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Cavitation *versus* debonding during deformation of rubber-modified poly(vinyl chloride)

D. Dompas and G. Groeninckx*
Catholic University of Leuven, Laboratory of Macromolecular Structural Chemistry, Celestijnenlaan 200F, B-3001 Heverlee, Belgium

and M. Isogawa and T. Hasegawa
Kaneka Corporation, Plastics Research Laboratories, 1–8 Miyamae-Machi, Takasago-cho, Takasago-shi, Hyogo, Japan

and M. Kadokura
Kaneka Belgium N.V., Head Office—Plant, Nijverheidsstraat 16, 2260 Westerlo-Oevel, Belgium
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The microvoiding mechanisms and mechanical properties of a blend of poly(vinyl chloride) (PVC) with methyl methacrylate–butadiene–styrene (MBS) graft copolymers are investigated. It is found that the toughening effect is independent of the type of microvoiding mechanism occurring in the blend. Both internal cavitation of the MBS particles and debonding at the PVC/MBS interface relieve the triaxial tension and thereby promote shear yielding of the PVC matrix.

(Keywords: interfacial adhesion; toughening mechanism; cavitation)

Introduction

The toughness of brittle or notch-sensitive polymers can be enhanced by the incorporation of small elastomeric particles in the matrix. In brittle polymers, such as polystyrene and poly(styrene-*co*-acrylonitrile), the toughness is enhanced by a multiple crazing mechanism[1], and adhesion between elastomeric particle and matrix is thought to be necessary because the rubber particles must be effective as craze stoppers[1]. On the other hand, in pseudoductile polymers such as polycarbonate, polyamides and poly(vinyl chloride) (PVC), the rubber particles promote shear yielding of the matrix, and strong adhesion between impact modifier and matrix resin is not required[2–4]. According to Wu[3], van der Waals' intermolecular adhesion is sufficient for toughening of nylon-6,6 in which the deformation mode is mainly shear yielding.

In spite of the low level of adhesion, most studies on rubber-toughened blends of pseudoductile matrices report that voiding, which is necessary to relieve the hydrostatic stress, occurs by internal cavitation of the rubber particles[5–11]. When the cativation resistance of the modifier is high, debonding at the modifier/matrix interface instead of internal cavitation can be expected. Debonding has indeed been reported as the predominant microvoiding mechanism in blends of polycarbonate with polyethylene[12,13].

However, to our knowledge, a comparative study of debonding *versus* cavitation, independently of the morphological or molecular properties of the rubbery modifier and of the matrix, has not yet been reported in the literature. The question therefore remains as to whether or not, for a given rubber-modified matrix, the toughness is influenced by the type of microvoiding mechanism. The role of the microvoiding mechanism is discussed in this paper for blends of PVC with methyl methacrylate–butadiene–styrene (MBS) graft copolymers. The different MBS types used in this study have the same chemical composition and particle size. The interfacial adhesion between the MBS particles and the PVC matrix is varied and will determine whether cavitation or debonding is occurring.

Experimental

MBS core–shell particles. The MBS graft copolymers are core–shell impact modifiers; they consist of an elastomeric core of a random styrene-*co*-butadiene (SBR) copolymer and a glassy shell composed of a random copolymer of styrene (St) and methyl methacrylate (MMA). The chemical composition of the MBS particles is constant in this study. The St/butadiene weight ratio in the core equals 23/77; the St/MMA weight ratio in the shell equals 50/50 and the core/shell weight ratio equals 60/40. This chemical composition produces transparent blends with PVC.

