Determination of the morphology and mechanical microprocesses in polymer combinations by electron microscopy

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Several non-conventional methods of determining the phase structure and the mechanical microprocesses of deformation and fracture of high-impact polymers are described. These include (i) methods of 'irradiation induced contrast enhancement', (ii) a method of 'straining-induced contrast enhancement', and (iii) a method of specimen deformation using a high voltage electron microscope. These methods, complemented by conventional techniques, enable improved correlations between structure and mechanical properties to be obtained. As an example, the rubber volume content and the fracture toughness of high-impact polystyrene are quantitatively correlated.

INTRODUCTION

A fundamental problem in polymer research today is the determination of correlations between structure and properties of polymers. In polymers structures of many differing sizes occur, from individual macromolecules to the largest supermolecular structures. Many recent studies have shown that mechanical properties can often be directly related to the supermolecular structure (or morphology). The so-called high-impact polymers (or rubber-modified polymers) are appropriate to show the possibilities of improving mechanical properties by modification of their morphology. The application of special electron-microscopic techniques enables not only the morphology of these polymers to be determined but also the deformation and fracture microprocesses.

Several well known high-impact polymers have been used for many years, for instance high-impact polystyrenes (HIPS) and ABS-polymers (acrylonitrile–butadiene–styrene). The traditional method of determining their morphology is to investigate ultra-thin sections by transmission electron microscopy (TEM)[1-4]. Before cutting the samples in an ultramicrotome, the polymeric materials are fixed or hardened and stained chemically, usually by osmium tetroxide as suggested by Kato[1]. However, recently many new rubber-modified polymers have been created, e.g. for outdoor application. These polymers contain rubber polymers highly resistant to chemical attack. Therefore, the usual fixation and staining techniques are often inappropriate. In some cases modified and new preparation and investigation methods have been tested successfully.

MORPHOLOGY INVESTIGATION

Investigation by irradiation effects

Investigation using irradiation methods is based on two effects which are a consequence of irradiation of polymeric materials:

(1) Several polymers show a clear tendency to crosslinking during γ- or electron irradiation[5]. Crosslinking between the macromolecules yields a fixation of the supermolecular structure often effective enough to protect the polymeric material against distortions during cutting in the ultramicrotome. *Figure 1a* shows the phase structure of a high-impact polystyrene with an ethylene–propylene–terpolymer (PS/EPT) rubber phase. The rubber phase was fixed and stabilized against distortion by γ-irradiation with a 10 MGy dose. The density of the rubber phase being lower than the density of the matrix causes bright particles to appear. The interior structure of the particles with a network of rubber and polystyrene inclusions can be easily identified. This network structure of the rubber particles is characteristic of high-impact polymers produced by solution polymerization[3,4]. The bright narrow bands between some of the rubber particles in *Figure 1b* are crazes, i.e. typical plastic deformation zones in this material (see also below).

