Structured polymer blends: 2. Processing of polypropylene/EDPM blends: controlled rheology and morphology fixation via electron beam irradiation

J. G. M. van Gisbergen, H. E. H. Meijer and P. J. Lemstra*

Eindhoven University of Technology, Department of Polymer Technology, PO Box 513, 5600 MB Eindhoven, The Netherlands

Electron beam irradiation has been used to improve the processability of polypropylene/ethylene–propylene–diene monomer (PP/EPDM) blends (controlled rheology) in combination with fixation of morphology by inducing crosslinks in the dispersed EPDM phase. An optimum morphology for impact toughening has been obtained via extrusion-blending high molecular weight PP with EPDM. Upon irradiation before subsequent processing (injection moulding) this morphology is fixated, whereas the viscosity of the blend decreases as a result of chain scission of the PP matrix. Impact strength and elongation at break of these irradiated blends are better than those of blends of low molecular weight PP with EPDM, which possess comparable overall viscosity.

(Keywords: PP/EPDM blends; irradiation; morphology; controlled rheology)

INTRODUCTION

Via extrusion (melt) blending of incompatible polymers, various morphologies can be realized, such as droplets or fibrils in a matrix, stratified or co-continuous structures, depending on the volume fraction of the constituents, their relative viscosities, shear stress (history) and interfacial tension[1]. The major complicating factor is the intrinsic instability, in the molten state, of the induced morphologies resulting from a local balance of stresses within the system, which change or adapt continuously depending on the processing conditions.

In principle, mixing devices can be optimized to induce a desired morphology in incompatible polymer blends, e.g. in pelletized form. However, subsequent processing, e.g. via injection moulding, of the pelletized blend could destroy this morphology completely as a consequence of different shear stresses. In previous papers we have shown that irradiation before subsequent processing could be used to fixate the morphology in polymer blends[2–4]. A schematic representation to illustrate this procedure is shown in *Figure 1*. Polymer B is dispersed in polymer A and pellets are obtained. Upon subsequent electron beam irradiation (EB) the dispersed phase B crosslinks and the morphology is fixated, provided of course that materials are selected with different beam response, e.g. a blend of a high T_g polymer (unsusceptible to irradiation) as matrix and a low T_g, crosslinkable, rubber as dispersed phase.

For rubber toughening of polypropylene (PP) with ethylene–propylene–diene monomer (EPDM), a homogeneous dispersion of EPDM particles with a diameter of about 0.3–0.5 μm is desired[5–8]. In incompatible polymer blends such a fine dispersion is most easily reached when the viscosities of matrix and dispersed phase are closely

matched[9,10]. For PP/EPDM blends this implies that to achieve the desired morphology, relatively high molecular weight PP is required, since the melt viscosity of EPDM is usually much higher than the viscosity of the PP matrix. For the subsequent processing step (injection moulding of the pelletized PP/EPDM blend), it would be beneficial to have a lower viscosity of the PP matrix. This contradiction can, in principle, be solved by irradiating the blend before the subsequent processing step. It is well known that the main reaction in PP as a result of electron beam irradiation is chain scission, whereas EPDM will crosslink[11–13]. Irradiation of a blend of high viscosity PP with EPDM will result in chain scission of the PP matrix, achieving a low viscosity, and the induced (optimum) morphology may be preserved as a result of radiation-induced crosslinks in the dispersed phase.

The influence of the irradiation dose on the chain scission reaction of the main chain of PP in both the pure homopolymer and the blend has been studied. Experiments concerning fixation via irradiation of an
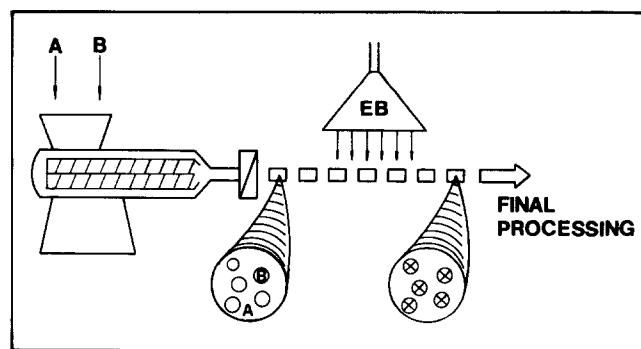

Figure 1 Schematic view of crosslinking a dispersed phase B, by using electron beam irradiation between the blending and final processing step to achieve morphology fixation

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* To whom correspondence should be addressed

optimum morphology, obtained by blending high viscous PP with EPDM, are presented. A comparison is made between rheology, morphology and mechanical properties of injection moulded blends with and without irradiation between the extrusion and processing step.

