Toughened thermoplastics: 2. Impact properties and fracture mechanisms of rubber modified poly(butylene terephthalates)

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The impact properties of commercial grades of rubber-toughened poly(butylene terephthalate) are investigated using various test procedures. Examination of fractured samples using transmission electron microscopy reveals that stress whitening results from cavitation of the rubber particles. Immediately behind the fracture surfaces, extensive plastic yielding of the matrix occurs which distorts the rubber particles into flattened ellipses.

(Keywords: poly(butylene terephthalate); impact strength; polymer blend; electron microscopy; rubber toughening; shear yielding)

INTRODUCTION

The commercial development of toughened polymer blends has increased rapidly in recent years. The impact properties of most thermoplastics can be considerably enhanced by the incorporation of a dispersed elastomeric phase, although the toughening mechanisms involved are influenced by the properties of the matrix material and by the morphology of the blend[1,2]. For example, in brittle polymers such as polystyrene[3–5] and poly(acrylonitrile-*co*-butadiene-*co*-styrene)[6,7] the rubber particles promote crazing of the matrix, whereas in blends which have a semi-ductile matrix such as polyesters[8–10] and polyamides[11–13], shear yielding is usually the dominant energy absorbing process.

A convenient way of controlling the particle size of the dispersed phase is the use of latex particles synthesized by emulsion polymerization[14,15]. Recent developments in this field have led to the manufacture of a wide range of impact modifiers of relatively complex structure (e.g. core-shell morphologies), notably by the Rohm and Haas company[15].

Although there have been many attempts to explain the toughening effect of a dispersed elastomeric phase[1,2], the subject remains controversial. However, it is generally accepted that relatively large particles (1–5 μm) are favoured in brittle polymers and that toughening is achieved by initiation of crazing and/or shear banding within the matrix[16]. In semi-ductile polymers, on the other hand, smaller particles (sub-micron) are required which lower the yield stress of the matrix and promote plastic flow (usually in the shear plane)[17–19].

In both types of blend, fracture is usually accompanied by stress-whitening, due to the generation of space within the sample. This may be either within the matrix (crazing or shear banding) or associated with the rubber particles themselves (debonding or cavitation). Although the processes of cavitation and debonding provide useful information concerning the strength of the matrix–particle interface, the stress-whitened region of toughened polymers has seldom been examined microscopically[20]. Beaumont and co-workers[21] have used *in situ* scanning electron microscopy (SEM) to observe crack propagation processes, but this technique does not provide information about the area behind the fracture surface, in which a significant amount of energy is being absorbed.

The measurement and analysis of the impact properties of polymers is another very controversial subject[2]. The amount of energy absorbed by a polymer during impact is dependent on many variables such as the sample geometry, test temperature, impact velocity, impacter shape, etc., and relatively minor changes in any of the factors can induce the material to undergo a sharp brittle–ductile transition.

Several methods have been developed for the analysis of impact data, depending on whether the material undergoes brittle, ductile or some intermediate mode of fracture. Linear elastic fracture mechanics (LEFM) which was originally developed for the analysis of metal failure[22], has been applied to the brittle fracture of polymers[23]. However, this procedure assumes that the sample fails under plane strain conditions, and it is likely that all polymeric materials absorb some energy, other than that which is stored elastically in the test specimen. Alternative procedures such as the *J*-contour integral method[24] and determination of the essential work of fracture[25] have been developed, which attempt to separate the elastic and plastic contributions to the total energy absorption. These methods have been successfully used to analyse the fracture of semi-ductile materials, but tend not to give satisfactory results with the new generation of super-tough blends.

However, Vu-Khanh has recently proposed a method

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for highly ductile polymers[26] in which he derives a fracture energy at initiation (essentially an elastic contribution), and a tearing 'modulus', which is a measure of the change in fracture energy as the crack grows (plastic contribution). He shows that a plot of U/A *versus* A (where A is the area of the fracture, and U is the total energy absorbed during fracture) is linear, with a slope of $T_a/2$ (the tearing modulus) and an intercept of G_i (fracture energy at initiation). The G_i values obtained from this method agree well with J_C values obtained from the J-contour integral method for a toughened nylon and polycarbonate/polyethylene blend.