(2) The second irradiation effect is the formation of radicals or new molecular groups. These irradiation products occasionally react more strongly with the chemical staining agents than with the original polymeric material. As an example *Figure 2* shows the morphology of a polymer system comprising styrene–acrylonitrile
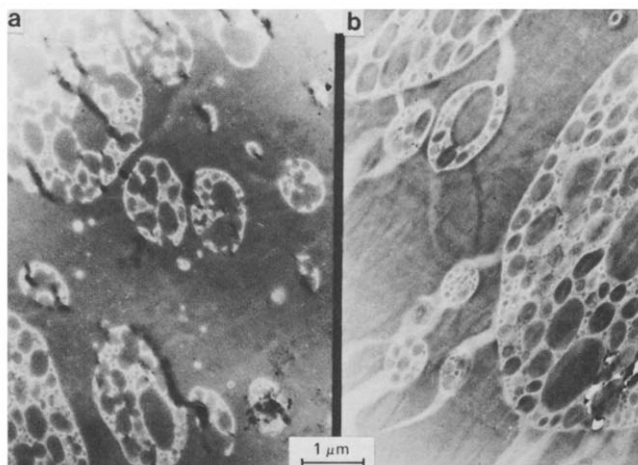
Figure 1 Morphology of high-impact PS/EPT. Preparation:(a) rubber particles fixed by γ-irradiation (dose 10 MGy); (b) ultra-thin section, TEM
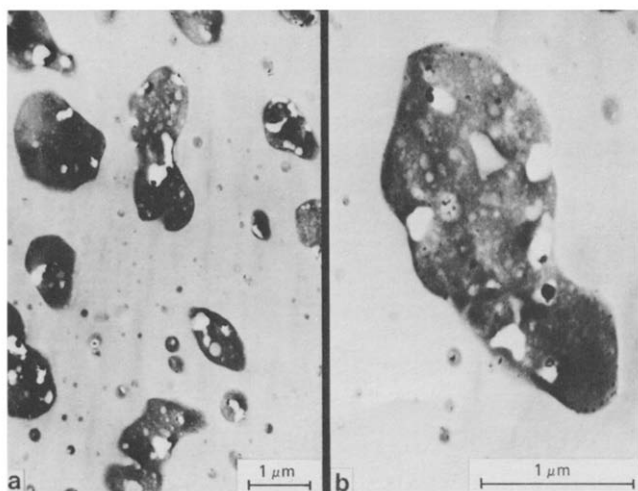

Figure 2 Morphology of a high-impact SAN/CPE (ACS-acrylonitrile-chlorinated polyethylene-styrene). Preparation: (a) rubber particles 'activated' by γ-irradiation and chemically stained with OsO_4; (b) ultra-thin section, TEM

copolymer and chlorinated polyethylene (SAN/CPE). The rubber particles are dark due to staining. During irradiation active radicals and groups are formed in the rubber phase, yielding a stronger chemical attack of staining reagents. In their interior the dispersed rubber particles show small bright particles. These domains of SAN-material are a result of grafting processes in the interior of the particles. Grafting at the surface of the particles is necessary for a good connection between particles and the matrix[3,6].

This effect of improved chemical staining due to irradiation ('irradiation-induced contrast enhancement') was also studied in semi-crystalline polymers[7,8].

Investigation by straining effects

The second possibility of structure determination arose from studies of the deformation processes of polymers using high voltage electron microscopy (HVEM[2b,9]). Thin polymeric specimens, usually 0.5 to 5 μm thick, were deformed outside or inside the HVEM. During deformation structural elements, which differ in Young's modulus or extensibility from the surrounding material, appear in a better contrast. This effect is called 'straining induced contrast enhancement' ('SICE'). Its applicability is demonstrated in the following (we will not discuss the

principles in detail here; for this see ref. 8). *Figure 3* shows two rubber modified high-impact polymers with clearly distinguishable polymer phases after a slight elongation. Micrograph (a) shows a system with dispersed rubber particles of chlorinated polyethylene (CPE). Due to the lower density and stretching, the rubber particles appear brighter than the matrix of the SAN. It is the same SAN/CPE system as in *Figure 2*, but here without any chemical treatment.

In micrograph (b) an opposite morphology is shown: a rubber network containing small particles of a hard polymer. Owing to the lower density and the predominant deformation of the rubber phase, the rubber network appears bright whereas the particles are dark. Such a network structure is characteristic of high-impact polymers based on PVC with e.g. rubbers of ethylene–vinyl acetate or chlorinated polyethylene. This effect of 'straining induced contrast enhancement' enabled several polymer combinations to be investigated, for which none of the chemical staining methods are apt.

Polymeric materials usually contain inorganic substances, e.g. stabilizers against heat or ultraviolet degradation and pigments. In investigating chemically stained ultra-thin sections it is often difficult to clearly determine these inorganic particles since small filler particles very much resemble the staining particles. However, for thin sections slightly strained it is easy to distinguish three components by the differences in their densities. An example is shown in *Figure 4*. A high-impact PVC clearly reveals the dark PVC particles, the bright rubber network phase and black small inorganic particles inside the rubber phase.

