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Influence of void formation on impact toughness in rubber modified styrenic-polymers

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Abstract

Impact modifiers in the form of rubber particles increase the toughness of styrene polymers and copolymers. It is thought that on impact cavitation in rubber particles occurs which reduces the detrimental dilatational stress in the bulk polymer without forming cracks in the brittle matrix or at the rubber–matrix interface. This void formation is thought to favour an increase of the energy dissipating deformation processes, namely by crazing in HIPS, where the voids are considered to ease craze formation, or by preferentially shear yielding in ABS at higher rubber concentration, where the voids support the plane stress situation which multiplies shear yielding.

To test this model the cohesion strength and consequently the resistance to void formation of the rubber particles was increased by thermal cross-linking, or decreased by adding oil to the rubber particles which acts as nuclei for void formation.

On annealing both the high impact polystyrene and rubber modified polystyrene–acrylonitrile copolymers embrittle. TEM of the fractured products showed that in the tough non-annealed products void formation in the rubber particles had occurred extensively, whereas after annealing this phenomena is hardly observed.

The addition of oil can improve toughness by facilitating void formation.

The reduction of voiding in the rubber particles of the annealed and more brittle products and toughening with oil as an additive to the rubber particles support the above proposed theory that void formation in rubber particles increases the energy dissipation on impact and thus the toughness of the products. © 2002 Published by Elsevier Science Ltd.

Keywords: Rubber modification; Cavitation; Toughness

1. Introduction

Polystyrene (PS) and poly(styrene-*co*-acrylonitrile) (PSAN) are polymers without secondary relaxation processes in the main chain. Therefore, they are brittle in impact testing [1–3] below their glass transition temperatures. To improve this sometimes disadvantageous situation caused by unstable craze deformation, the materials are often modified with rubber particles, leading to HIPS, ABS or ASA (acrylonitrile–styrene–acrylate). It is well known that in rubber modified polymers impact energy can be dissipated by intensified stable crazing (e.g. HIPS) which is triggered in the stress field near the rubber particles if deformed in plane strain mode in the bulk. This is favoured by relatively large particles of ca. >0.8 μm. Increasing the rubber content with small rubber particles (0.1–0.2 μm) favours local plane stress situation in the region between them, with the consequence that a transition from crazing to shear deformation and macro crazing can occur as, for example, in ABS [4]. The role and importance of void formation within the rubber particles in these materials is still not clear but has been a centre of interest recently. Bucknall [5] postulates that void formation is an essential prerequisite for crazing. However, it is also conceivable that crazes are initiated first in the matrix in the stress field of the rubber particles according to the original model by Argon [6–8] but that these centres for craze initiation cannot open to macroscopic crazes unless the adjacent rubber particles form voids to compensate for the dilatation of the craze. Therefore, in both cases cavitation in rubber particles is helpful. In the following report the rubber particles have been thermally cross-linked to increase their cohesion energy and thus impede voiding. Also the reverse effect was tested namely to toughen the materials by nucleating cavitation by oil in the rubber particles.

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Table 1
Characteristic data of HIPS and ABS

Polymer	MI (ml/10 min) (test conditions)	Base rubber concentration (wt%)	Diameter of rubber particles (μm)
HIPS	113.3 (200 °C, 5 kp)	7	1
ABS	3.5 (220 °C, 10 kp)	24	0.08
ABS	6 (220 °C, 21.6 kp)	30	0.08, 0.4

2. Experimental and discussion

2.1. Materials

The experiments were mainly performed with commercial rubber modified products (Table 1), if no exceptions or modifications are mentioned in the text.

2.2. Cross-linking

It is well known that HIPS and ABS can embrittle if the rubber particles are further cross-linked. This may occur via chemical, radiation or thermal techniques, e.g. in the latter case by too high processing or storage temperatures. This embrittlement may be caused by the increased resistance to void formation in the rubber particles due to their higher cross-link density. Cigna [9] describes the embrittlement for chemically cross-linked HIPS, Steenbrink [10] found similar effects in ASA. Bergmann, Scharf and Schmiedberger also showed that the notched impact strength of an ABS decreases with increasing cross-linking (Fig. 1). The ABS (MI 6) was molten in the barrel of an injection moulding machine at 250, 265 and 280 °C for 18, 28 and 30 min. After this annealing the material was injection moulded to the small standard bars for impact testing ($4 \times 6 \times 50\ \mathrm{mm}^3$). The first four specimens have been rejected to avoid specimens with damaged material by the oxygen, diffused through the die into the material during annealing. The other specimens were notched and measured in impact at 23 °C according to the former standard DIN 53457. The reduction in mobility by thermal cross-linking was qualitatively characterised by an NMR procedure [11].

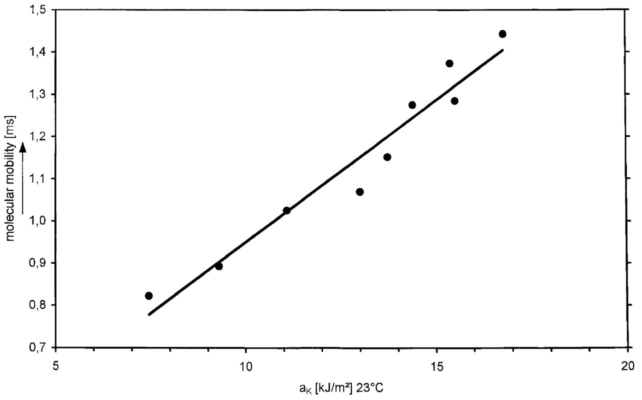


Fig. 1. Increasing notched impact strength with increasing molecular mobility in the rubbery phase of ABS (MI 6) as determined by NMR relaxation measurements [11].