The size of MBS core–shell particles can be controlled by agglomeration, aggregation or grow-out of the particles[14]. Details of these three different procedures are described elsewhere[15]. Particles termed MBS-1 and MBS-2 are prepared by aggregation and grow-out, respectively, and have an average size of 255 nm. Particles termed MBS-3 and MBS-4 are prepared by agglomeration and have an average size of 260 and 300 nm, respectively. The average particle sizes were determined by transmission electron microscopy (TEM) on ultrathin sections of the PVC/MBS blends, after

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* To whom correspondence should be addressed

Table 1 Characteristics of the core–shell MBS particles employed in this study

Particle	Polymerization technology	Core/shell ratio	SBR core diameter (nm)
MBS-1	aggregation	60/40	255
MBS-2	grow-out	60/40	255
MBS-3	agglomeration	60/40	260
MBS-4	agglomeration	60/40	300

staining with osmium tetroxide (OsO_4). Since OsO_4 only stains the double bonds of butadiene, the particle sizes that are obtained by this method are the sizes of the SBR rubber cores. The characteristics of the different particles are summarized in *Table 1*.

Blend preparation. Blends of 100 phr PVC (K value = 57), 10 phr MBS, 2 phr heat stabilizer (octyltin mercaptide) and 1 phr lubricants (0.8 phr glycerine rincinolate and 0.2 phr of an ester of montanic acid) were compounded by roll-milling at 170°C for 5 min. The films obtained were then pressed into sheets by compression moulding at 190°C for 15 min. The sheet thickness was set at 2 mm for the tensile sheets and at 5 mm for the Izod impact tests.

Uniaxial tensile tests. Stress–strain experiments were performed on an Instron series 1121 draw-bench at a crosshead speed of 10 mm min^{-1} at room temperature (20°C). Dumb-bell shaped test specimens were used with a cross-section of 10×2 mm^2 and a gauge length of 20 mm.

Izod impact tests. The notched Izod impact strength was determined according to ASTM D-256. The impact speed was 3.46 m s^{-1}; the energy of the hammer was 10.8 J. Specimens ($63.5 \times 12.7 \times 5$ mm^3) were cut from the mid-sections of the compression-moulded sheets ($250 \times 160 \times 5$ mm^3). A notch of 0.25 mm was machined on all specimens and checked for notch defects. The impact tests were carried out in a conditioned room at a constant relative humidity of 50% and at temperatures ranging from 23 to 45°C. Prior to the experiment, the samples were conditioned overnight at the test temperature. For each PVC/MBS blend, the average Izod impact strength from seven measurements was taken at each temperature.

Transmission electron microscopy. Prior to ultrathin sectioning, the blends were stained for 3 days in a 2 wt% solution of OsO_4 in distilled water. When preparing thin sections for TEM, care was taken to make sure that the damage features observed were not due to the ultrathin sectioning process. The undeformed blends were subjected to the same procedure, and cavitation or debonding was not observed on the corresponding TEM micrographs. This indicates that the dispersed rubber particles are sufficiently hardened by OsO_4 and that the observed rubber cavitation and debonding in the deformed blends are not artefacts from the cutting process.

The deformation mechanisms were investigated on the necked part of PVC/MBS specimens, deformed in a tensile experiment at a strain rate of 10 mm min^{-1} at room temperature. The ultrathin sections were cut in such a way that the sections were parallel to the deformation direction. This allows for the visualization of crazes, elongated particles, rubber cavitation and debonding whenever present.

Results and discussion

The mechanical properties at low strain rates of the different PVC/MBS blends were examined in a uniaxial tensile test at a strain rate of 10 mm min^{-1} at room temperature. The tensile stress–strain curves of the different PVC/MBS blends are shown in *Figure 1*. Clearly, the tensile mechanical properties at low strain rates are not influenced by the type of MBS modifier used in this study. In particular, the Young's modulus and the yield stress were found to be the same, within experimental error, for all the blends and depend only on the effective rubber volume fraction. Also, the strain at fracture is not influenced by the type of MBS modifier and was found to be 190 ± 30%. Note that in *Figure 1*, the stress–strain curves are only shown up to 100% elongation.