Accurate determination of particle size distributions

The investigation of semi-thin sections in the HVEM implies another advantage. It is easier to determine shapes and real sizes of the dispersed particles using semi-thin sections than by using ultra-thin ones. *Fibure 5* shows rubber particles of a commercial HIPS after the usual staining with osmium tetroxide in sections of enlarged thicknesses. Micrograph (c) shows particles the whole or the greater part of which is lying inside the section. Therefore, in comparison with the ultra-thin sections, this relatively thick specimen reveals the real diameters of the particles with a higher probability. *Figure 5d* compares frequency distributions of the particle diameters,
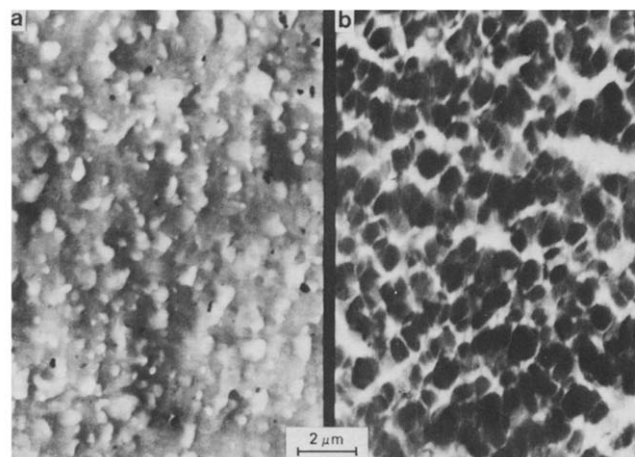

Figure 3 Morphology of high-impact polymers. Preparation: staining of semi-thin sections (1 μm thick) in a HVEM (the rubber-phase appears brighter due to its lower density and preferred deformation); (a) rubber particles (SAN/CPE), (b) rubber network (PVC/EVA)
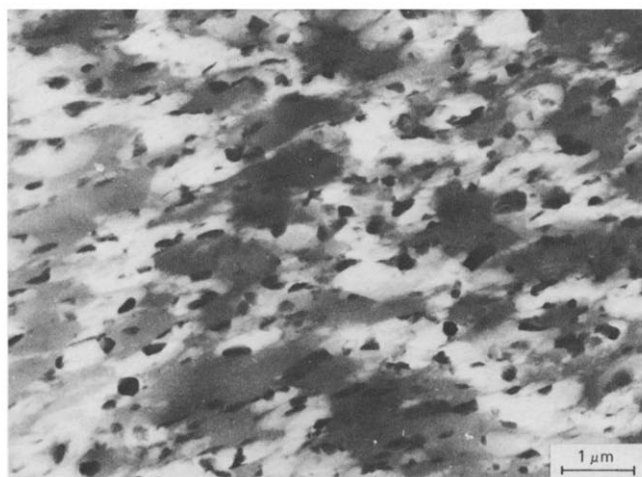
Figure 4 Three components in a high-impact PVC/EVA, visible in a strained semi-thin section in a HVEM, dark-PVC primary particles; bright-rubber network phase; black-inorganic particles of a heat stabilizer
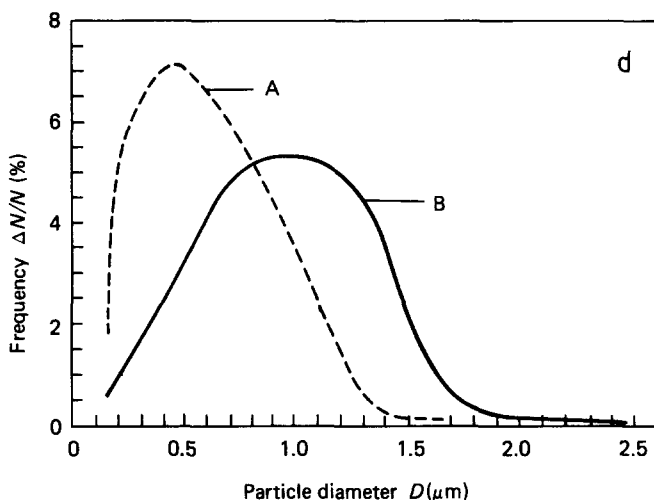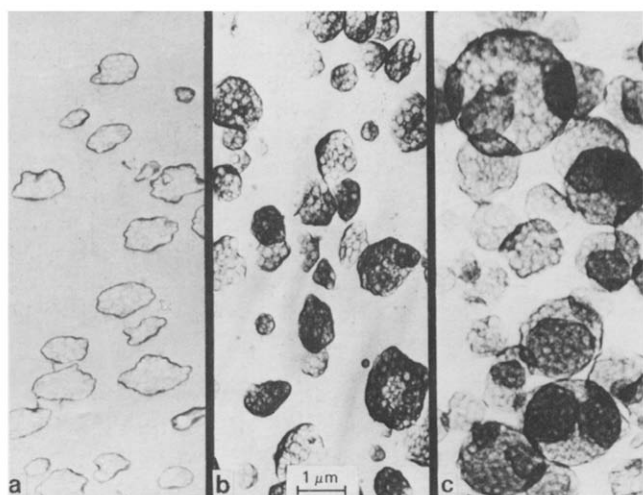

