Impact strength of reactively extruded polystyrene/ehtylene-propylene-diene rubber blends

Please check the document version of this publication:

• A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
• The final author version and the galley proof are versions of the publication after peer review.
• The final published version features the final layout of the paper including the volume, issue and page numbers.

[Link to publication](#)

B U T T E R W O R T H
H E I N E M A N N

Impact strength of reactively extruded polystyrene/ethylene–propylene–diene rubber blends

J. J. Crevecoeur*, L. Nelissen, M. C. M. van der Sanden and P. J. Lemstra

Centre for Polymers and Composites (CPC), Eindhoven University of Technology, PO Box 513, 5600 MB Eindhoven, The Netherlands

and H. J. Mencer

Faculty of Chemical Engineering and Technology, University of Zagreb, PO Box 177, Marulićev trg 19, Zagreb, Croatia

and A. H. Hogt

Akzo Nobel Central Research, Location Deventer, PO Box 10, 7400 AA Deventer, The Netherlands

The impact strength of blends consisting of polystyrene (PS) and ethylene–propylene–diene rubber (EPDM) could be increased by adding a poly(styrene/ethylene–propylene) (SEP) compatibilizer and an organic peroxide during reactive extrusion. The increased impact strength could be related to an enhanced adhesion between the dispersed EPDM phase and the PS matrix, as a consequence of radical graftlink or co-crosslink reactions between the rubbery part (EP) of the compatibilizer and the dispersed EPDM rubber. The morphology of the blend proved to be dependent upon the type and amount of peroxide used, as well as on the residence time (feeding position) of the peroxide in the extruder. The dependence of the mechanical properties of the blends on the type and concentration of peroxide used, is discussed in relation to the distribution of the peroxide between the PS and the EPDM phases.

(Keywords: polystyrene; EPDM rubber; polymer blend)

INTRODUCTION

The toughening of brittle polymers by the dispersion of rubbery particles is a topic of major interest in polymer blend research[1–4]. The morphology, i.e. the state of dispersion of the rubber in the matrix, as well as the adhesion between the rubbery phase and the matrix, have been considered to be important parameters in matrices which craze upon loading, e.g. polystyrene[1,2]. Van Gisbergen *et al.* reported a strong increase in the Izod impact value upon the electron beam (e.b.) irradiation of injection moulded blends of PS and EPDM rubber when using a polystyrene/polybutadiene diblock copolymer as a compatibilizer[5]. This increase in impact properties was explained by a graftlink reaction between the compatibilizer and the EPDM rubber, which increased the adhesion between the dispersed phase and the matrix.

Impact improvements, comparable with the results reported by Van Gisbergen *et al.*[5], are presented in this paper, using several organic peroxides as graftlinking agents, instead of e.b. irradiation. The peroxides were added during the melt extrusion of a PS/EPDM rubber blend, using a poly(styrene/ethylene–propylene) (SEP) diblock copolymer as a compatibilizer.

Some important differences exist when using peroxides instead of the e.b. irradiation technique, which increase the adhesion between the matrix and the dispersed phase. The main difference is that during extrusion a peroxide can initiate a crosslink or grafting reaction *in situ*, whereas the e.b. technique requires an additional irradiation step in order to achieve the same result. The second difference is that the peroxide-induced reaction takes place under conventional processing conditions (i.e. high temperature, shear forces), whereas e.b. irradiation is usually carried out at room temperature (glassy state) in the absence of shear forces. Depending on the molecular structure of the particular peroxide, as well as on its solubility/miscibility in the matrix and the dispersed phase, a certain distribution of peroxide in both phases might be expected. Therefore, the use of a peroxide could provide the possibility of targeting reactions in the desired phase.

The relationships between the impact properties of a PS/EPDM extrusion blend containing a SEP diblock compatibilizer and the degree of graft- and crosslinking, initiated by several peroxides in different amounts, were the topics of this research.