The uniaxial deformation applied during stress–strain experiments generates intensive stress whitening in the initially transparent PVC/MBS blends. In order to find out the origin of this stress whitening, TEM micrographs were taken from the stress-whitened zone in the samples. The results are shown in *Figures 2a*, *b* and *c* for the blends of PVC with MBS-1, MBS-2 and MBS-4, respectively. Plastic flow of the matrix is evident from the stretched rubber particles. The microvoiding mechanism of the three blends, however, is entirely different.

MBS-1 has been prepared by the aggregation technology. One global MBS particle in reality consists of several individual MBS particles held together by an appropriate clustering agent[14,15]. The high magnification TEM micrograph of *Figure 2a* shows a multiple cavitation mechanism in the blend of PVC with MBS-1; more than one SBR core in the aggregated MBS particle can cavitate internally. Debonding from the matrix and crazes in the matrix were not observed on the TEM micrographs of this blend.

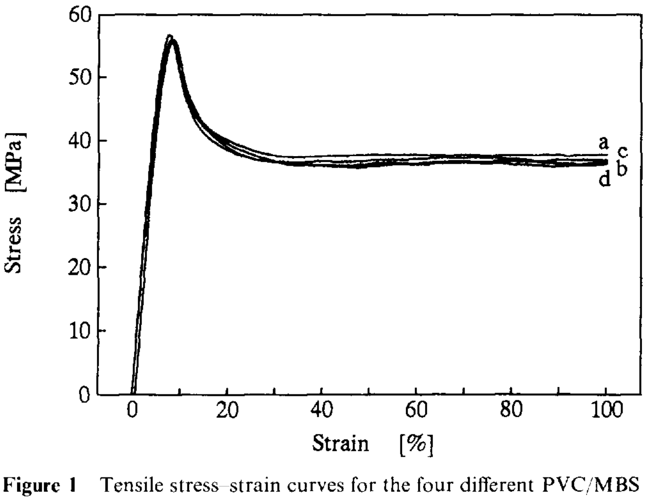

Figure 1 Tensile stress–strain curves for the four different PVC/MBS blends: (a) MBS-1 (255 nm, internal cavitation); (b) MBS-2 (255 nm, internal cavitation); (c) MBS-3 (260 nm, debonding); (d) MBS-4 (300 nm, debonding)