In this paper various methods for characterization of the fracture behaviour of commercial grades of impact modified poly(butylene terephthalate) (PBT) are compared. The results of a detailed examination of the process zone, using transmission electron microscopy (TEM) are also presented.

EXPERIMENTAL

Impact testing

Plates (60 cm × 60 cm × 2 mm) and bars (105 mm × 10 mm × 4 mm) were cut from plaques which had been compression moulded at 240°C for 5 min, using a pressure of 20×10^3 kg on a 10 cm ram, and the bars were machine-notched. High-speed impact experiments were carried out using a Rosand instrumented impact tester at an impact velocity of $3\ \mathrm{m\ s^{-1}}$. Hemispherical and wedge-shaped strikers were used for the plates and bars, respectively. The mass of the impacter was 4.95 kg and the raw data were filtered using a frequency of 1 kHz (notched bars) or 2 kHz (plates). A modified Nene MC3000 tensometer (operated in compression mode) was used for the fracture experiment performed at lower strain rate ($10\ \mathrm{mm\ min^{-1}}$), and strain was measured by crosshead displacement.

Samples were cooled in ice (0°C), or by adding solid carbon dioxide to methanol (−30°C), and were tested no more than 5 s after being removed from the coolant. Stress intensity factors (K_C) and strain release rates (G_C) are the average of at least four samples and were obtained using a computer program which calculates the geometrical correction factor (ϕ) from a series of linear interpolations.

Values of G_i and T_a were obtained using a linear least squares analysis of the Vu-Khanh equation:

$$U = G_i A + 0.5 T_a A^2$$

The dynamic impact modulus was calculated from the expression

$$E = S\frac{a^2}{t^3}\frac{3}{16\pi}\left[\frac{(3+\nu)}{(1+\nu)} + \left(\frac{d}{a}\right)^2 \log_e\left(\frac{d}{a}\right) - \left(\frac{d}{a}\right)\frac{7+3\nu}{4(1+\nu)}\right]$$

where ν is the lateral contraction ratio (a value of 0.4 was used in these experiments), d is the diameter of the hemispherical striker, a is the radius of the support, t is sample thickness and S is the maximum gradient of the force–displacement curve prior to yield.

Instruments

Transmission electron micrographs were obtained using a Hitachi HU-11B microscope, and a Philips 525M instrument was used for SEM. Samples for TEM were stained with osmium tetroxide before sectioning, and those for SEM were etched in boiling dichloromethane and then sputtered with gold, using a Polaron E5000M sputter coater. Differential scanning calorimetry thermograms were obtained using a Perkin Elmer series 7 differential scanning calorimeter at a heating rate of $10^\circ\mathrm{C\ min^{-1}}$. Dynamic mechanical thermal analyses (d.m.t.a.) were performed using a Polymer Laboratories dynamic mechanical thermal analyser at a frequency of 10 Hz, a heating rate of $3^\circ\mathrm{C\ min^{-1}}$ and the single cantilever mode of clamping.

RESULTS AND DISCUSSION

The two impact modified grades of PBT used in this work were Pocan S-1506 (ex. Bayer) and Ultradur 4071 (ex. BASF). It is believed that the latex particles in Pocan have a poly(styrene-*co*-butadiene) core and a poly(acrylonitrile) shell, which is supported by the d.m.t.a. thermogram shown in *Figure 1*. The structure of the modifier in Ultradur is not known, but the d.m.t.a. thermogram and characteristic odour of nitrile rubber are consistent with a random poly(butadiene-*co*-acrylonitrile) copolymer. Pure PBT (Arnite T06 204; ex. Akzo) was used as a reference material.

Fracture experiments

Two different types of fracture experiment have been used to characterize these materials, employing notched bending bars and square plates, and force *versus* displacement curves were obtained in both types of test. The notched samples were fractured by a wedge-shaped impacter using a three-point bend loading geometry at velocities of $3\ \mathrm{m\ s^{-1}}$ and $10\ \mathrm{mm\ min^{-1}}$. The results of these experiments are shown in *Tables 1* and *2*, respectively. The blends did not exhibit any stress whitening at an impact velocity of $3\ \mathrm{m\ s^{-1}}$, indicating a brittle (or semi-brittle) mode of failure. However, it is likely that fracture of these samples did not occur under conditions of perfect plane strain, and therefore, the K_C and G_C values given in *Table 1* will not be true material parameters. Nevertheless, they give a good indication of the relative strengths of the blends.