---

* To whom correspondence should be addressed

EXPERIMENTAL

Materials

Polymers. Polystyrene (Styron 638[TM] (Dow); $M_n = 70$ kg mol^{-1}; $M_w = 200$ kg mol^{-1}); EPDM (Keltan 514[TM] (DSM); $M_n = 45$ kg mol^{-1}; $M_w = 180$ kg mol^{-1}); poly-(styrene/ethylene-propylene) diblock copolymer (SEP) (Kraton G-1701X[TM] (Shell); $M_n = 82$ kg mol^{-1}; $M_w = 88$ kg mol^{-1}; PS content = 37 wt%), were used in this work.

Peroxides. 2,5-Bis(t-butylperoxy)-2,5-dimethylhexane (Trigonox 101[TM]), 2,5-bis(t-butylperoxy)-2,5-dimethylhex-3-yne (Trigonox 145[TM]), t-butylcumylperoxide (Trigonox T[TM]), and 1-(α-t-butylperoxyisopropyl)-3-isopropenyl-benzene (Initiator D-120[TM]), were supplied by Akzo Nobel, and were used as received. The peroxides were impregnated on a solid carrier, i.e. a porous polypropylene powder (Accurel EP 100SR[TM] (Akzo Fibres)), up to the level of 40 or 50 wt% peroxide, in order to facilitate and increase the efficiency of the addition during the extrusion process.

Blend preparation and testing

Blends of PS, EPDM and SEP were prepared on a co-rotating 30 mm twin screw extruder (Werner and Pfleiderer ZSK 30, 12 zones; $l/d = 36$). The composition of the reference blend was PS:EPDM:SEP = 78:19:3 wt%. The various peroxides were added to the blend in concentrations, respectively, of 1, 2, 3, 5, and 7 mmol of peroxide groups per 100 g of blend. Peroxides were fed to the blend, either in the hopper together with the polymers (position a), or close to the end (position b) of the extruder, i.e. just before the last two zones. The temperature in the last part of the extruder was 235°C. The homogeneity of the dispersed peroxide was optically checked with a tracer, with the latter (and consequently the peroxide) being homogeneously dispersed.

The extruded strands were quenched in a water bath and subsequently pelletized. The granules were injection moulded at 220°C (using an Arburg 221/150R machine) into rectangular bars (10 × 4 × 80 mm), and subsequently

Table 1 Characteristics of the peroxides used in this study

Peroxide	Trigonox 101	Trigonox 145	Trigonox T	Initiator D-120
H_v (kJ mol^{-1})	66.5	76.8	66.3	63.8
V_m (mol^{-1})	335	324	224	272
α ($\times 10^{-4}$ K^{-1})	10.4	11.5	10.2	9.4
δ_0 at 235°C (J cm^{-3})$^{1/2}$	10.5	11.2	12.9	11.9

Table 2 Impact strength (notched Izod impact) of the polymer blends studied in this work

Material	Impact strength (kJ m^{-2})
PS	1.0
PS/EPDM	1.8
PS/EPDM/SEP	4.5
PS/EPDM/SEP/Trigonox 101[a]	2.5
PS/EPDM/SEP/Trigonox 101[b]	10.1

[a] Peroxide feed in the hopper
[b] Peroxide addition at the end of the extruder

notched according to the ISO standard (ISO1982(E)). After 24 h of annealing at a temperature of 80°C, the bars were subjected to a notched Izod impact test, using a Zwick 5102 impact tester, and a fast tensile test on a Zwick r_{el} (type SB 3122) tensile machine, using a test speed of 1 m s^{-1}.

Characterization

Heat of vaporization. The molar heats of vaporization (ΔH_v) of the peroxides were measured in aluminium cups (Mettler ME 27811) using a Mettler TA 2000 differential scanning calorimeter, operating at a reduced pressure (2 mbar) and at a heating rate of 5 K min^{-1}, as described in ref. 6. Solubility parameters (δ_0s) of the peroxides were calculated from the equation $\delta_0 = (\Delta H_v - RT/V_m)^{1/2}$, where R is the gas constant (in J mol^{-1} K^{-1}), T is the absolute temperature (K) and V_m is the molar volume (l mol^{-1}). The δ_0 values at 235°C were calculated from equation (1), taken from reference 7:

$$\ln\delta_T = \ln\delta_{298} - 1.25\alpha(T - 298) \qquad (1)$$

Values obtained for the coefficients of thermal expansion (α) are determind from density measurements[6], at temperatures up to 80°C, and are listed in *Table 1*. The solubility parameters of PS and EPDM were taken from Barton[8]. δ_0 values at 235°C were calculated from equation (2), taken from reference 9:

$$\ln\delta_T = \ln\delta_{298} - \alpha(T - 298) \qquad (2)$$

using for the volume coefficient of thermal expansion, α, the following values: PS = 1.9×10^{-4} K^{-1} below T_g and 5.6×10^{-4} K^{-1} above T_g[10,11]. EPDM = 2.3×10^{-4} K^{-1} (calculated from the coefficients of thermal expansion of PE[12,13] and PP[12,14,15]). The δ_0 values (at 235°C) of PS and EPDM were 16.9 and 15.9 (J cm^{-3})$^{1/2}$, respectively.

Scanning electron microscopy (SEM). The morphologies of the blends were observed by 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.

Gel fractions. The degree of crosslinking in the rubber was measured after extraction in boiling xylene for 12 h. The samples were washed with acetone, dried at 150°C for 30 min and subsequently weighed. The fraction of crosslinked material was normalized to the amount of rubber being present in the blend.

RESULTS AND DISCUSSION

Impact strength

Typical impact strength values of the materials investigated are listed in *Table 2*. By blending polystyrene with EPDM rubber, the resulting impact strength is increased. By adding a compatibilizer, in this case 3 wt% of a SEP diblock copolymer, the impact strength increases further, due to a reduced particle size[16] of the dispersed rubber and an increased adhesion between the PS and EPDM phases. If a peroxide is also introduced via addition in the hopper (position a), the impact strength is increased to a lesser extent. Addition of the same peroxide close to the end of the extruder (position b),

resulted in a substantial increase in impact strength of the blend.

Morphology

Scanning electron micrographs of the blends (*Figure 1*) show that the differences in impact behaviour for the two different peroxide feed positions, may be related to the morphology that is obtained.

Figure 1a shows the morphology of a PS/EPDM/SEP blend in which the peroxide (Trigonox 101) was added in the hopper. A coarser morphology (average rubber particle size of ~4 μm) was obtained in this case, when compared to the morphology of the same blend without peroxide (average particle size of ~2 μm). Morphology coarsening is caused by crosslinking of the rubber phase, which is initiated by the peroxide added in the hopper. A shift of the dynamic equilibrium between breaking up and coalescence of the rubber particles, in favour of coalescence/coarsening, can be assumed.

Figure 1b reveals the finer morphology of a PS/EPDM/SEP blend in which the peroxide was added close to the end of the extruder (average rubber particle size of ~2 μm).

From comparison between *Figures 1a* and *1b* it is obvious that besides the size, the shape of the rubbery particles also is influenced by the peroxide feed position. This difference in shape may influence the impact
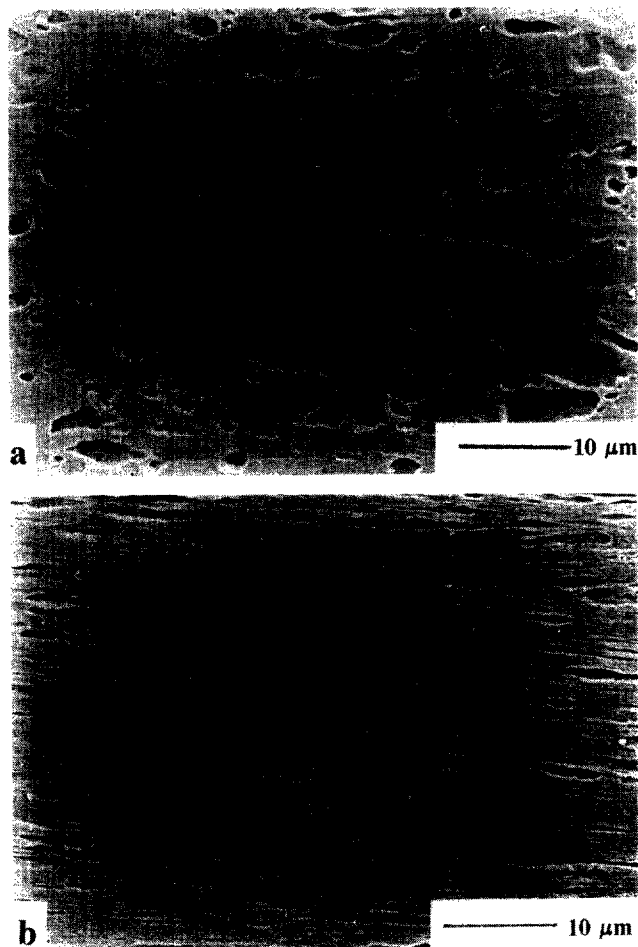