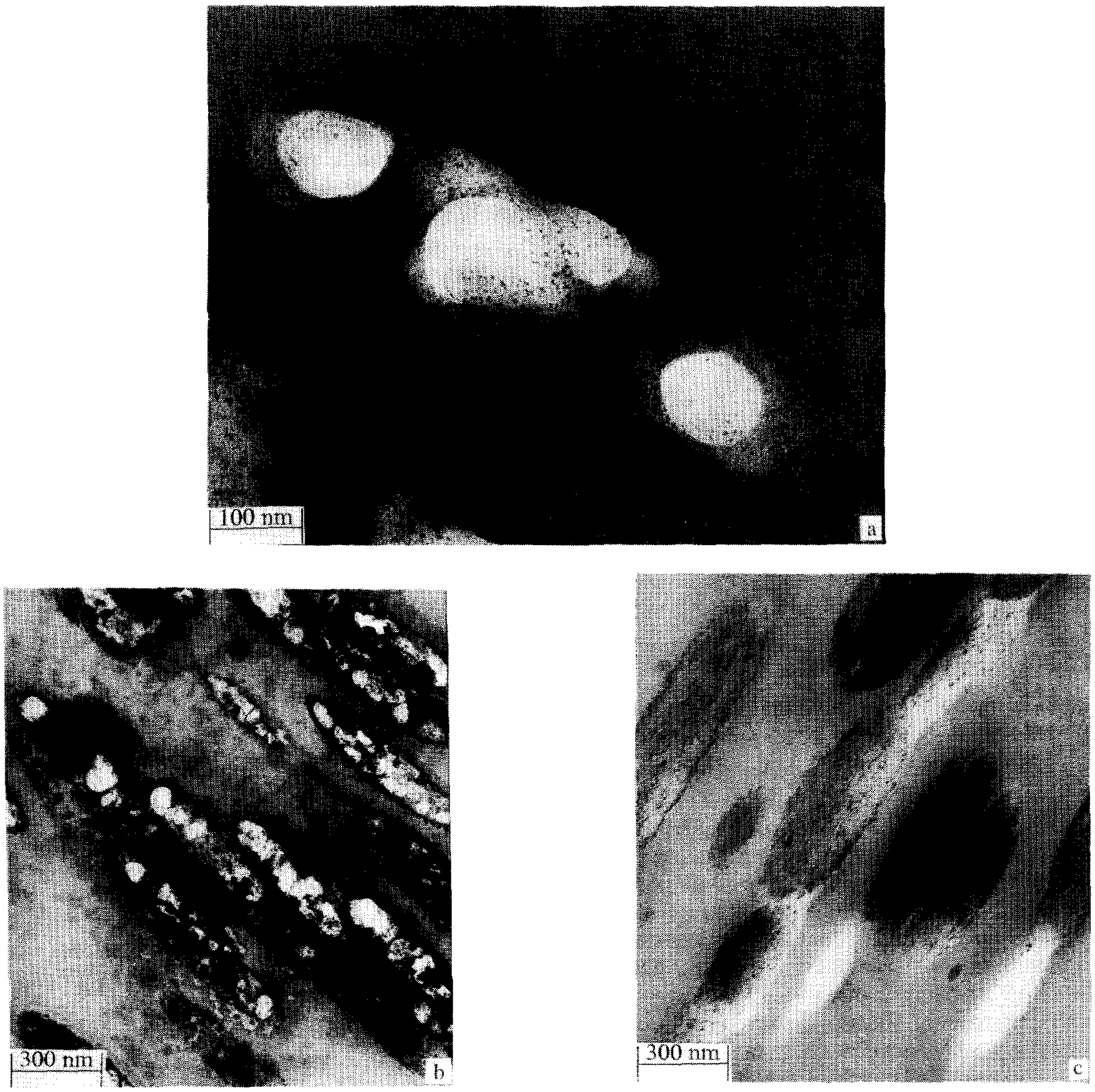

Figure 2 Transmission electron micrographs of ultrathin sections of the stress-whitened zone of PVC/MBS blends deformed at a strain rate of 10 mm min^{-1}: (a) PVC/MBS-1; (b) PVC/MBS-2; (c) PVC/MBS-4

Internal cavitation is also the only microvoiding mechanism in the blend of PVC with MBS-2 (*Figure 2b*). However, MBS-2 is manufactured by grow-out of the SBR rubber core and each particle consists of one SBR rubber core surrounded by a grafted shell of P(MMA-*co*-St) copolymer[14,15]. Consequently, the cavities in the rubber particles are not clearly separated by P(MMA-*co*-St) boundaries, although one still has the impression that more than one cavity is produced per particle. In particular, at the poles of the particles, an individual cavity seems to be separated from the rest of the cavitated rubber particle. Again, crazes and debonding from the matrix were not observed on the TEM micrographs of this blend, in agreement with earlier findings[6].

Finally, in the blend of PVC with MBS-4, the MBS-4 particles, prepared by agglomeration of SBR rubber cores[15], are clearly detached from the PVC matrix (*Figure 2c*). Crazing and internal cativation were not observed on the TEM micrographs. In addition, TEM micrographs of the undeformed blend of PVC with MBS-4 did not show any debonding at the modifier/matrix interface, indicating that the detachment of the particles is not a consequence of thermal stresses at the PVC/MBS-4 interface after cooling down from the melt, but is a consequence of the applied deformation on the sample.