At the slower strain rate, all test bars of both blends failed via a ductile mechanism, with extensive stress whitening and plastic deformation in the process zone.

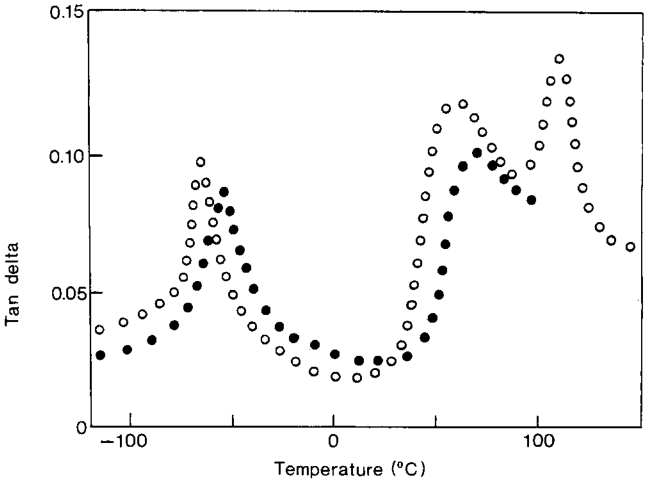

Figure 1 Plots of tan δ *versus* temperature for Pocan S-1506 (○) and Ultradur 4081 (●)

Table 1 Impact test data (3 m s^{-1})

Sample	Temperature (°C)	K_c (MN m$^{-3/2}$)	G_c (kJ m^{-2})
Pocan	23	3.27	10.94
	0	3.38	7.85
	−30	3.08	5.72
Ultradur	23	3.23	9.76
	0	2.62	6.28
	−30	2.84	5.22
PBT	23	1.77	2.36
	0	2.07	2.43
	−30	2.69	3.91

Table 2 Fracture test data (10 mm min^{-1})

Sample	F_C/A (MPa)	E_C/A (kJ m^{-2})	E_F/A (kJ m^{-2})
Pocan	5.84	11.7	56.8
Ultradur	4.25	5.3	16.2
PBT	8.79	6.9	7.6

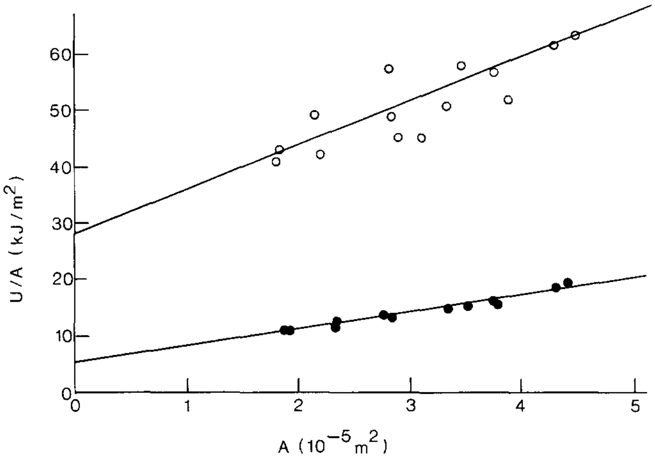

Figure 2 Vu-Khanh plots for Pocan S-1506 (○) ($G_i = 27.15$ kJ m^{-2}; $T_a = 1.67 \times 10^9$ J m^{-4}) and Ultradur 4081 (●) ($G_i = 5.14$ kJ m^{-2}; $T_a = 0.63 \times 10^9$ J m^{-4})

Since the LEFM method is inappropriate for ductile mechanisms of fracture, the results of these experiments have been analysed using the Vu-Khanh procedure described above. Plots of *U/A versus A* are linear, with a positive slope as shown in *Figure 2*. It can be seen that under these test conditions Pocan absorbs considerably more energy than Ultradur in both the initiation and propagation stages of fracture.

The plates, which were only tested at 3 m s^{-1}, were placed on a circular support and struck by a hemispherical impacter. The results of these tests are shown in *Table 3*. Relatively thin plates of the type used in this work tend to induce conditions of plane stress, which will favour a ductile mode of fracture. Indeed, even at 0°C some of the unmodified PBT plates were punched rather than smashed. A circular region of stress whitening was observed when the blends were punched, but this behaviour was never seen with the pure PBT.