Figure 1 Scanning electron micrographs of PS/EPDM/SEP/Trigonox 101 blends: (a) peroxide added in the hopper; (b) peroxide added close to the end of the extruder
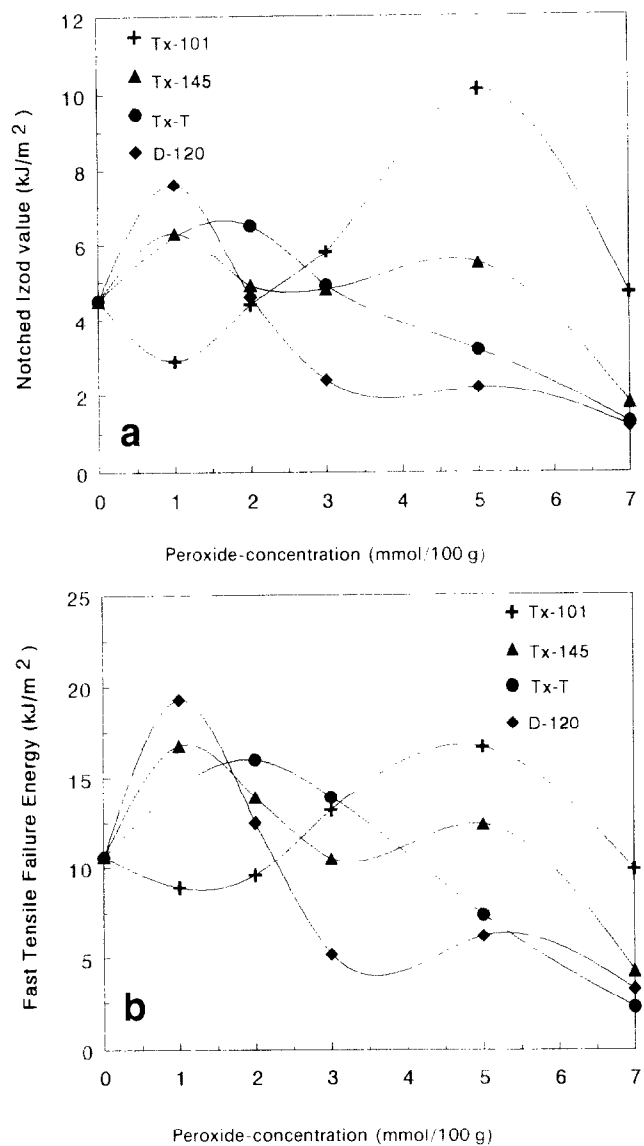

Figure 2 Impact values of various PS/EPDM/SEP/peroxide blends *versus* the concentration of the different peroxides, with the latter added close to the end of the extruder: (a) notched Izod value; (b) fast tensile (1 m s^{-1}) failure energy

behaviour, since truncated edges tend to initiate crazes more efficiently than smooth boundaries with a relatively large radius of curvature[17]. However, when considering the morphologies presented here, the differences in size are assumed to be more important than the shape of the rubbery particles.

Considering these data, one can conclude that the residence time of the peroxide in the extruder gives the opportunity of a tailoring of the desired impact strength. Optimal residence time can provide a sufficient homogeneity of the peroxide within the blend, a reasonable amount of crosslinks and graftlinks, and a proper morphology, as a result of the competition between breaking up and coalescence of the dispersed phase.