Figure 5 Comparison of visible particle sizes in HIPS in dependence on the section thickness t (sections stained with OsO_4, HVEM); section thickness t; (a) 0.1 μm, (b) 1 μm, (c) 4 μm, (d) frequency distribution of particle diameters, determined on sections of a thickness of 0.1 μm (curve A) and 4 μm (curve B)

determined on the 0.1 μm ultra-thin sections (curve A) and on 4 μm thick sections (curve B). In each case almost 1200 particles are measured. With increasing section thickness the maximum of the frequency distribution is shifted towards the larger particles. However, of more interest is the finding that the largest particles appear only in the

thick section with measurable probability. The information concerning their existence is necessary to assess the mechanical behaviour of the high-impact polymers, since the largest particles have a negative influence on the mechanical properties, particularly on fracture toughness[10].

The determination of the true particle diameters by measuring their sectional areas (which are usually smaller than the particles) on the ultra-thin sections (0.1 μm thick) is a well known problem of 'stereology'[11]. For many years mathematical solutions[12] and numerical calculations[13] existed for spheres and other regularly shaped particles. These mathematical corrections yield a shift of the maximum of frequency distribution towards larger particles. However, an important disadvantage (nevertheless rarely taken into consideration) is that the maximum particle diameter has to be known. However, this is not realized in the most cases. Therefore, investigating thicker sections in the HVEM is practically speaking very useful for determining true particle diameters.

MECHANICAL MICROPROCESSES

Rubber particles, particularly the rubber phase in high-impact polymers, increasingly favour energy absorbing processes, e.g. crazing in HIPS. The various structural parameters (size, size distribution, rubber particle shape, volume content of the rubber phase, Young's modulus of the rubber, connection between the phases, etc.) influence the formation of crazes and other micromechanical processes of deformation and fracture, and the fracture energy. The micromechanical processes of deformation were studied directly on thin deformed samples in a HVEM. Thin sections of the polymeric material about 0.5 to 5 μm thick were deformed using a tensile device. Here two advantages are implied:

(1) The morphology can be determined by the effect of 'SICE' (see above).

(2) The microprocesses of deformation can be studied due to the dependence on the morphology actually present.

The electron irradiation inside the HVEM destroys the molecular structure of the polymeric materials and changes their mechanical behaviour. To avoid any falsification of the results, direct *in-situ* deformation tests were performed at relatively very low electron beam intensities using highly sensitive photographic films[14]. Furthermore, several other methods have been used to investigate deformation structures[9,15].