EXPERIMENTAL

The materials used, polypropylene (Stamylan P) with EPDM rubber (Keltan), were obtained from DSM and their characteristic properties are listed in *Table 1*. The third monomer in the EPDM rubber is ethylidene norbornene (ENB). The polypropylene grades were isotactic homopolymers.

Blends were either made on a two-roll mill (Schwabenthan, $T=185°C$) and subsequently compression moulded into 1 mm thick sheets or prepared on a co-rotating twin screw extruder (Berstorff ZE 25, $T=220°C$) and pelletized. Both sheets and pellets (also for PP) were exposed to a 3 MeV electron beam 'Van de Graaff' accelerator at IRI, Delft. Irradiation was performed at room temperature in air. Irradiated and non-irradiated pellets were injection moulded on an Arburg Allrounder (221-55-250) at a temperature of 240°C and with a mould temperature of 50°C into test pieces for Izod impact testing and stress–strain experiments.

From the compression moulded sheets, samples were cut for rheological measurements using a Rheometrics RDS-II. A cone and plate geometry was used. The test temperature was 190°C, rather low for PP and PP/EPDM samples. Measurements at higher temperatures, however, were not possible since the low viscosity of irradiated high molecular weight PP caused experimental difficulties.

Morphologies of the blends were characterized with a Cambridge 200 stereoscan scanning electron microscope. Samples were cut at low temperature and the rubber particles were then extracted. A method described by Stehling[14] was used and somewhat modified. After microtoming, the rubber particles were extracted for 2 min in n-hexane in an ultrasonic bath. To extract even partly crosslinked particles in some cases a method described by Rose et al.[15] was used: the smooth surfaces were held in boiling xylene vapour for 5 s. After extraction the surface was covered with a thin gold layer.

Izod impact testing was performed according to ASTM (D 256) at room temperature. Tensile testing was performed on dumb-bell shaped specimens at a rate of 100 mm min^{-1} (ISO-R-37, type 2). Yield stress (σ_y), modulus (E) and elongation at break (ε_b) were determined.

Molecular weights were determined via gel permeation chromatography (g.p.c.) (Waters Model 200) using TCB as a solvent at 135°C and four columns packed with styragel (10^2, 10^3, 10^4, 10^5 nm). The g.p.c. facilities at DSM Research Geleen, The Netherlands, were used.

Table 1 Specifications of the materials

Material	MFI 230°C (dg min^{-1})	Mooney viscosity ML(1+4), 125°C	Ethylene content (mol%)	ENB content (mol%)	Code
PP 13E10,	1.1	–	–	–	PP-H
PP 112Mn10, K 514, EPDM	45	–	–	–	PP-L
rubber	–	46	52	8	EPDM

Table 2 Molecular weights of polypropylene (PP-H) as a function of radiation dose, determined by high temperature g.p.c.

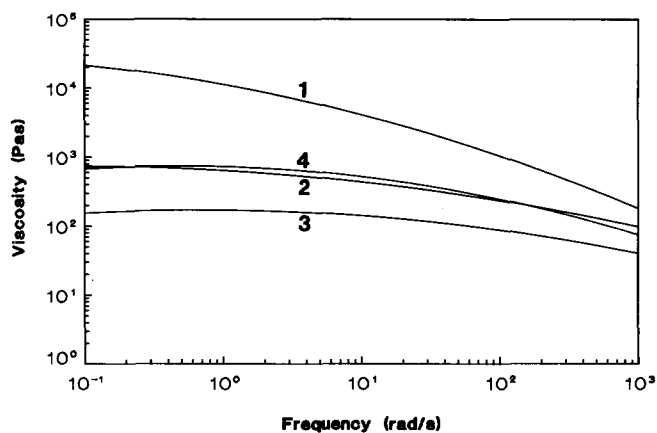| Dose (kGy)	M_w (kg mol^{-1})	M_n (kg mol^{-1})	M_w/M_n
0	570	82	6.9
26	250	65	3.8
44	220	68	3.2
88	180	48	3.7

Figure 2 Complex viscosity of irradiated PP-H: curve 1, 0; 2, 44; 3, 88 kGy. For comparison curve 4 is for the low molecular weight PP-L. Measurements were performed at $T=190°C$, as explained in the experimental section

RESULTS AND DISCUSSION

Irradiation of polypropylene homopolymer

Table 2 shows the results of irradiating high molecular weight PP homopolymer (PP-H) as revealed by g.p.c. measurements. A large decrease in absolute values for M_w and M_n is observed as well as a narrowing of the molecular weight distribution.