Impact strength versus peroxide concentration

In *Figures 2a* and *2b*, the notched Izod impact values and the failure energies of the fast tensile testing of various PS/EPDM/SEP blends, with peroxide added close to the

end of the extruder, are presented, with both sets of data showing similar patterns.

For all of the peroxides an optimum concentration exists, resulting in optimum impact properties, which is in agreement with the results presented by Teh and Rudin[18]. The appearance of this optimum peroxide concentration is most likely related to an increasing adhesion between the dispersed phase and the matrix, (increasing impact), and with a morphology coarsening, (decreasing impact)[19,20]. The increase in adhesion can be explained by a radical-induced co-crosslinking (graft-linking) of the rubbery part of the compatibilizer with the EPDM phase. (Possibly, the unsaturation of the diene segment of the dispersed EPDM phase reacts with a tertiary radical, formed previously at a propylene segment of the SEP copolymer.) The adhesion between the rubbery phase and the polystyrene phase is dependent on the number of graftlinks between the rubbery part of the compatibilizer and segments of the EPDM. It is expected that the number of graftlinks will increase with the peroxide concentration, because the number of graftlinks generated will be proportional to the number of radicals present. This is not the case for the whole range of applied peroxide concentrations. The shapes of the curves in *Figure 2* point to the other superimposed effect.

Above a certain optimum peroxide concentration, the impact values and fast tensile failure energies start to decrease and the amount of gel fractions starts to increase substantially (*Figure 3*). This implies that the crosslinking of the EPDM, at peroxide concentrations higher than the optimum, becomes more pronounced.

In the scanning electron micrographs presented in *Figure 4* the morphologies of the PS/EPDM/SEP blends with different peroxide (D-120) concentrations are shown. Above the optimum peroxide concentration (1 mmol of peroxide groups/100 g of blend) an increasing coarsening in morphology takes place as a result of extensive crosslinking.

Morphology coarsening at peroxide concentrations higher than the optimum results in decreasing impact
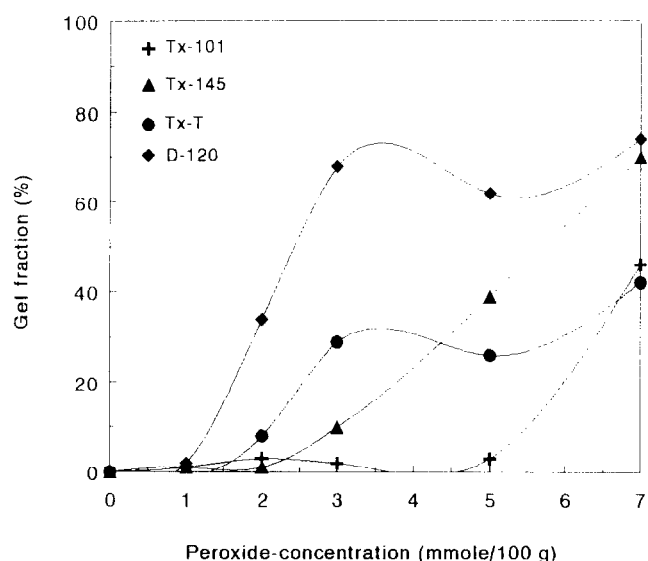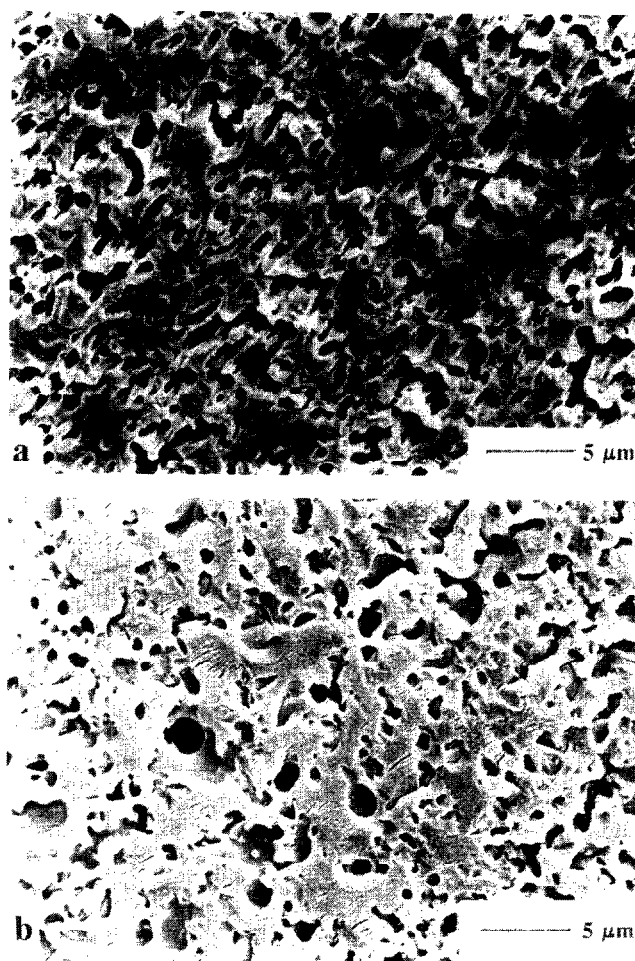

