phase due to shielding effects of the polystyrene matrix. In a polystyrene/EPDM blend only a moderate degree of crosslinking was achieved and consequently complete fixation of morphology was not possible. Nevertheless, electron beam irradiation of this blend could increase the impact strength significantly. In this paper we report some preliminary results concerning impact improvement of polystyrene/EPDM blends using polystyrene/polybutadiene diblock copolymers as compatibilizers.

Experimental

The materials used are listed in *Table 1*. The compatibilizers used, later referred to as BC, are diblock copolymers of polystyrene (PS) and polybutadiene (PB).

Blends were prepared on a co-rotating twin screw extruder (Berstorff ZE 25) with a standard screw geometry (two kneading sections), at an average barrel temperature of 200°C. Strands were quenched and subsequently pelletized. One part of the pelletized blends was injection moulded at a temperature of 200°C into square plaques with length 80 mm and thickness 4 mm. The plaques were subsequently irradiated at room temperature in air, using a 3 MeV van de Graaff electron beam accelerator (IRI, Delft). The other part of the pellets was first irradiated and subsequently injection moulded.

The injection moulded plaques were prepared for notched Izod impact testing (ASTM D256) and were annealed for 3 weeks at room temperature before testing.

Morphologies of the blends were observed using scanning electron microscopy (Cambridge Stereoscan 200). Samples were cut at liquid nitrogen temperature with a glass knife, subsequently etched in an oxygen plasma and finally covered with a gold layer.

The degree of crosslinking was measured via soxhlet extraction in (boiling) xylene for 24 h. The samples were dried under vacuum at a temperature of 60°C for 24 h and subsequently weighed. The fraction of crosslinked

Table 1 Specifications of the materials used

	M_n (kg/mole)	M_w (kg/mole)	M_w/M_n	PS content (%)	PS block (%)	Code
Polystyrene, styron 638 (Dow)	70	200	2.85	100	–	–
EPDM rubber, Keltan 514 (DSM)	45	180	4	–	–	–
PS-b-PB, Kraton D-1118X (Shell)	53	63	1.19	30	±30	1-PS
PS-b-PB, Finaprene F-410 (Fina)	70	78	1.09	48	±32	h-PS