The decrease in molecular weight is reflected in the melt viscosity, as shown in *Figure 2*. The irradiated samples also show more pronounced Newtonian behaviour indicative of a narrowing of the molecular weight distribution[16,17]. It can be concluded, as published previously[4,12–14] that the molecular weight of PP can easily be controlled by irradiation, at least up to doses of 100 kGy. The viscosity of the low molecular weight PP (PP-L) is also shown in *Figure 2* (curve 4). This type of PP, prepared via peroxide shifting of a high molecular weight PP, possesses about the same viscosity as the PP-H irradiated with a dose of 44 kGy.

Blending and fixation of morphology

Morphologies of extruded strands of blends with 70% PP and 30% EPDM, obtained via mixing in a co-rotating twin screw extruder, are shown in *Figure 3*. The dispersed EPDM particles in the PP-H matrix are small and uniformly distributed, whereas the EPDM particles in the PP-L matrix are irregular and rather large.

The importance of using high viscosity PP to obtain small particles is evident from these micrographs. *Figure 4a* shows that this optimum morphology may rapidly develop into another as a consequence of subsequent processing. After injection moulding of the unirradiated, pelletized, blend the EPDM particles are still very small but orientation of the particles in the direction of injection is visible (compare *Figure 3a*). For the extruded, pelletized,
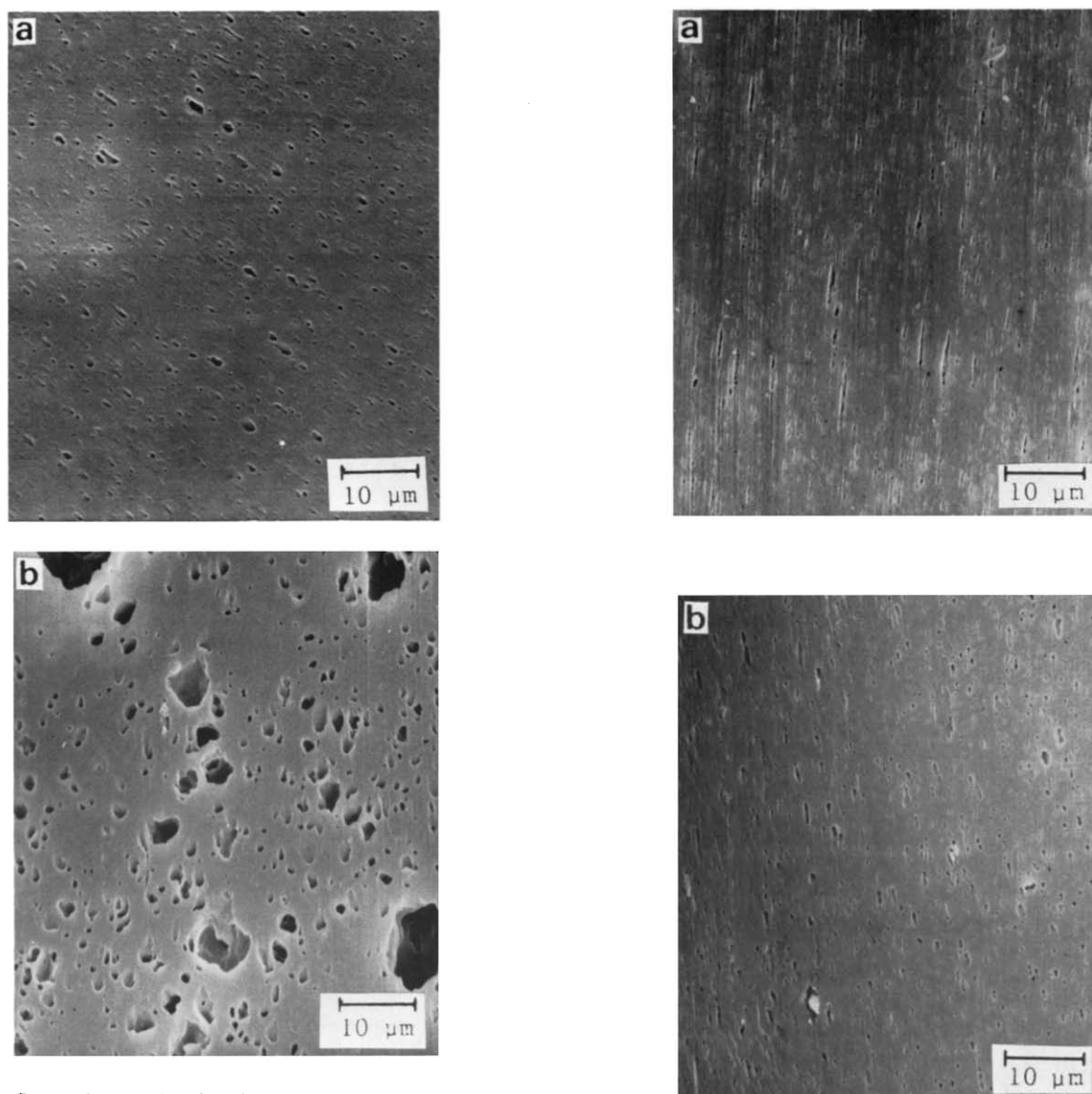
Figure 3 SEM micrographs of PP/EPDM 70/30 blends (extrudate), parallel to the direction of extrusion, etched in n-hexane for 2 min: (a) PP-H/EPDM; (b) PP-L/EPDM