It is interesting to compare the results of the notched experiments with those of the plate tests. Whereas the unmodified PBT is substantially weaker than the blends in the notched tests, the situation is reversed when plates are used. This marked difference in behaviour illustrates how the geometry of the test samples can influence the ability of the material to respond to an applied load. It is well known that PBT has very good unnotched impact properties, and under favourable test conditions, it can absorb considerably more energy than the rubber-modified blends. Indeed, we have found that relatively minor changes in the geometry or rate of fracture of the notched bars will induce a ductile–brittle transition in both blends.

However, in the notched tests it is apparent that with both ductile and 'brittle' modes of fracture, the blends always absorb more energy than the unmodified PBT. This indicates that at least two toughening mechanisms could be operating under these conditions, only one of which results in ductile fracture. In the brittle mode of fracture, the toughening effect is associated only with the initiation process, since the subsequent crack propagation is unstable. Indeed, SEM analysis of a brittle fracture surface of Pocan reveals an area of plastic deformation immediately above the notch, as seen in *Figure 3*. Further confirmation of this crack blunting mechanism is the presence of pronounced yielding in the force *versus* displacement curve, which is not seen for the pure PBT.

Electron microscopy

In order to obtain ductile failure of Pocan under relatively severe conditions, a notched sample was fractured at a velocity of 1 m s^{-1}. Scanning electron micrographs of ductile and brittle (3 m s^{-1}) fracture

Table 3 Plate test data (3 m s^{-1})

Sample	Temperature (°C)	F_C (N)	E_C (J)	E_F (J)	Modulus (MPa)
Pocan	23	1770	10.6	22.8	2440
	0	1920	10.4	19.0	2790
Ultradur	23	1340	8.1	12.2	2050
	0	1270	6.1	7.3	2300
PBT	23	2240	13.5	21.5	3780
	0	2530	12.1	16.9	4700

Figure 3 Scanning electron micrograph of the brittle fracture surface of Pocan S-1506 in the region of the notch tip

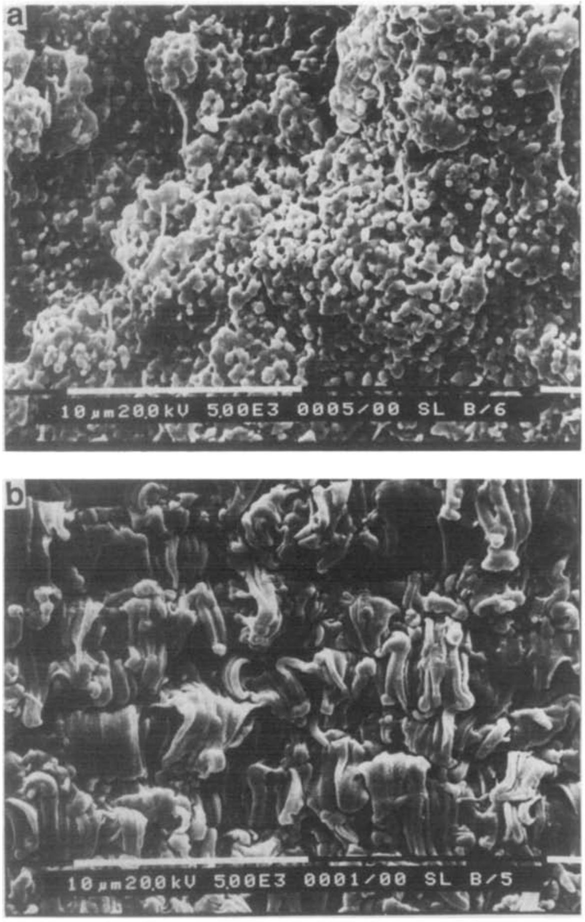

Figure 4 Scanning electron micrographs of (a) brittle and (b) ductile fracture surfaces of Pocan S-1506. The samples were etched with dichloromethane

surfaces of Pocan are shown in *Figure 4*. Both specimens were etched by boiling in dichloromethane for 12 h. As expected, the ductile fracture surface shows extensive plastic deformation, resulting from the drawing of matrix ligaments, and spherical rubber inclusions are not observed. However, the sample fractured at 3 m s^{-1} has a characteristically brittle fracture surface, with approximately spherical cavities from which the rubber particles have been etched. Similar micrographs were obtained for the Ultradur material, although the average particle size is somewhat smaller than that of Pocan.