0263–6476/90/050162–03

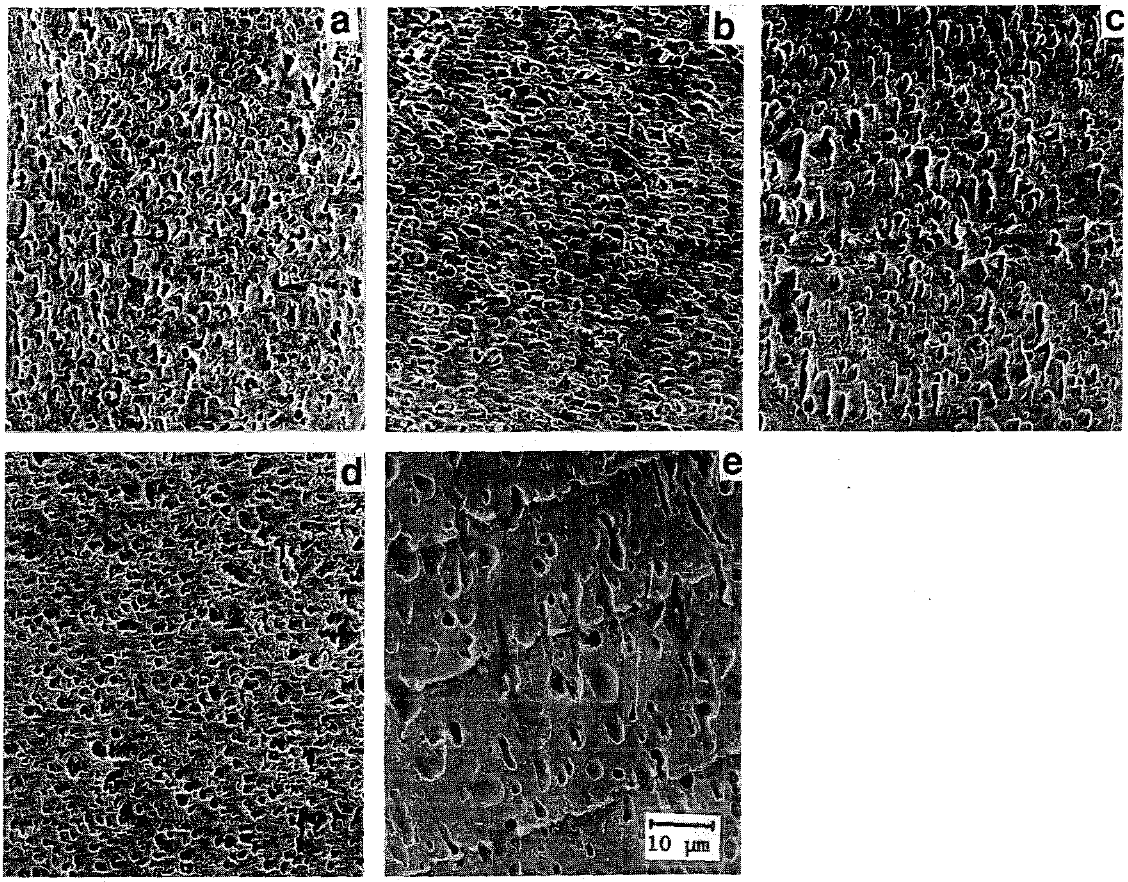

Figure 1 SEM micrographs of injection moulded blends (all magnifications are the same). (a) PS/EPDM/l-PS 78/19/3; (b) PS/EPDM/l-PS 78/19/3, irradiated with a dose of 100 kGy before injection moulding; (c) PS/EPDM/h-PS 78/19/3; (d) PS/EPDM/h-PS 78/19/3, irradiated with a dose of 100 kGy before injection moulding; (e) PS/EPDM 80/20

material was based on the amount of rubber present in the blend.

Results and discussion

Figure 1 shows the morphologies of various injection moulded blends. As can be inferred, and as expected, the addition of block copolymer reduces the average EPDM particle size: compare *Figure 1e* with *Figures 1a–d*. Both compatibilizers used seem equally effective in reducing the average EPDM particle size. Irradiation before injection moulding (irradiation of the pelletized strands, see experimental section) only slightly affects the EPDM particle shape and size: compare *Figure 1a* with *1b* and *1c* with *1d*. Further details with respect to the combined effect of processing and irradiation on the resulting morphology are beyond the scope of the present communication and will be discussed elsewhere[9]. Based on the micrographs in *Figure 1* one may conclude qualitatively that the morphology of the processed blends is determined primarily by the addition of block copolymers, at least for the processing conditions employed for these experiments.

The impact strength data are presented in *Figure 2*. *Figure 2a* shows that an increase in impact is obtained from approximately 1 to 2.8 kJ m^{-2} by the addition of 20 wt% EPDM and a further increase from 2.8 to 5 kJ m^{-2} is achieved with the addition of the compatibilizers. This effect is related, as well documented in the literature, to the combined effect of reduced particle size and an increased adhesion[1,2].

Although electron beam irradiation of the pelletized blend before injection moulding has no profound effect on morphology, in terms of fixation of specific structures, a major increase in impact strength is observed if PS/EPDM/block copolymer blends are subjected to irradiation before (*Figure 2b*) as well as after (*Figure 2c*) injection moulding. Via the latter route all influences of processing on impact strength are ruled out, i.e. there is no difference in morphology between the irradiated and non-irradiated samples. A strong increase in impact strength is already observed at a relatively low radiation dose, notably for the PS/EPDM blend with the high PS content (h-PS) block copolymer, where an Izod value of approximately 14 kJ m^{-2} is obtained. The differences in absolute Izod values between the two processing routes might be related to finer details in morphology which cannot yet be explained.

The main reason for the strong increase in impact strength however, should be related to grafting at the interface. Crosslinking as such of the dispersed EPDM phase cannot explain these effects. For example PS/EPDM blends, without compatibilizer, do not change in impact strength upon irradiation (see *Figure 2b*). Moreover the increase in impact strength in the case of PS/EPDM/BC blends is already achieved at a dose of 36 kGy, whereas the degree of crosslinking of the dispersed EPDM phase increases continuously, see *Figure 3*.