blend irradiated with a dose of 44 kGy the degree of orientation as a result of injection moulding is decreased (*Figure 4b*). The particles in the injection moulded blend of low viscous PP-L and EPDM are more regular and smaller than in the reference blend (compare *Figures 4c* and *3b*) but the average particle size is still too large for good impact properties (see below).

A more extreme example of morphology change during processing of polymer blends is shown in *Figure 5a,b* for a PP-H/EPDM 80/20 blend. A droplet in matrix structure obtained in the extrusion step develops into a co-continuous structure as a result of injection moulding the pelletized blend. Irradiation of the blend after extrusion but before injection moulding preserves the original morphology to a large extent, as shown in *Figure 5c*. The SEM micrographs (*Figures 5b* and *5c*) were made from parts of the injection moulded samples where deformation stresses were high, i.e. near edges of the injection moulded samples.

Rheology, processing and properties

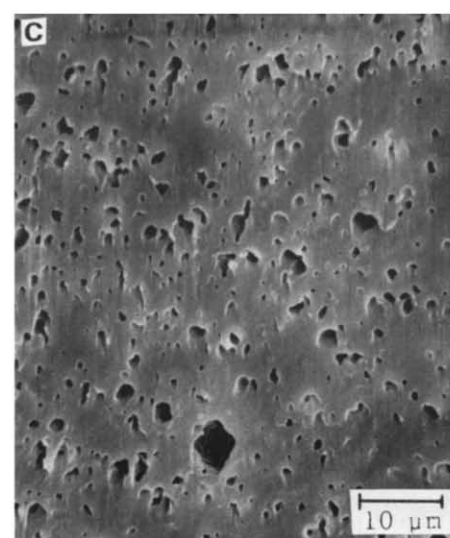The detailed rheological behaviour of dispersed polymer systems is beyond the scope of our study. The prime goal