Debonding can arise from a high interfacial tension between the two phases. In such a case, one should expect a poor dispersion of the MBS particles in the PVC matrix. A low magnification TEM micrograph of the stress-whitened zone of the blend of PVC with MBS-4 demonstrates, however, that this is not the case (*Figure 3*). *Figure 3* clearly indicates that the MBS particles are homogeneously dispersed in the blend in spite of their low interfacial adhesion to the PVC matrix. In an independent study[16,17] the interfacial tension between the shell of the MBS particles and the PVC matrix is estimated on the basis of a miscibility study and using Helfand's equations. A value for the interfacial tension of only $0.9 \times 10^{-3}\,\mathrm{J\,m^{-2}}$ is found. Such a low interfacial tension indeed explains the good dispersion of the MBS particles in the PVC matrix. It is therefore believed that

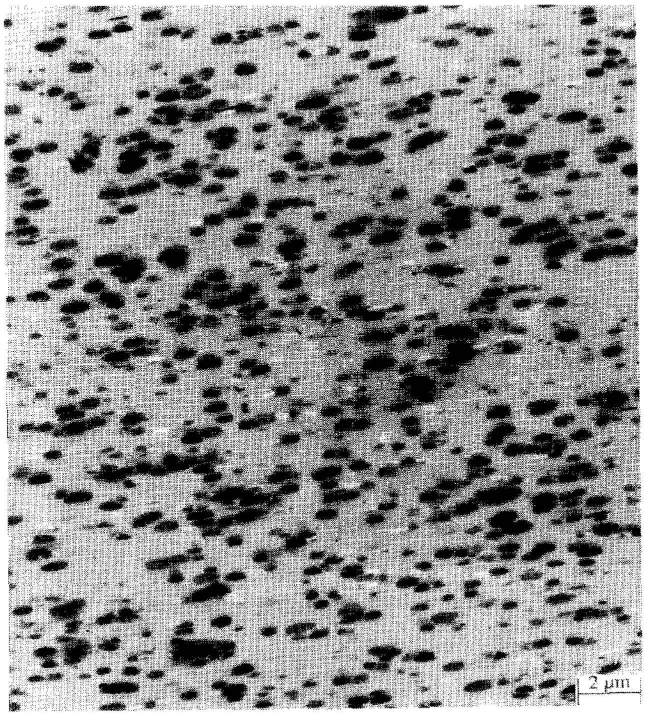

Figure 3 Transmission electron micrograph of an ultrathin section of the stress-whitened zone of PVC/MBS-4 deformed at a strain rate of 10 mm min^{-1}

the poor adhesion between modifier and matrix arises from other factors. It can be expected that the chemicals used to control the size of the MBS core–shell particles also affect the molecular weight of the grafted chains. These chemicals are different for the agglomeration, aggregation or grow-out technology[16]. If the level of adhesion is close to being critical in all of the blends, then a small decrease in the molecular weight of the grafted chains in combination with a small increase in the particle size of the MBS modifier is probably sufficient to tilt the balance towards debonding as opposed to particle cavitation. However, at the present time the effect of the chemicals used during polymerization on the molecular weight of the grafted chains is not well known. As a consequence, it is difficult to determine why MBS-1 and MBS-2 deform by internal cavitation, and MBS-4 by debonding at the particle/matrix interface. An understanding of the fundamental relation between chain microstructure and microdeformation mechanisms will therefore require further study.

Figure 1, in connection with the deformation study, reveals that the difference in microvoiding mechanism does not affect the mechanical properties at low strain rates. This can be understood from the fact that the mild test condition of a tensile test at low strain rate does not require the relief of hydrostatic tension in the blend by microvoiding of the rubber for the initiation of matrix shear yielding. The ultimate proof of this statement is that even the unmodified PVC matrix deforms by shear yielding under these conditions. Consequently, the yield stress should simply be a function of the effective load-bearing area, where the rubber particles are assumed not to bear stresses. This effective load-bearing area is only a function of the effective rubber volume fraction in the blend and this is constant for the different blends considered here. Therefore, the yield stress is expected to be the same for the different PVC/MBS blends, as is indeed observed in *Figure 1*.