Using the above techniques enables the micromechanical processes of several high-impact polymers to be determined. For high-impact PS and related polymers the processes of deformation and fracture have been arranged in three stages[15]:

Stage 1—craze-initiation (Figure 6)

Each rubber particle concentrates the stress. In the particles' surroundings matrix material will be transformed into crazes; this mechanism was first deduced by Bucknall[16,17]. The micrograph in *Figure 6* shows such crazes around rubber particles in a sample of high-impact polystyrene. The rubber particles appear somewhat brighter than does the polystyrene matrix; they are elongated in the direction of tension (see arrow). The
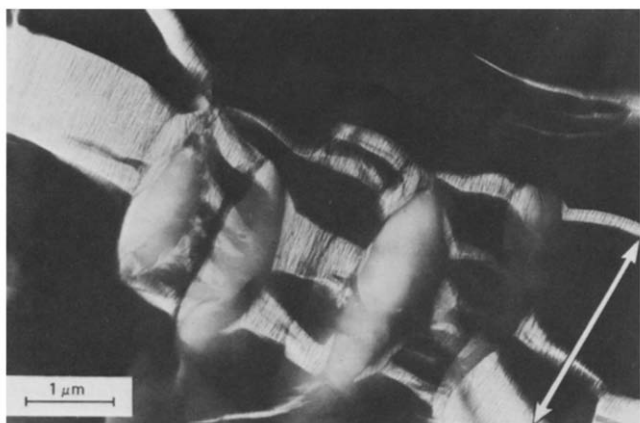
Figure 6 Initiation of crazes at rubber particles in HIPS (1 μm thick section, deformation direction see arrow, HVEM)

highest concentration of stress is along the equatorial zones of the rubber particles; these are the zones vertical to the tension direction. The crazes start from the equatorial zones of the particles and propagate perpendicularly to the tension direction. The separate initiation of crazes around the particles is the basic mechanism.

Stage 2—superposition effect (Figure 7)

For a rubber content of more than 15 vol% the stress-fields of neighbouring particles and of particles and craze-tips superimpose, favouring the formation of broad crazes, and broad long craze bands. These long craze bands propagate in large polymer areas, in which the original stress concentration was too low for craze initiation. Here the energy absorption essentially increases.

Stage 3—crack propagation (Figure 8)

High-impact polymers fracture by rupture of the crazes, as happens with glassy polymers. However, the modified structure modifies crack propagation. *Figure 8* shows the successive stages of crack propagation: the main crack is from above. In front of the main crack crazes are visible. In the stress field ahead of the crack crazes rupture and crazes that in micrograph (a) are intact are ruptured in micrograph (b). The length of the cracks is limited by length of the crazes. These mechanisms of crack stop and, restricting the crack lengths, delay the propagation of cracks and the ultimate fracture.

QUANTITATIVE STRUCTURE–PROPERTY CORRELATIONS

Detailed knowledge of the microprocesses of deformation and fracture enables quantitative correlations between morphology and fracture toughness to be obtained. An example is the influence of the volume content of the rubber particles on the energy absorption. The influence of the rubber content on the mechanical properties (impact toughness, fracture elongation etc.) has been described in many previous papers[2,3,18-20]. On the other hand, only a few investigations have been made on the corresponding changes of the mechanical microprocesses. The variation of crazing depending on rubber content has been described qualitatively recently[21].

Figure 9 compares the craze formation of three ABS polymers of different rubber content. The upper micrographs show stress-whitened areas at small magnifications whereas the micrographs at the bottom show particles and crazes at higher magnifications. In (a) the rubber content is low (0.6 vol%), yielding large spacings between the rubber particles. Only a few longer crazes are formed. In (b) the rubber content is somewhat higher (2.4 vol%), so that more crazes are formed. In (c), with a rubber content of about 21 vol%, the superposition effect is operative, yielding a large number of crazes and craze-bands over a large area.