Figure 4 SEM micrographs of PP/EPDM 70/30 blends, etched in n-hexane for 2 min: (a) PP-H/EPDM, extruded, pelletized and injection moulded; (b) as (a), but in pelletized form irradiated with a dose of 44 kGy before injection moulding; (c) PP-L/EPDM, extruded, pelletized and injection moulded
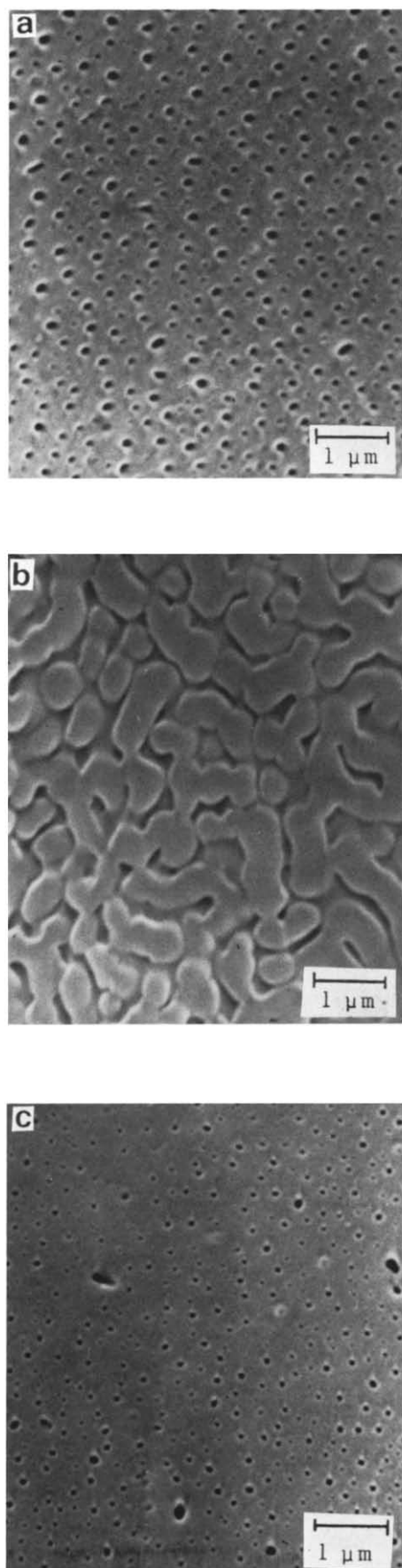
is to improve the processability of PP/EPDM blends in combination with good mechanical properties via morphology fixation, using electron beam irradiation. To make a fair comparison between mechanical properties, two systems were selected, possessing a similar overall viscosity, in other words comparable processing characteristics. PP-H/EPDM irradiated with a dose of 44 kGy and PP-L/EPDM were chosen, with melt viscosities given, respectively, by curves 1 and 2 in *Figure 6*.

The similarity of the viscosity curves at the injection moulding temperature (240°C) is questionable, however, since the viscosities were measured at a temperature of 190°C. Therefore, experiments were also performed with an unirradiated PP-H/EPDM 70/30 blend and with a blend irradiated with a dose of 88 kGy, possessing a higher and lower viscosity, respectively, compared to the two blends shown in *Figure 6*.

Figure 6 also shows that the rheological behaviour of the blends is more complex than for pure PP. For the blends there is a strong dependence of viscosity on frequency, even at low frequencies, and the average viscosity is much higher than for the pure PP. Moreover, experiments with other types of EPDM elucidated that after irradiation the overall viscosity of the blend was determined to a large extent by the type of EPDM used. Reactions occurring at the PP–EPDM interface may play an important role both in the determination of the overall blend viscosity and in the morphology fixation process. Results of these experiments will be published in the near future.

In *Table 3* the results of the mechanical tests are listed. The mechanical properties of the PP-H/EPDM blend irradiated with a dose of 44 kGy are superior to the PP-L/EPDM blend. In particular, the impact value of the Izod test is much higher. The properties of the PP-H/EPDM blend irradiated with a dose of 88 kGy are also better, bearing in mind that the melt viscosity is even
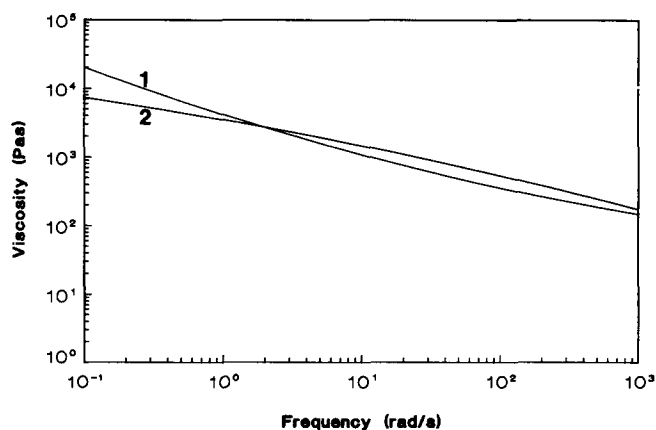

Figure 6 Complex viscosity for PP/EPDM 70/30 blends: curve 1, PP-H/EPDM, 44 kGy; 2, PP-L/EPDM, 0 kGy. $T = 190°C$