An increased cross-link density causes an increase in the glass transition temperature of the rubber phase with a corresponding shift of the brittle/ductile transition in rubber modified materials. However, as long as the test temperature is higher than the rubber glass transition temperature and the cross-linked rubber particles are still in the rubbery phase, crazes should be generated in the stress fields of the soft rubber particles. Thus the higher glass transition temperature due to an annealing step cannot be the main reason for embrittlement beyond the glass transition temperature of the rubbery phase. This embrittlement may be caused by the concomitant resistance to voiding. Therefore, our interest turned to investigate the effect of void formation in the rubber particles on impact strength.

Figs. 2 and 3 show the dynamic mechanical properties for HIPS (rubber phase polybutadiene) and for an ABS (MI 3.5) with a copoly(butadiene–butylacrylate) rubber phase. The dynamic mechanical properties were determined according to ISO 6712-7 in forced oscillation (1 Hz) during heating up with 1 °C/min. In both materials the glass transition temperature of the rubber-phase is shifted by 10 °C to higher values after annealing at 280 °C for 30 min. The embrittlement of both materials is quantified by the impact strength which decreases on annealing in the case of HIPS from 72 to 58 kJ/m^2 and for ABS from 154 to

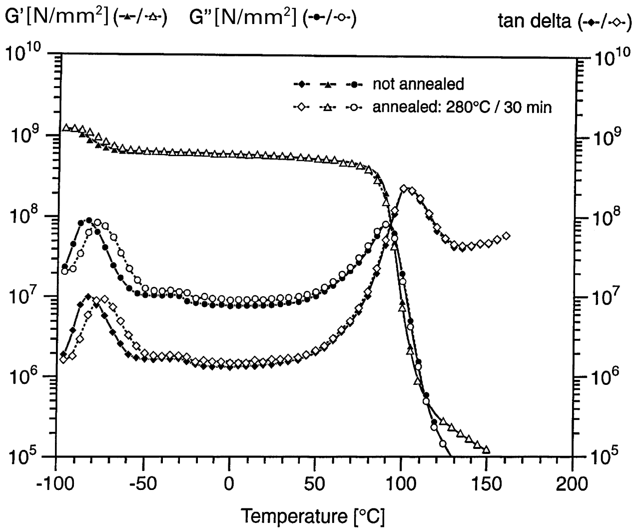


Fig. 2. Complex torsion modulus [N/mm^2] of HIPS before and after annealing at 280 °C for 30 min.

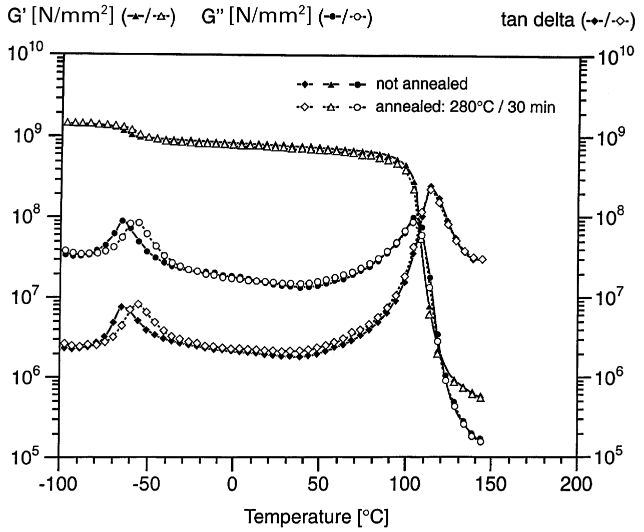


Fig. 3. Complex torsion modulus [N/mm^2] of ABS (MI 3.5) before and after annealing at 280 °C for 30 min.

109 kJ/m^2. Reduced deformation at fracture of the annealed specimens and not a drop in the matrix strength, at least not in HIPS, is the reason for embrittlement as can be seen from the force deflection diagrams recorded during the three point bent impact test (Fig. 4). To make it more clear, the deformation curves of the annealed specimens were shifted along the deformation axis in relation to the original specimens by 5 mm deformation, the curves for the HIPS additional by 20 mm. Thus in both materials the deformation at fracture is reduced by annealing from 15 to 10 mm.

The influence of annealing with the reduction of molecular mobility on the brittleness can only be assessed if during the annealing procedure the morphology has not changed simultaneously. TEM-images of ABS show (Fig. 5) that during the annealing process agglomeration of small particles had occurred, as is often observed in this kind of material. However, this agglomeration effect normally increases instead of decreasing toughness, if no cross-linking has occurred [12].