However, even when tensile stress–strain curves of different blend systems are equal, the impact mechanical behaviour can vary considerably. For Izod impact experiments with a pronounced triaxiality at the notch tip, the relief of the hydrostatic tension by microvoiding of the rubber is essential for the initiation of matrix shear yielding. Therefore, Izod impact measurements were carried out to examine whether the type of microvoiding mechanism has any influence on the impact strength of the different blends. In *Figure 4* the Izod impact strength is plotted as a function of temperature for the four different PVC/MBS blends studied.

All the brittle blends, at low temperature, have a notched impact strength of 9–15 kJ m^{-2}, independent of the type of MBS modifier used, and the fractured samples only show intensive stress whitening in a small volume of the material near the notch tip. All the ductile blends, at high temperature, have a notched impact strength between 90 and 110 kJ m^{-2} and the fractured samples show intensive stress whitening as well as lateral contraction of the Izod impact bar in a large volume of the test sample. The variations in impact toughness among the different blends are within experimental error.

The brittle–ductile transition temperature also is nearly independent of MBS type. The brittle–ductile transition temperature is 34°C for PVC/MBS-1, PVC/MBS-3 and PVC/MBS-4. *Figures 2a* and *c* have shown that in a uniaxial tensile experiment at low strain rate, the first blend deforms by multiple cativation, while the latter two blends deform by debonding from the matrix. Examination of the microvoiding mechanism in an Izod impact experiment has not yet been carried out on these PVC/MBS blends. However, as far as we know from the literature, there are no transitions in the type of microvoiding mechanisms (debonding or cavitation) reported when going from low to high strain rates. For instance, in blends of nylon-6 with ethylene-*co*-propylene rubber, cavitation is reported[18] in a wide range of strain rates from 10^{-5} to $10\,\mathrm{m\,s^{-1}}$. Likewise, in blends of polycarbonate with polyethylene, debonding at the modifier/matrix interface has been reported[12] independently of the strain rate between 2.54×10^{-4} and

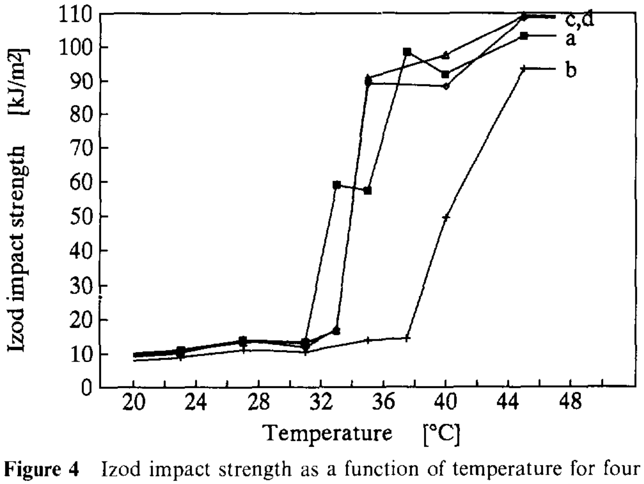

Figure 4 Izod impact strength as a function of temperature for four different PVC/MBS blends with nearly the same average particle size: (a) MBS-1 (255 nm, internal cavitation); (b) MBS-2 (255 nm, internal cavitation); (c) MBS-3 (260 nm, debonding); (d) MBS-4 (300 nm, debonding)

2.54 m s^{-1}. It is therefore believed that when PVC/MBS-3 and PVC/MBS-4 deform by debonding in a low-strain-rate experiment, they also deform by debonding at impact speeds. Likewise, since PVC/MBS-1 and PVC/MBS-2 were found to deform by internal cavitation at low strain rates, they are assumed to deform by internal cavitation in the Izod impact experiments too. The type of microvoiding mechanism therefore seems not to affect the impact mechanical behaviour of the blend; the brittle–ductile transition temperature is the same (34°C) for PVC/MBS-1 (internal cavitation), PVC/MBS-3 (debonding) and PVC/MBS-4 (debonding) and is only slightly higher (40°C) for the blend of PVC with MBS-2 (internal cavitation). The slightly inferior mechanical performance of the latter blend, with MBS particles prepared by the grow-out procedure, has been reported earlier[14]. A sound argument for this behaviour cannot be given, but the shift of 6°C in brittle–ductile transition temperature is small compared to the effect of particle size or volume fraction[19]. The Izod impact data therefore demonstrate that the impact mechanical behaviour is not significantly altered by the type of microvoiding mechanism of the rubber particles.