The changes in size and shape of crazes, depending on the volume content of rubber particles, were measured directly from the micrographs of the deformed specimens.

Figure 7 Formation of broad long-craze-bands in HIPS due to the superposition of stress fields (deformation direction horizontal)
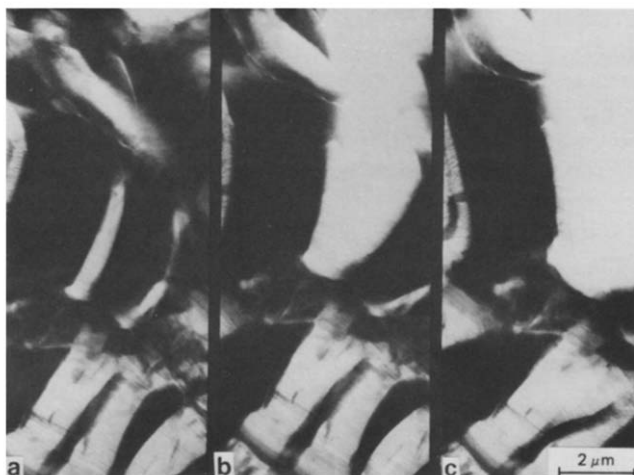

Figure 8 Crack propagation hindered by mechanisms of crack stop at rubber particles and by these limiting the crack length (successive stages of crack propagation in an *in situ* deformed HIPS sample in HVEM; deformation direction horizontal)
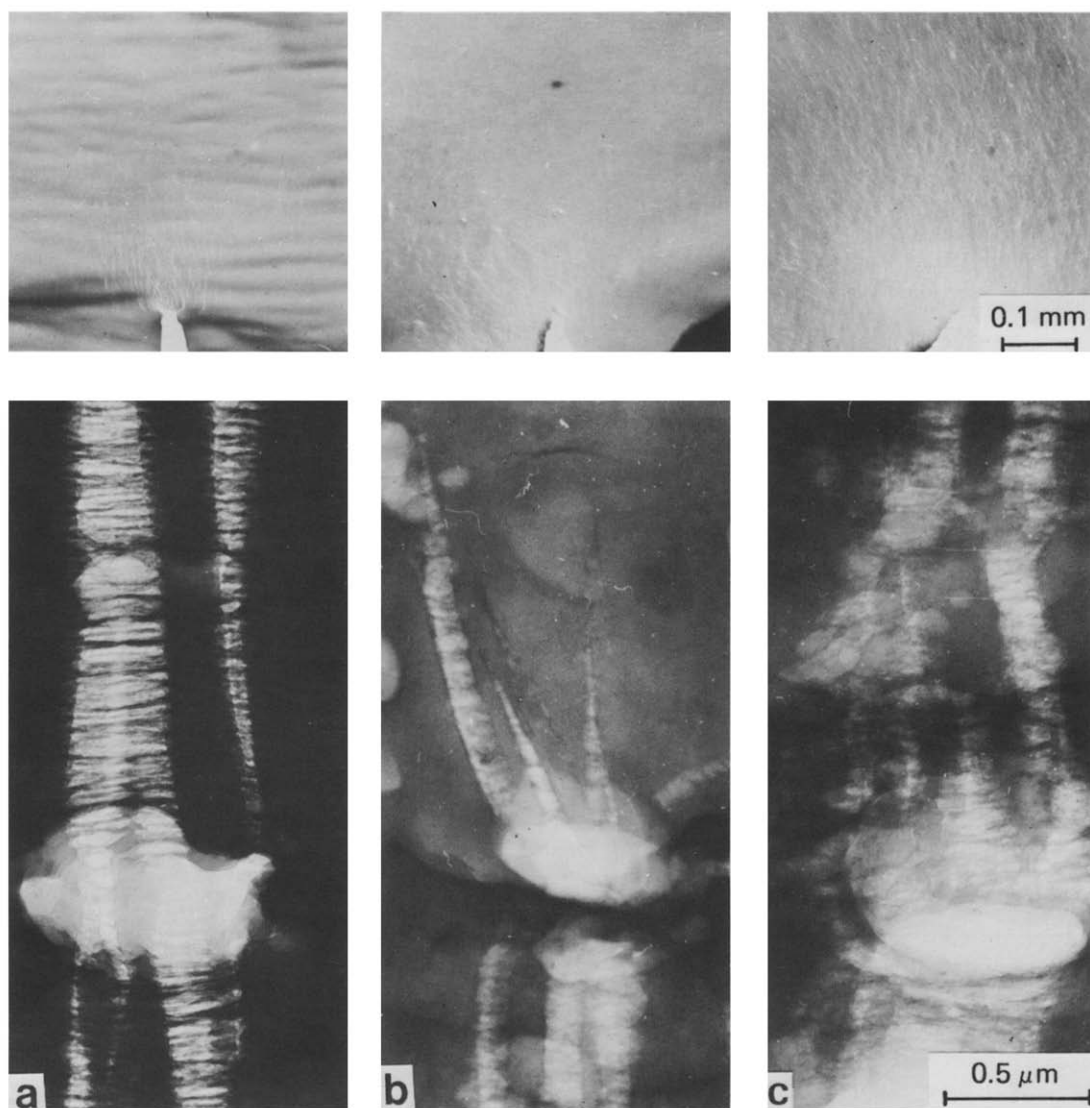
Figure 9 Influence of the rubber volume content on the size of the crazed area ('stress-whitened' area ahead of the crack tip) in the micrographs at the top and the size and shape of crazes in the micrographs at the bottom. Rubber volume content: (a) 0.6%, (b) 2.4%, (c) 21%