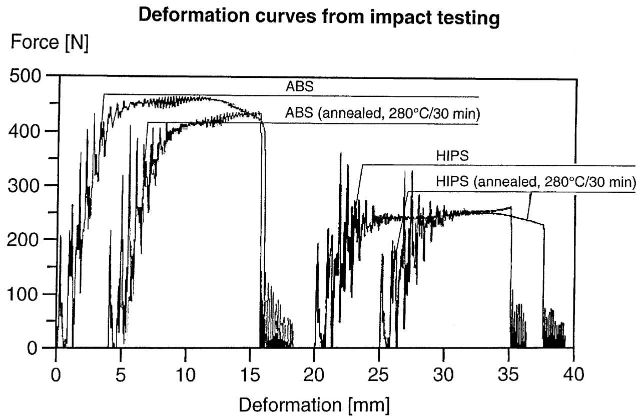
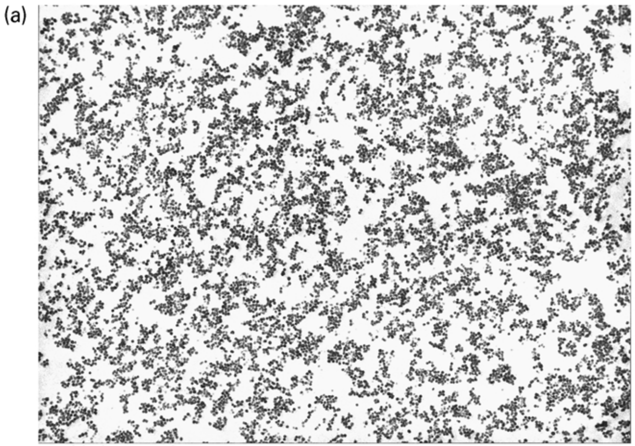
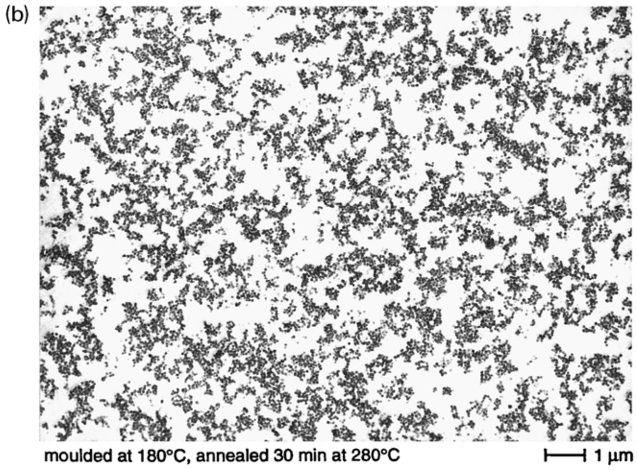


Fig. 4. Force–deflection diagrams in impact strength tests of HIPS and ABS (MI 3.5) before and after annealing for 30 min at 280 °C.



moulded at 180°C



moulded at 180°C, annealed 30 min at 280°C

Fig. 5. TEM micrographs of undeformed ABS (MI 3.5) before and after annealing (OsO_4-staining) showing some agglomeration after annealing.

The embrittlement by annealing appears to be caused by a transition in the deformation mechanism. The influence of annealing on crazing and void formation was studied in a Zeiss EM 902 TEM by means of ultra thin sections obtained after staining with OsO_4. The TEM is equipped with an energy filter where images can be obtained with elastically scattered electrons or with electrons, which are inelastically scattered. Figs. 6 and 7 show TEM micrographs of HIPS after impact for the cases where the HIPS had been/not been annealed before mechanical testing. Figs. 6a and 7a are bright field images, Figs. 6b and 7b are images obtained from the same region with inelastically scattered electrons. Imaging with inelastically scattered electrons helps to differentiate optically between voids and polystyrene inclusion. In the bright field image inclusions and voids are white, whereas in images with inelastically scattered electrons voids are black, because no electron can be inelastically scattered where no material is present. Whereas according to Fig. 6 numerous crazes and voids have developed during impact, these deformation structures are formed much less in the annealed material (Fig. 7). Obviously the crazes cannot be formed in the abundant

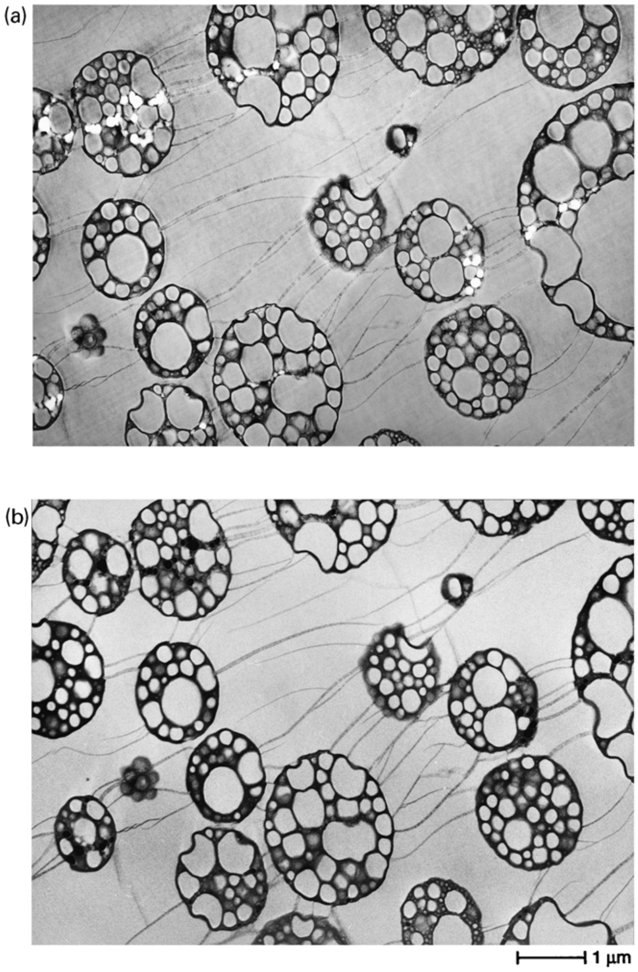


Fig. 6. TEM micrographs of compression moulded, non-annealed HIPS after deformation at 23 °C in impact; OsO_4-staining. (a) Bright field image; (b) Image taken with inelastically scattered electrons ($\Delta E = 59$ eV).