The present study therefore suggests that the toughening effect in the PVC/MBS blends is independent of the starting microvoiding mechanism of the MBS particles. This is in agreement with the idea that the most important function of the dispersed rubber particles is to generate voids during the deformation process. From a mechanical point of view, there is no difference between void formation by cavitation or debonding. Whether plastic deformation starts with internal cavitation or debonding of the MBS particles, both microvoiding mechanisms relieve the triaxial tension in front of the notch tip of the Izod impact bar. As soon as the hydrostatic tension is relieved, massive shear yielding in the matrix can occur, leading to ductile behaviour.

Conclusions

The precursors of the toughening mechanism in PVC/MBS blends are found to be internal cavitation or debonding at the modifier/matrix interface. This is followed by extensive shear yielding of the matrix. The present study demonstrates that debonding at the modifier/matrix interface is as effective as internal cavitation with respect to the initiation of plastic deformation in the matrix. Some kind of microvoiding mechanism must occur in the elastomer or at the modifier/matrix interface to relieve the triaxial stress state. Subsequently, this relief of the hydrostatic tension promotes shear yielding in the matrix, leading to ductile behaviour.

References

1 Bucknall, C. B. 'Toughened Plastics', Applied Science, London, 1977
2 Hobbs, S. Y., Bopp, R. C. and Watkins, V. H. *Polym. Eng. Sci.* 1983, **23** (7), 380
3 Wu, S. *Polymer* 1985, **26**, 1855
4 Borggreve, R. J. M. and Gaymans, R. J. *Polymer* 1989, **30**, 63
5 Parker, D. S., Sue, H.-J., Huang, J. and Yee, A. F. *Polymer* 1990, **31**, 2267
6 Breuer, H., Haaf, F. and Stabenow, J. *J. Macromol. Sci. — Phys.* 1977, **B14** (3), 387
7 Tse, A., Shin, E., Hiltner, A., Baer, E. and Laakso, R. *J. Mater. Sci.* 1991, **26**, 2823
8 Hourston, D. J., Lane, S. and Zhang, H. X. *Polymer* 1991, **32**, 2215
9 Borggreve, R. J. M., Gaymans, R. J. and Schuijer, J. *Polymer* 1989, **30**, 71
10 Borggreve, R. J. M., Gaymans, R. J. and Eichenwald, H. M. *Polymer* 1989, **30**, 78
11 Wu, S. *J. Appl. Polym. Sci.* 1988, **35**, 549
12 Yee, A. F. *J. Mater. Sci.* 1977, **12**, 757
13 Sue, H.-J., Huang, J. and Yee, A. F. *Polymer* 1992, **33**, 4868
14 Dunkelberger, D. L. and Dougherty, E. P. *J. Vinyl Technol.* 1990, **12** (4), 212
15 Dompas, D., Groeninckx, G., Isogawa, M., Hasegawa, T. and Kadokura, M. in preparation
16 Dompas, D. PhD Thesis, Catholic University of Leuven, Belgium, 1994
17 Dompas, D., Groeninckx, G., Isogawa, M., Hasegawa, T. and Kadokura, M. in preparation
18 Dijkstra, K. PhD Thesis, University of Twente, The Netherlands, 1993
19 Dompas, D., Groeninckx, G., Isogawa, M., Hasegawa, T. and Kadokura, M. *Polymer* 1994, **35**, 4760