Transmission electron micrographs of undeformed samples of the two blends are shown in *Figure 5*. In both cases the sections were stained with osmium tetroxide to reveal latex particles with relatively narrow size distributions. A series of transmission micrographs were also obtained in the three orthogonal planes through the process zone of a Pocan sample which had undergone ductile fracture (*Figure 6*). These planes are defined in *Figure 6*, and the sections were taken towards the middle of the fracture surface. The micrographs taken in the x-plane reveal that the stress whitening is a result of cavitation within the rubber particles rather than debonding at the matrix–particle interface. The proportion of cavitated particles increases through the process zone, and is almost 100% immediately behind the fracture surface. It is also apparent that the matrix material has yielded, causing substantial, irreversible deformation of the rubber particles. When the micrographs of the y and z planes are examined, it can be seen that this plastic deformation has occurred predominantly in the shear plane, causing the rubber particles to adopt a flattened, elliptical shape.

CONCLUSIONS

It has been shown that, under certain test conditions, the impact properties of PBT can be significantly improved by the addition of composite latex particles. Pocan absorbs considerably more energy than Ultradur, especially when fracture occurs in a ductile manner.

Electron microscopy reveals that the origin of stress whitening in these materials can be attributed to cavitation of the rubber particles, rather than particle debonding, or voiding within the matrix (e.g. crazing or shear banding). The cavitation may be incidental to the toughening process since stress whitening is always observed when plates of rubber modified blends are punched, and yet, pure PBT which does not stress whiten absorbs far more energy. Also, in notched samples, the region of cavitation extends well beyond that of plastic deformation. The cavitation process may simply be a response to the triaxial (or uniaxial in tension) stress which is imposed by the loaded matrix prior to yielding.

It is therefore reasonable to conclude that tough blends which undergo extensive plastic deformation will usually whiten as a result of the lower cohesive energy density

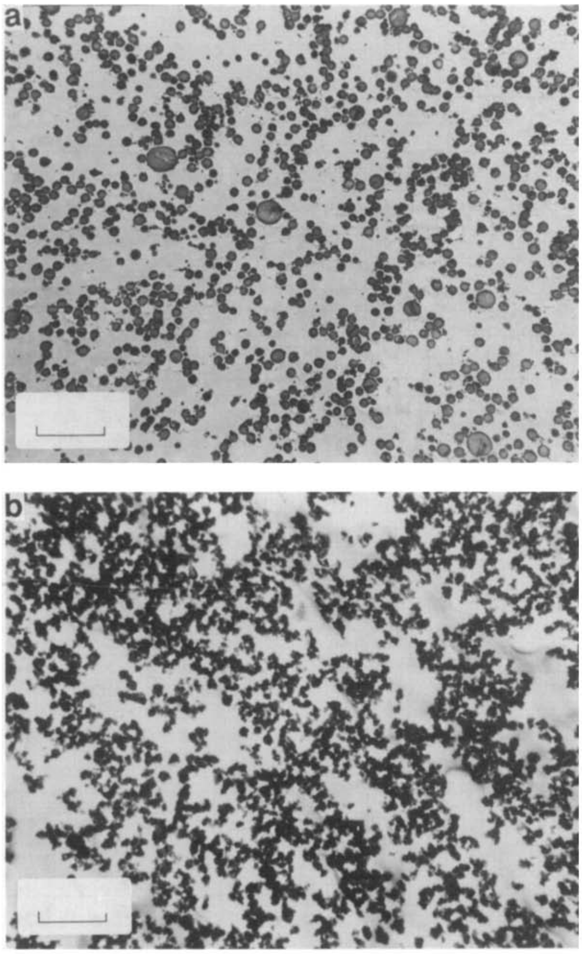

Figure 5 Transmission electron micrographs of (a) Pocan S-1506 and (b) Ultradur 4081. The samples were stained with osmium tetroxide. The scale bar = 3 μm