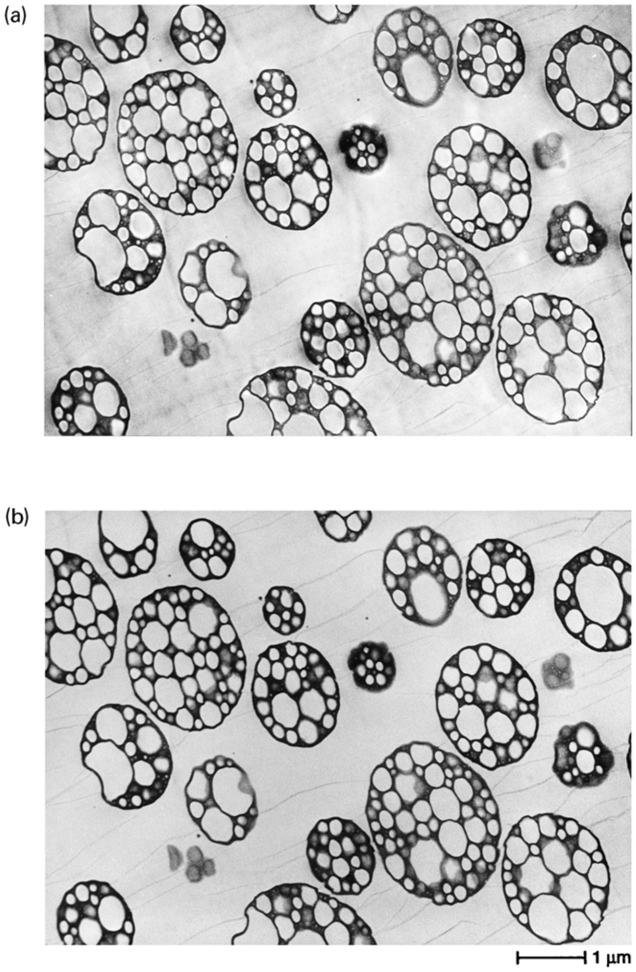


Fig. 7. TEM-micrographs of compression and annealed (30 min at 280 °C) HIPS after deformation at 23 °C in impact; OsO_4-staining. (a) Bright field image; (b) Image taken with inelastically scattered electrons ($\Delta E = 60$ eV).

way after thermal cross-linking because in accordance with Bucknall's model the cohesion energy of the rubbery phase is too high for void formation. Additionally reduced deformability via crazing after annealing may hamper blunting of detrimental local high stress fields and as a consequence cracks are initiated which cannot be stabilised thus leading to material failure. Changes in the morphology by annealing are not seen in HIPS.

Figs. 8 and 9 show TEM images of deformed ABS (MI 3.5). In the non annealed material (Fig. 8) much void formation has occurred during impact. Perpendicular to the tensile direction 'Macro Crazes' [4] have formed consisting of voids and stretched material-like fibrils between the voids in the tensile direction. Void formation facilitates this shearing in the locally plane stress situation between the cavitated particles in ABS (Fig. 8) after the plain strain was reduced by the voids. In annealed ABS, however (Fig. 9), cavitation is drastically reduced and some conventional crazes have appeared which bridge the larger regions between the agglomerations of the rubber particles. Shearing and stretching combined with voiding obviously dissipates the impact energy in the non-annealed product before fracture can occur. However, in the annealed product the increased resistance to void formation due to the increased cross-links also hinders the formation of Macro Crazes and thus reduces the impact resistance to failure.

Concluding, by cross-linking HIPS and ABS embrittlement occurs which can be attributed to higher resistance to void formation. Crazing and shearing are facilitated by cavitation in the rubber particles.

2.3. Addition of oil

Morbitzer et al. [13] have shown that the addition of small amounts of oil can influence the mechanical properties of ABS. Therefore, for a better understanding of this effect it is important to know where the oil is located. In rubber modified polymers the oil can be in one or more of the following states:

- in the matrix either segregated or dissolved on a molecular basis,

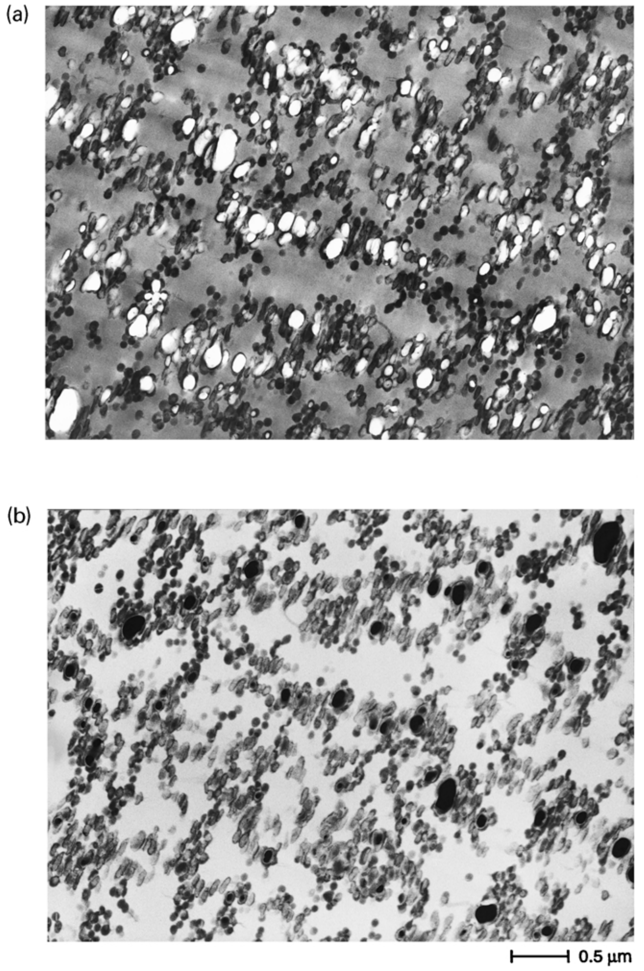


Fig. 8. TEM-micrographs of compression moulded ABS (MI 3.5) after deformation at 23 °C in impact; OsO_4-staining. (a) Bright field image; (b) Image taken with inelastically scattered electrons ($\Delta E = 60$ eV).