Figure 4 Scanning electron micrographs of PS/EPDM/SEP blends with different concentrations of peroxide D-120: (a) 1 mmol of peroxide groups per 100 g; (b) 5 mmol of peroxide groups per 100 g

Figure 3 Gel fraction (normalized to the amount of rubber present in the blend), *versus* the concentration of peroxide added during the extrusion process

properties (see *Figure 2*) as a consequence of the reduced number of craze initiating rubber particles. The average particle size should be minimized (but not below 2 μm, because of the decreasing ability of craze initiation)[19,20]. Apparently, the occurrence of crosslinking is undesirable. Although crosslinking in the dispersed rubbery phase, as such, can have a direct influence on the fracture resistance of the blend[21], the observed effects on the impact behaviour cannot be explained by the level of crosslinking achieved in the EPDM phase. This has been demonstrated by the electron beam irradiation experiments of PS/EPDM blends carried out by Van Gisbergen *et al.*[5]

At low peroxide concentrations, no significant crosslinking occurs, but the graftlink reaction is the predominant one, thus causing the impact improvement.

Evidently the peroxide radicals initiate selectively, with respect to the crosslink reaction in the EPDM phase, a graftlink reaction between the rubbery part of the block copolymer and the EPDM chains. This selectivity in favour of the graftlink reaction could be explained by the migration process of the peroxide from the polystyrene phase (the largest fraction in the blend) towards the rubber. During this process, the peroxide will encounter the compatibilizer first, because this component is positioned at the interface.

Because the desired reactions take place at the interface in the rubbery phase (gel permeation chromatography

measurements show that no significant molecular weight reduction of the polystyrene is caused by the peroxide at the applied temperature), the peroxide content in the rubbery phase is of great importance. The distribution of the peroxide between the matrix and the dispersed phase can be qualitatively considered as being a consequence of the different mobility and solubility of the peroxide in the two phases. This distribution depends therefore upon the molar mass of the peroxide and the Hildebrand solubility parameters of both the peroxides and the polymers. It is well known that the mutual affinity between the peroxide and the polymer increases if the difference in the δ_0 values (*Table 1*) decreases, although for a more exact discussion each specific contribution[12] (δ_d = dispersive term, δ_p = polar term and δ_h = hydrogen bonding term) to the total solubility parameter (δ_0) should be considered. A correlation between the Hildebrand solubility parameter (δ_0) and the peroxide concentration at which crosslinking starts (*Figure 3*) does appear to exist, since the amount of peroxide required for crosslinking decreases with increases in δ_0. The exception is initiator D-120, which possesses, in addition to the peroxide group, a double bond which may increase the ability to induce the crosslink and graftlink reactions.