The results are shown in *Figure 10*. At lower rubber contents (0.02–0.05) only individual crazes with wedge-shaped cross-sections appear. At higher rubber contents the length of crazes is limited by the mean distance between the rubber particles. The width B of the crazes increases with increasing stress between the rubber particles due to the stress-field superposition. The curves in *Figure 10* show the decrease in the length L and the increase in the width B of the crazes.

From the above the volume of a single craze around a rubber particle was calculated and in addition knowledge of the number of rubber particles (and of the number of crazes) enabled the total volume of all crazes to be calculated. With increasing rubber content an appreciable increase of the total craze volume is observed (*Figure 11a*). The formation of the crazes requires energy and recently[15] the amounts of energy of the main energy-absorbing processes of deformation and fracture have been evaluated. It was shown that in intensively crazed materials the amount of energy required to form crazes is more than 90% of the total fracture work. Therefore, the curve in *Figure 11a* reveals rather well the increase in the total fracture work with increasing rubber volume

content. *Figure 11b* shows the values of the impact strength measured[15]. Comparing these curves verifies the same dependence on the rubber content, implying a good description of the toughening mechanism on the basis of the micromechanical processes.

Other structure–property relations were also determined in this way, e.g. the influence of the diameter of the rubber particles, the distribution of the particle diameter, and of the Young's modulus on the fracture work[15]. Thus it becomes possible to determine to what extent the various structural parameters influence the fracture work.

CONCLUSIONS

High-impact or rubber modified polymers can be studied using several electron microscopical methods.

Traditional methods of determining the morphology are TEM investigations of chemically fixed and stained ultra-thin sections. For several polymers these methods are not appropriate; however, new or modified techniques have been successfully applied.