- in the rubber phase, again either dissolved or as a separate phase,
- in the interface between the rubbery particles and the matrix.

HIPS with mineral oil. In the screening test HIPS was modified with 4 and 17.5% mineral oil (Mink 70). The TEM images (Fig. 10) show no optical indication of the 4% oil. But at higher oil concentrations holes are seen in the rubbery phase which are likely to be segregated inclusions of oil. The contrast is bright, because the oil is assumed to be extracted during preparation by the ultra thin sectioning technique. The dynamic mechanical properties reveal (Fig. 11) that the glass transition temperature of the rubber phase is not shifted by 4% mineral oil whereas the glass transition temperature of the matrix is decreased by 6 °C which indicates its plasticising effect. Fig. 12 reproduces the deformation curves of compression moulded HIPS, with and without mineral oil, at room temperature in tension by three point bending and in uniaxial compression. The bending data were recalculated to tension values according to the known equations (ISO 178). In both cases oil reduces the yield strength. In tension where crazes play an important role the difference in the yield point is much more pronounced than in compression where crazes are absent. Due to the high plasticising of the matrix by mineral oil it is difficult to separate the effects of the oil in the matrix from

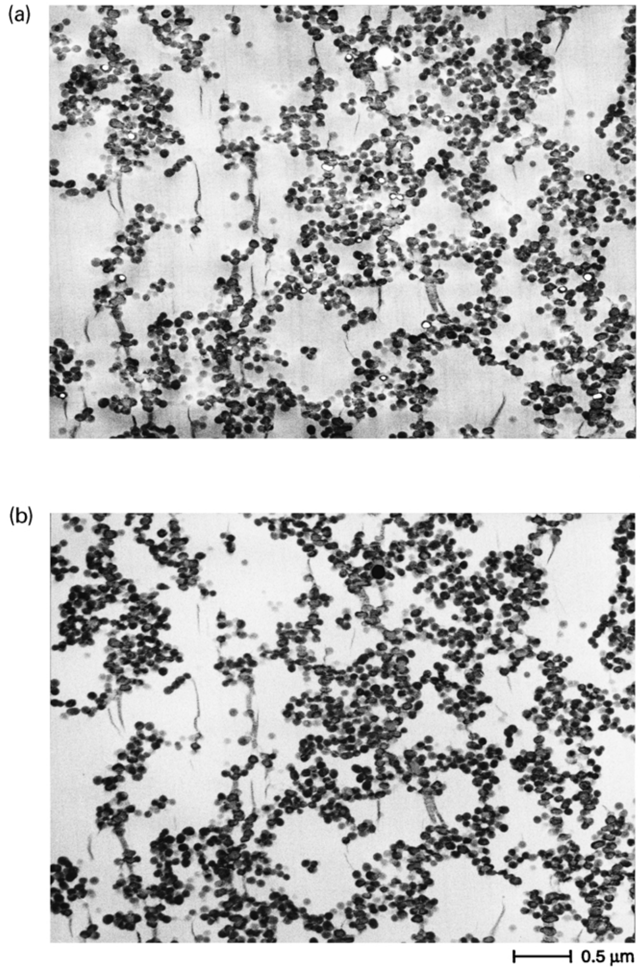


Fig. 9. TEM-micrographs of compression and annealed (30 min at 280 °C) ABS (MI 3.5) after deformation at 23 °C in impact; OsO_4-staining. (a) Bright field image; (b) Image with inelastically scattered electrons ($\Delta E = 60$ eV).

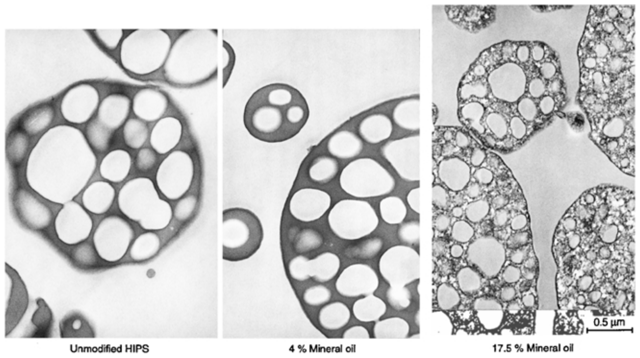


Fig. 10. TEM-micrographs of ultra thin sections of HIPS with 4 and 17.5% mineral oil, stained with OsO_4.

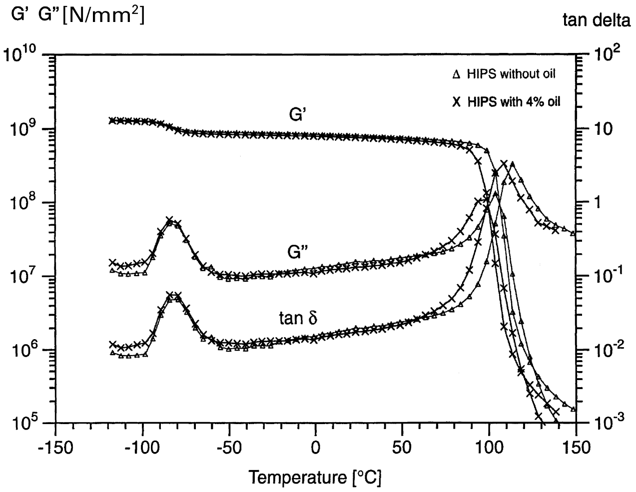


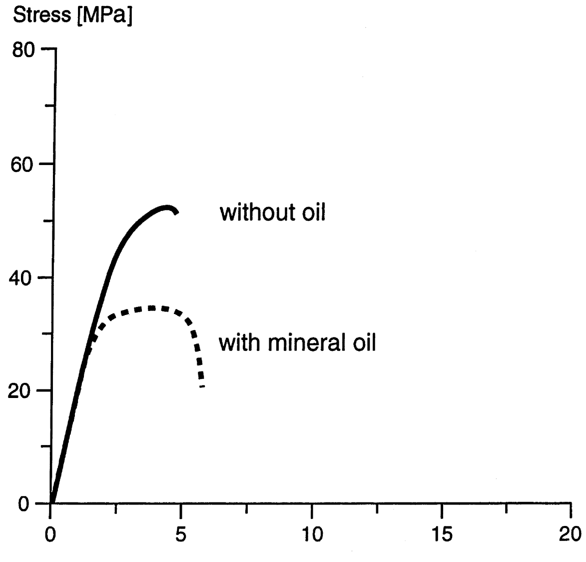
Fig. 11. Dynamic mechanical properties of HIPS with (4%) and without mineral oil.