Figure 5 SEM micrographs of PP-H/EPDM 80/20 blends, etched in xylene vapour for 5 s: (a) extrudate, parallel to the direction of extrusion; (b) same blend as (a), but after injection moulding the pelletized blend; (c) same blend as (b), but in pelletized form irradiated with a dose of 44 kGy before injection moulding

Table 3 Mechanical properties for PP/EPDM 70/30 blends

Material	Izod (kJ m^{-2})	σ_y (N mm^{-2})	E (N mm^{-2})	ε_b (%)
PP-H/EPDM, 0 kGy	66.6	24.5	826	472
PP-H/EPDM, 44 kGy	57.3	17.2	804	597
PP-H/EPDM, 88 kGy	51.6	17.7	722	345
PP-L/EPDM, 0 kGy	8.1	16.4	828	460

lower than for the PP-L/EPDM blend. Compared with the unirradiated PP-H blend, irradiation causes a small decrease in impact strength, modulus and yield strength. A possible explanation for the first decrease is the crosslinking of the EPDM, resulting in poorer impact strength of the EPDM itself. Scission of the PP matrix could explain the decrease in modulus and yield strength and the increase in elongation at break[18].

CONCLUSIONS

An optimum morphology for toughening can be obtained by mixing high molecular weight PP (PP-H) with EPDM. Radiation-induced crosslinks stabilize this optimum morphology during subsequent injection moulding, resulting in good mechanical properties. Although these preliminary experiments are encouraging, optimization with respect to composition and dose is necessary.

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REFERENCES

1 Meijer, H. E. H., Lemstra, P. J. and Elemans, P. H. M. *Makromol. Chemie. Macromol. Symp.* 1988, **16**, 113–135
2 Van Gunst, C. A., Hoen, N. G. M., Lemstra, P. J. and Schrijver, J. Patent NL 8304161, 1983
3 Elemans, P. H. M., Van Gisbergen, J. G. M. and Meijer, H. E. H. 'Integration of Fundamental Polymer Science and Technology: Part 2' (Eds P. J. Lemstra and L. A. Kleintjens), Elsevier Applied Science Publishers, Barhing, 1988, pp. 261–266
4 Van Gisbergen, J. G. M., Meijerink, J. I. and Overbergh, N. 'Integration of Fundamental Polymer Science and Technology: Part 3' (Eds P. J. Lemstra and L. A. Kleintjens), Elsevier Applied Science Publishers, London, 1989, p. 128
5 Karger-Kocsis, J., Kallo, A., Szafner, A. and Bodor, G. *Polymer* 1979, **20**, 37–43
6 Jang, B. Z., Uhlmann, D. R. and Vander Sande, J. B. *Polym. Eng. Sci.* 1985, **25**, 643–651
7 Jang, B. Z., Uhlmann, D. R. and Vander Sande, J. B. *J. Appl. Polym. Sci.* 1985, **30**, 2485–2504
8 Thamm, R. C. Proc. Joint Meeting of the Rubber Division (ACS) and International Rubber Conference, 1976, *Elastomerics*, 1977, **50**, 24–34
9 Grace, H. P. *Chem. Eng. Commun.* 1982, **14**, 225–277
10 Elmendorp, J. J. A study on polymer blending microrheology, *PhD Thesis*, Delft University, 1986
11 Charlesby, A. 'Atomic Radiation and Polymers', Pergamon Press, Oxford, 1960
12 Makhblis, F. A. 'Radiation Physics and Chemistry of Polymers', Keter Publishing House, Jerusalem, 1975 (transl. from Russian)
13 Black, R. M. and Lyons, B. J. *Proc. Roy. Soc. Lond.* 1959, **A253**, 322–330
14 Stehling, F. C., Huff, T. and Speed, C. S. *J. Appl. Polym. Sci.* 1981, **26**, 2693–2711
15 Rose, W. and Meurer, C. H. *Siemens Forsch.-u. Entwickl.-Ber. Bd.* 1987, **16**(3), 127–130
16 Zeichner, C. R. and Patel, P. D. 'A Comprehensive Evaluation of Polypropylene Melt Rheology', Report Hercules Inc., Wilmington, 1985
17 Pahl, M. H. 'Praktische Rheologie der Kunststoffschmelzen und Lösungen', VDI Verlag, Düsseldorf, 1983
18 Levy, M. and Drummen, M. (DSM) personal communication