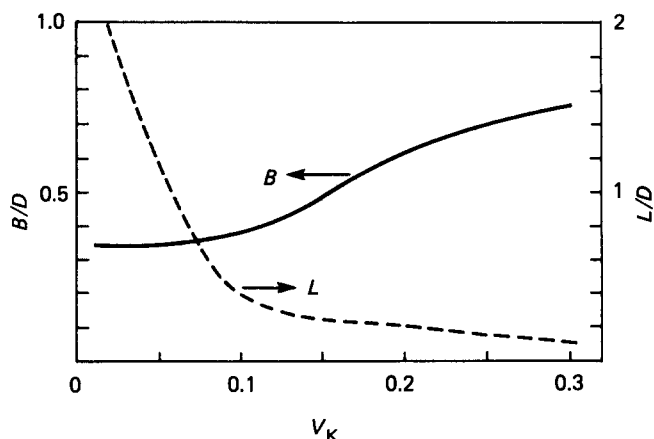| Rubber volume V_K	≤ 0.02	0.05	0.1	0.15	0.20	0.25	0.30
Craze shape	D $L \leqslant A$		B $L = A/2$ A		$L = A/2$		
Craze size B/D	0.35	0.35	0.35	0.50	0.62	0.70	0.75
L/D	2	1.2(=A)	0.37(=$\frac{A}{2}$)	0.26	0.19	0.14	0.10

Figure 10 Influence of rubber volume content on size and shape of crazes; dependence of the length L and the width B of crazes on the rubber volume content

Fracture processes are usually studied on fracture surfaces by SEM. However, HVEM investigations of thin deformed specimens yield far more detailed information on the deformation processes.

To get the most information concerning many high-impact polymers it is useful or indeed necessary to combine the traditional methods with new techniques. On this basis improved (and at best quantitative) correlations between the two-phase morphology and the mechanical properties can possibly be gained.
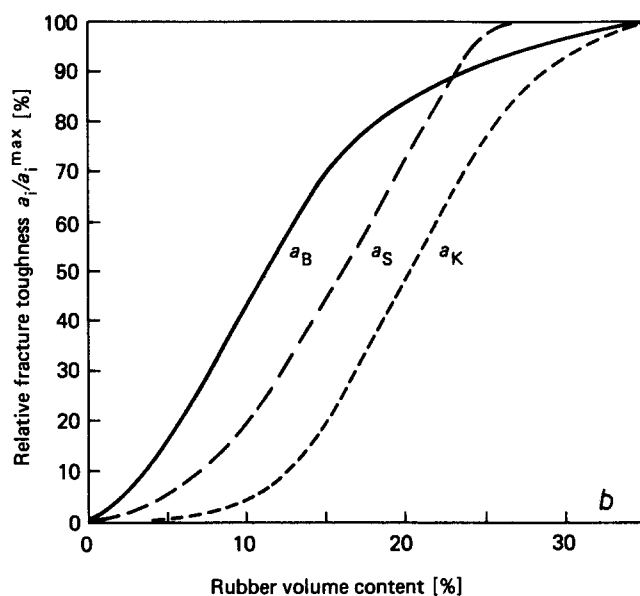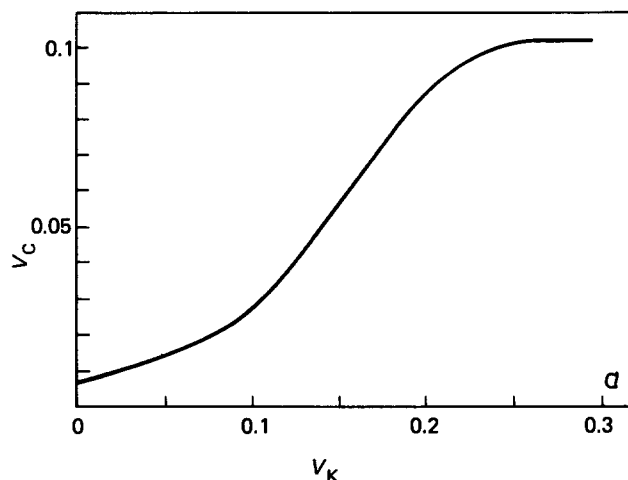
ACKNOWLEDGEMENTS

Figure 11 (a) Calculated increase of the total craze volume and the total energy for the craze formation with increasing rubber volume content. (b) Measured increase of the impact strength (a_K, notched; a_S, unnotched; a_B, tension test)

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