those of the oil in the rubber phase on the toughness of the oil modified HIPS. Both effects, void formation and matrix plasticising seem to be active. In our case the impact strength and the notched impact strength were increased at room temperature by 10% with 4% oil compared to unmodified HIPS (Table 2). Anderson et al. [14] regarded the plasticising effect on the matrix as being responsible for the increase in toughness; void formation is not considered.

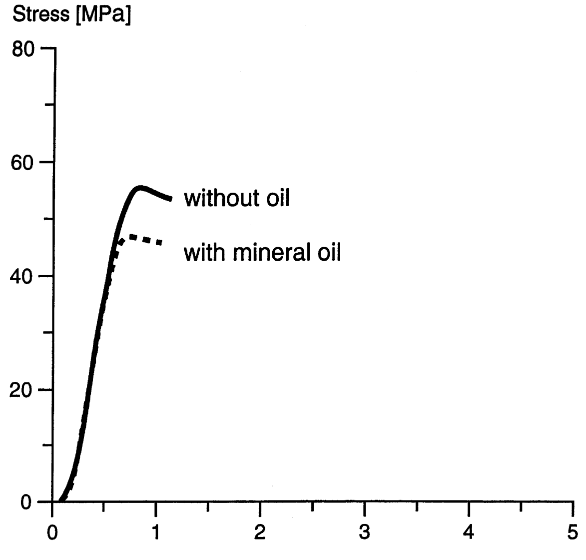
HIPS with silicone oil. In contrast to mineral oil the silicone oil is insoluble in HIPS. This can be seen in Fig. 13 from the dynamical torsion measurements. Neither the glass transition temperature nor that of the rubber phase is influenced by 4.2% silicone oil. In SEM-images of sliced pellets obtained with the backscatter detector (Fig. 14) bright spherical areas are seen which are attributed to oil filled holes and also to dark empty holes. Both features are absent in the pure material. For this product with silicone oil mechanical embrittlement was observed which can be attributed to the unblunted, and therefore, detrimental stress field around the holes of the oil in the matrix. Thus no further studies have been performed with this material.

ABS with silicone oil. The ABS used was an emulsion produced product containing a pure rubber core grafted with PSAN. This impact modifier was blended with PSAN to give the ABS product.

Since Morbitzer showed the strong influence of silicone oil on the mechanical properties of ABS this system was studied in more detail.



a) tension in bending



b) compression

Fig. 12. Stress–strain deformation curves of HIPS with (4%) and without mineral oil in three point bending and uniaxial compression.

Dynamic mechanical measurements reveal (Fig. 15) no influence of the silicone oil on the glass transition temperature of the SAN-matrix. The glass transition temperature of the rubber phase, however, is broadened by

Table 2
Mechanical properties of pure HIPS and HIPS modified with 4% mineral oil

HIPS with % oil	Impact strength (kJ/m^2)	Notched impact strength (kJ/m^2)	Yield strength tension (23 °C) in (N/mm^2)	in compression
0	27	6.57	35.6	57
4	31	7.5	23.4	47

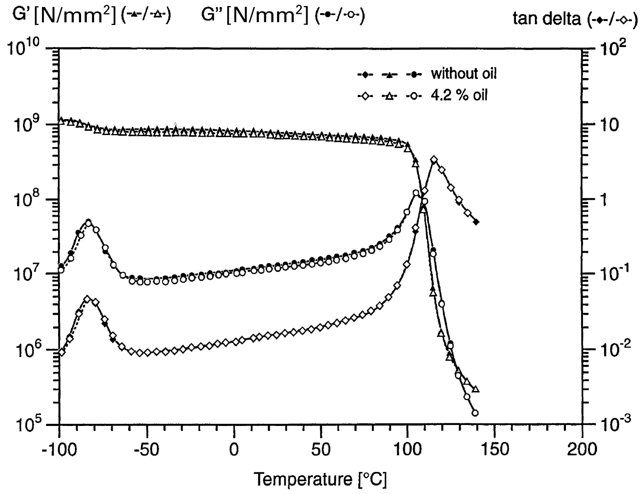


Fig. 13. Dynamic mechanical properties of HIPS with (4.2%) and without silicone oil.

oil to higher temperatures. As Hennig [15] has shown, the oil crystallises at this low temperature leading to a stiffening of the rubber particles. These measurements show that silicon oil is at least partly soluble in the rubber phase of ABS. The SEM images with backscattered electrons in Fig. 16 confirm the presence of abundant silicon oil droplets. From their size of up to 4 μm it can be concluded that these droplets are in the hard phase. The annular bright rings around the dark droplets (holes) are due to the so-called edge-effects. At an edge more electrons are emitted compared to the compact materials. This feature is not present in the pure ABS.

Usually silicone oil is added to ABS in much lower concentrations so that no abundant silicone oil droplets develop in the hard phase. To investigate by TEM where smaller concentrations of silicone oil are localised, the concentration of the silicone oil was reduced to 0.43% and the ABS was further diluted with the PSAN matrix to give a 2.7% end rubber phase concentration. Thus overlapping particles in the ultra thin sections are avoided and excess oil is absent.