However, differences in the migration velocity and crosslink efficiency[6] of the peroxides may also influence the optimum peroxide concentration. Therefore, it is not possible to derive a reliable correlation between the Hildebrand solubility parameter and the optimum concentration of the peroxides, on just the basis of these few tested peroxides.

CONCLUSIONS

The impact strength of a PS/EPDM/SEP blend can be doubled by adding a peroxide to the polymer blend during the melt extrusion process. By thermal decomposition the peroxides form radicals, which most likely initiate a graftlink reaction between segments of the dispersed EPDM rubber and the rubbery part of the compatibilizer. This reaction enhances the adhesion between the PS and the EPDM phases, thus resulting in an improved impact strength.

As a result of crosslinking of the EPDM, which takes place if the amount of added peroxide is too high, or if the position of the peroxide feed to the extruder is unfavourable, a morphology coarsening can take place, resulting in inferior impact properties, despite an improved adhesion between the dispersed and matrix phases.

The positive contribution of the adhesion, and the negative contribution of the morphology coarsening to the impact behaviour, give rise to an optimum peroxide concentration. It is possible that the value of this optimum might be correlated with the distribution of the peroxides over the PS and the rubbery phases, and consequently with the molecular structure of the peroxide.

REFERENCES

1   Bucknall, C. B. 'Toughened Plastics'. Applied Science, London, 1977
2   Bucknall, C. B. in 'Polymer Blends' (Eds D. R. Paul and S. Newman), Vol. 2, Academic, New York, 1978, pp. 91–127
3   Borggreve, R. J. M. *PhD Thesis*, Twente University, 1988
4   Wu, S. *Polymer* 1985, **26**, 1855
5   Van Gisbergen, J. G. M., Borgmans, C. P. J. H., Van der Sanden, M. C. M. and Lemstra, P. J. *Polymer* 1990, **31**, 162
6   Hogt, A. H. Proceedings of the Conference on Advances in Additives and Modifiers for Polymer Blends, Philadelphia, PA, 24–26 February 1993, paper 5
7   Hildebrand, J. H. and Scott, R. L. 'The Solubility of Nonelectrolytes', 3rd edn, Dover Publications, New York, 1964, p. 432
8   Barton, A. F. M. 'Handbook of Solubility Parameters and Other Cohesion Parameters', CRC Press, Boca Raton, 1985
9   Krause, S. in 'Polymer Blends' (Eds D. R. Paul and S. Newman), Vol. 1, Academic, New York, 1978, pp. 15–113
10   Boundy, R. H. and Boyer, R. F. 'Styrene, its Polymers, Copolymers and Derivatives', Reinhold, New York, 1952
11   Spencer, R. S. and Gilmore, G. D. *J. Appl. Phys.* 1949, **20**, 502
12   Brandrup, J. and Immergut, E. H. 'Polymer Handbook', 2nd Edn, Wiley, New York, 1975
13   Hahn, F. C., Macht, M. L. and Fletcher, D. A. *Ind. Eng. Chem.* 1945, **37**, 526
14   Crespi, G. and Luciana, L. in 'Kirk Othmer Encyclopedia of Chemical Technology' (Eds M. Grayson and D. Eckroth), Vol. 16, 32nd Edn, Wiley, New York, 1981, p. 453
15   Frank, H. P. 'Polypropylene', Gordon and Breach, New York, 1968
16   Shaw, S. and Singh, R. P. *Eur. Polym. J.* 1989, **25**, 445
17   Kawai, H., Hashimoto, T., Miyoshi, K., Uno, H. and Fujimura, M. *J. Macromol. Sci.-Phys. (B)* 1980, **17**, 427
18   Teh, J. W. and Rudin, A. 'Proceedings of the Conference on Polymeric Materials Science and Engineering', Vol. 67, American Chemical Society, Washington, DC, 1992, pp. 309–310
19   Donald, A. M. and Kramer, E. J. *J. Mater. Sci.* 1982, **17**, 1765
20   Donald, A. M. and Kramer, E. J. *J. Mater. Sci.* 1982, **17**, 2351
21   Birkinshaw, C., Buggy, M. and O'Neill, M. *J. Appl. Polym. Sci.* 1990, **41**, 1913