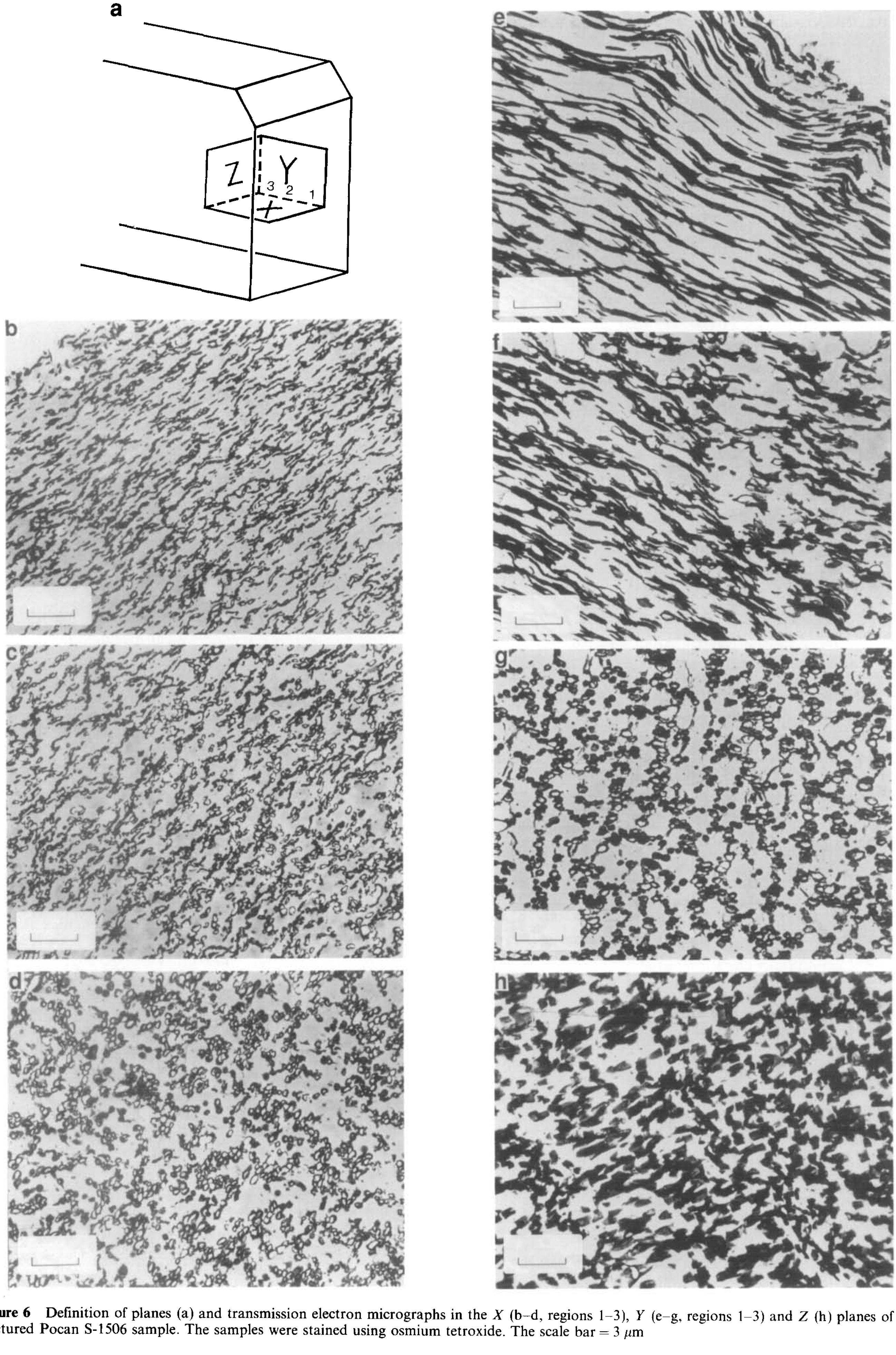

Figure 6 Definition of planes (a) and transmission electron micrographs in the X (b–d, regions 1–3), Y (e–g, regions 1–3) and Z (h) planes of a fractured Pocan S-1506 sample. The samples were stained using osmium tetroxide. The scale bar = 3 μm

of the rubber compared with that of the matrix. With a weak particle–matrix interface debonding will be more likely than cavitation. Thus although the rubber particles seem to promote yielding of the matrix, the cavitation and elongation of the particles may not contribute significantly to the overall absorption of energy.

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