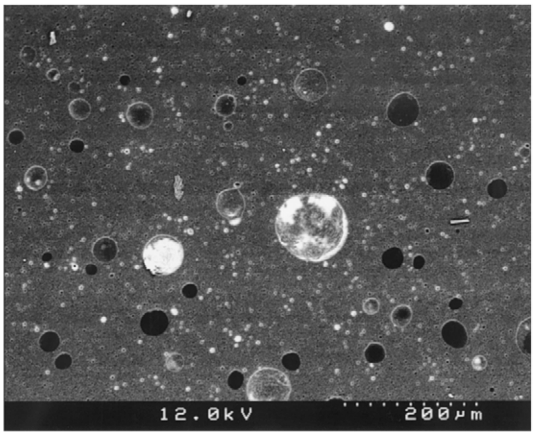


Fig. 14. SEM backscattered electron micrographs of HIPS modified with 4.2% silicone oil.

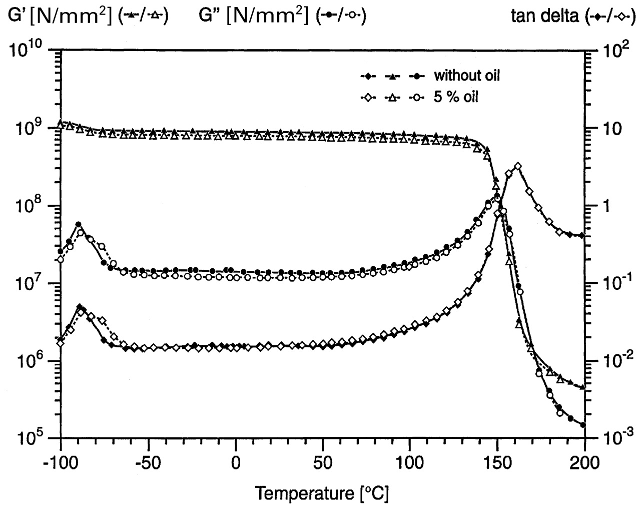
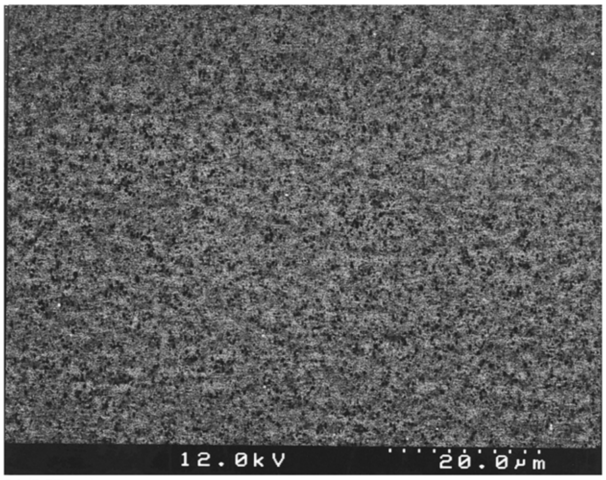
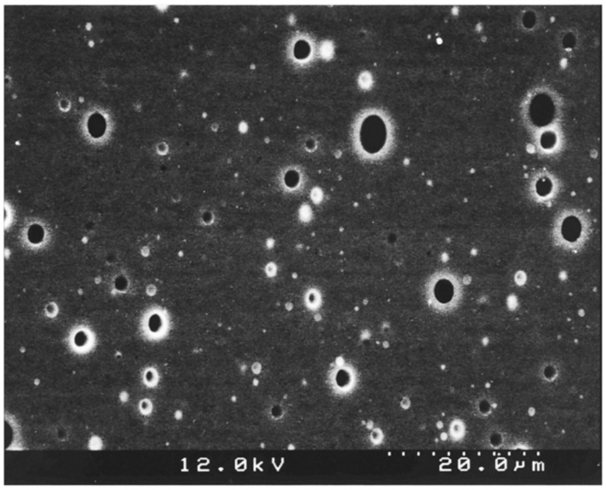


Fig. 15. Dynamic mechanical properties of ABS (MI 3.5) without and with 5% silicone oil.



without silicone oil



5 % silicone oil

Fig. 16. SEM backscattered electron images of sliced pellets of ABS (MI 3.5) without and with 5% silicone oil.