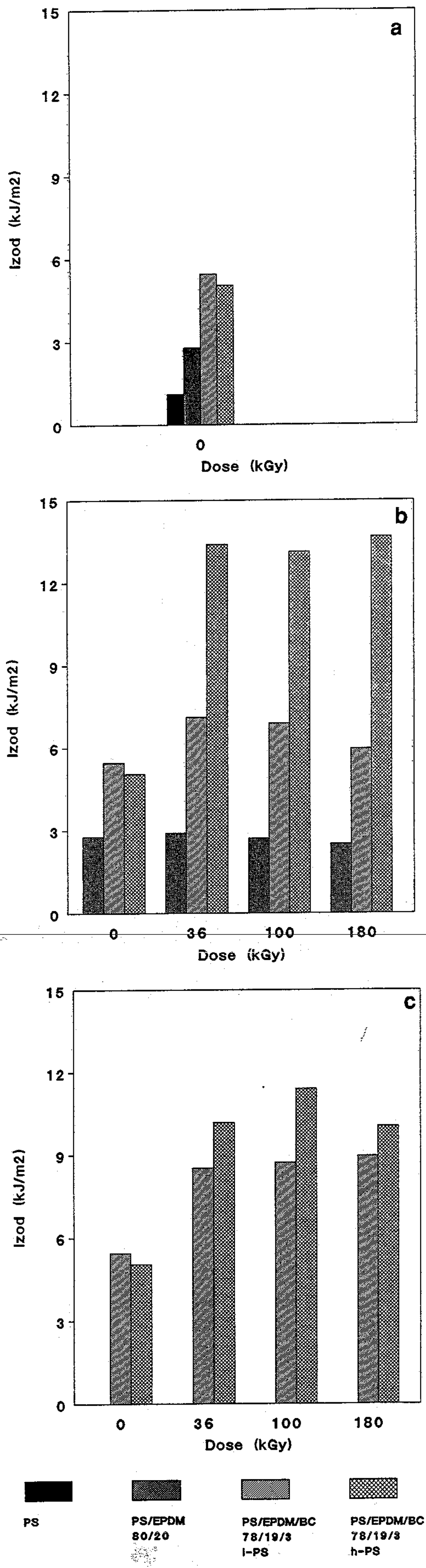

Figure 2 Izod values for injection moulded blends as a function of irradiation dose (l-PS and h-PS used as compatibilizer). (a) Non-irradiated blends; (b) irradiated before injection moulding; (c) injection moulded before irradiation

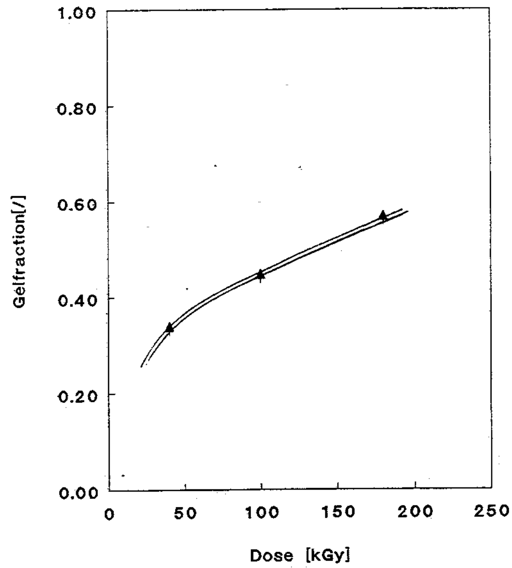

Figure 3 Crosslinked fractions for PS/EPDM/BC 78/19/3 blends as a function of irradiation dose. l-PS (+) and h-PS (▲) used as block copolymer

It has been reported in the literature that polybutadiene is not completely miscible with EPDM but that there is compatibility to some extent[10,11]. Assuming that the block copolymer is located at the PS/EPDM interface, the unsaturated (and consequently reactive) butadiene block may be grafted onto the EPDM phase resulting in an increased adhesion between EPDM rubber and matrix. The ultimate adhesion will now be determined by the interaction between the PS block and the PS matrix, which is still of a physical nature since polystyrene is inert at these radiation doses. In this respect the larger effect with the h-PS block copolymer can be explained by the higher PS content, leading to a better interaction between PS block and PS matrix.

Acknowledgement

One of the authors, J.G.M. v. G., is indebted to TNO, Delft for financial support.

References

1 Bucknall, C. B. 'Toughened Plastics', Applied Science Publishers, Barking, 1977
2 Bucknall, C. B. in 'Polymer Blends' (Eds. D. R. Paul and S. Newman), Academic Press, New York, Vol. 1, 1978
3 Borggreve, R. J. M. 'Toughening of Polyamide 6', PhD thesis, Twente University, The Netherlands, 1988
4 Wu, S, *Polymer* 1985, **26**, 1855
5 Elemans, P. H. M., Van Gisbergen, J. G. M. and Meijer, H. E. H. in 'Integration of Fundamental Polymer Science and Technology' (Eds. P. J. Lemstra and L. A. Kleintjens), Elsevier, Amsterdam, Vol. 2, 1988, pp 261–266
6 Van Gisbergen, J. G. M., Meijer, H. E. H. and Lemstra, P. J. *Polymer* 1989, **30**, 2153
7 Charlesby, A. 'Atomic Radiation and Polymers', Pergamon Press, Oxford, 1960
8 Spenadel, L. *Rad. Phys. Chem.* 1979, **14**, 683
9 Van Gisbergen, J. G. M. and Meijer, H. E. H. in preparation
10 Olabisi, O., Robeson, L. M. and Shaw, M. T. 'Polymer/Polymer Miscibility', Academic Press, 1979
11 Corish, P. J. in 'Polymer Blends and Mixtures' (Eds. D. J. Walsh, J. S. Higgins and A. Maconnachie), Martinus Nijhoff Publishers, Dordrecht, 1985