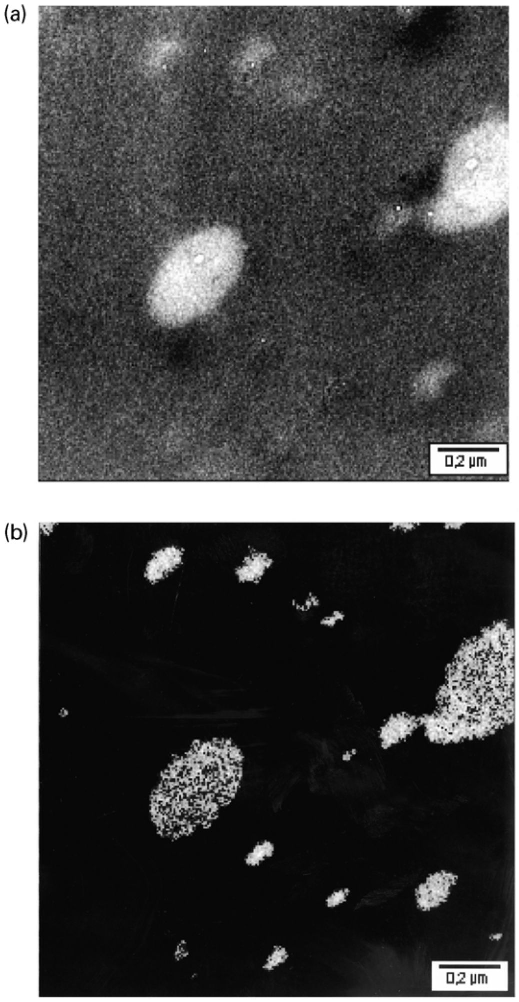
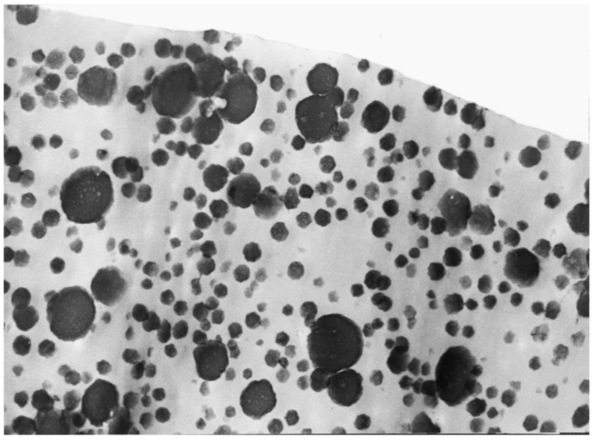
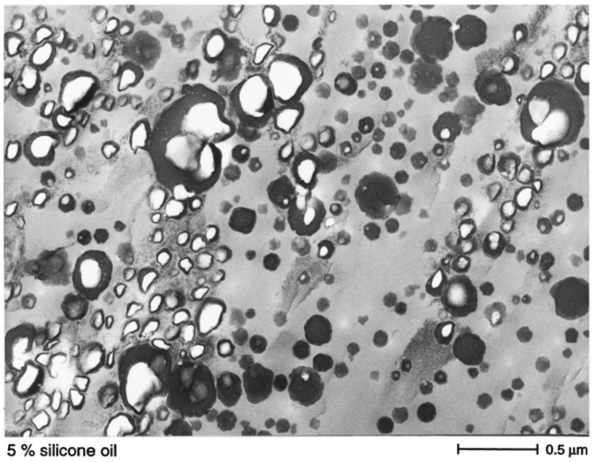


Fig. 17. ABS (2.7% rubber) modified with 0.43% silicone oil. (a) TEM bright field image (unstained); (b) corresponding Si elemental distribution map of ABS.

In order to investigate this we recorded a silicon elemental distribution map by means of electron spectroscopic imaging. This can be done by an analytical electron microscope where an energy filter is integrated in the column as realised in the LEO 912 Omega. The energy filter consists of magnetic prisms, which deflect electrons of different energy loss to different extents. In the back focal plane of the filter the electron energy loss spectrum is produced. With an energy-selecting slit electrons of a special energy loss can be selected and used for imaging. In the case of our samples we used the Si L2,3 edge for imaging because under the K edge the signal is too weak. Normally a total of three images with a 5–10 eV energy window are recorded. The two images in front of the edge are used to calculate the background, which is subtracted from the image under the edge. The result is a Si elemental distribution map as shown in Fig. 17.



without silicone oil



5 % silicone oil

Fig. 18. TEM micrographs of ultra thin sections stained with OsO_4 immediately after cooling to liquid nitrogen for 1 min.

Obviously the silicone oil has concentrated in the rubber particles and not at the interface or in the matrix. Thus it is to expect that any improvement of toughness by small amounts of silicone oil is mainly caused by a promotion of deformation process at the rubber particles. If the ABS is quenched for 1 min in liquid nitrogen and subsequently warmed up to room temperature and stained with OsO_4 the TEM images of thin section of this material show the enhanced void formation in the rubber particles in contrast to the unmodified ABS (Fig. 18). Void formation occurs simply by the thermal stress during cooling in accordance with Bucknall's procedure [16]. The notched impact strength of this ABS was increased by 0.025% silicon oil from 18 to 23 kJ/m^2. Therefore, it is to be concluded, that in ABS with a small amount of silicone oil toughness is increased by enhanced void formation in the rubber particles on impact. The toughening of rubber modified PMMA on the basis of microcracks inside the rubber particles with a small amount of silicone oil was recently discussed by Yamashita and Nabeshima [17].

3. Conclusion

It was shown that void formation in rubber particles in HIPS and ABS has a more important influence on the impact strength than was supposed in the past. Rubber modification of brittle polymers is based either on enhanced crazing or shear yielding. Crazing and shearing are facilitated, if the rubber particles can easily cavitate. This can be achieved by either avoiding too much cross-linking or by adding adequate oil into the rubber particles which act as nuclei for void formation. By thermal cross-linking of the rubber particles in the HIPS and ABS-types studied in this paper, the particles become more resistant to cavitation resulting in embrittlement of both materials, independent of which deformation mechanism, namely crazing or shearing, is operating. It can be concluded that the experimentally observed embrittlement caused by processing of these materials at a higher temperature is essentially due to a higher degree of cross-linking of the rubber particles, which in turn reduces the ability of the rubber particles to cavitate. Adding adequate oil into the rubber particles facilitates void formation at least in ABS by a nucleation effect leading to tougher products.

It is still open to question, which of the following three mechanisms prevails, namely

- whether crazes are initiated after void formation,
- whether the precursor of a craze in the matrix can only easily form a real craze, if the adjacent rubber particle cavitates to compensate the local volume strain or
- both deformation structures occur simultaneously.

Further kinetic examinations must follow to decide this question.

Thus in order to optimise the toughness of rubber modified thermoplastics well grafted rubber particles should be weak enough for internal cavitation but be strong enough to bridge deformation zones like crazes.

Acknowledgements

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