Improved low temperature impact strength of polypropylene by modification with polyethylene

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The deformation behaviour of polypropylene is briefly described. Using the *SEM* and *TEM* techniques the morphology and the dilatational processes during deformation have been studied in order to elucidate the improvement of impact strength of polypropylene at low temperatures by modification with polyethylene. The segregation of polyethylene in polypropylene appears to be a prerequisite in producing a structure capable of forming energy dissipating deformation zones (crazes).

Keywords Polypropylene; polyethylene; copolymers; structure; deformation behaviour; shear bands; crazes; impact strength

INTRODUCTION

Polypropylene (PP) is a widely used thermoplastic material. Its deficiency in low temperature applications is its tendency to embrittlement. PP is known to belong to those materials in which the brittle–ductile transition in impact tests is related to the glass transition temperature[1]. *Figure 1* shows the log decrement of PP determined by the torsion pendulum method (DIN 53 445 alt. ISO/R 537), and the oscilloscope traces of the force–deflection diagrams taken during the Charpy impact flexural test (DIN 53 453 alt. ISO/R 179). Below the glass transition temperature at 10°C the impact strength of compression-moulded PP is given mainly by the elastic absorption energy, whereas at higher temperatures additional energy dissipation by wide range plastic deformation takes place. The most commonly applied method to improve toughness of PP below its glass transition temperature is by its modification by the addition of rubber particles, blending it with polyethylene (PE), or by copolymerization of PP with PE[2–5]. The latter two procedures are discussed here in more detail with emphasis on structural phenomena taking place during deformation. Two materials are considered here: one is a blend of PP/PE copolymer with 20% HDPE (CO/HDPE) and the second is a PP/PE block copolymer (PP/PE-copolymer).

DEFORMATION MECHANISMS IN POLYPROPYLENE HOMOPOLYMER

The glass transition temperature of PP is coupled with a change in the main deformation mode. At low temperatures, voiding processes are predominant which tend to form cracks followed by the fracture of the material. At high temperatures shear processes dominate which entail a reduced tendency to fracturing. The transition in the deformation mode can be shown by dilatational measurements (*Figure 2*) during the deformation (for method see ref. 1): At low deformation temperature (0°C) the volume of the PP specimen increases with the deformation strain due to the formation of cavities, whereas at a higher deformation temperature (40°C) the volume of the specimen tends to remain more or less constant, neglecting elastic swelling. After deformation near the glass transition temperature (e.g. at 23°C) both deformation modes are discernable in the specimen. At lower strains (outside the necking zone) cracks are observed perpendicular to the tensile direction, which cross the spherulites without seeming to be influenced by them (*Figure 3*). Under other deformation conditions this may be different[6,7]. However, the cracks will initiate the fracture of the material, at least at lower temperatures. Inside the necking zone shear bands are detectable (*Figure 4* a). In the regions of intersection of these shear bands, spherical voids are formed (*Figure 4* b), by virtue of the high local stresses generated there[8]. Additionally, the material splits (*Figure 4* c) along the tensile direction at high strains. Further confirmation of these different structural phenomena is afforded by small angle X-ray scattering (SAXS), as far as structures with reduced density are concerned. As the SAXS pattern (*Figure 5*) from inside the necking zone reveals, scattering occurs mainly perpendicular to the tensile direction (splitting) and from spherical voids. Outside the necking zone, scattering from thin openings lying perpendicular to the tensile direction predominates. This changing of the SAXS pattern by going from outside to inside the necking zone is in accordance with observations by Garton *et al.*[9]

MORPHOLOGY AND DEFORMATION MECHANISMS IN MODIFIED POLYPROPYLENE

Voiding in plain PP during deformation at low temperatures is the precursor of a crack entailing the fracture of the material. The basis of impact strength improvement is to bring this voiding under control. With this aim in mind, PP was modified either by blending a

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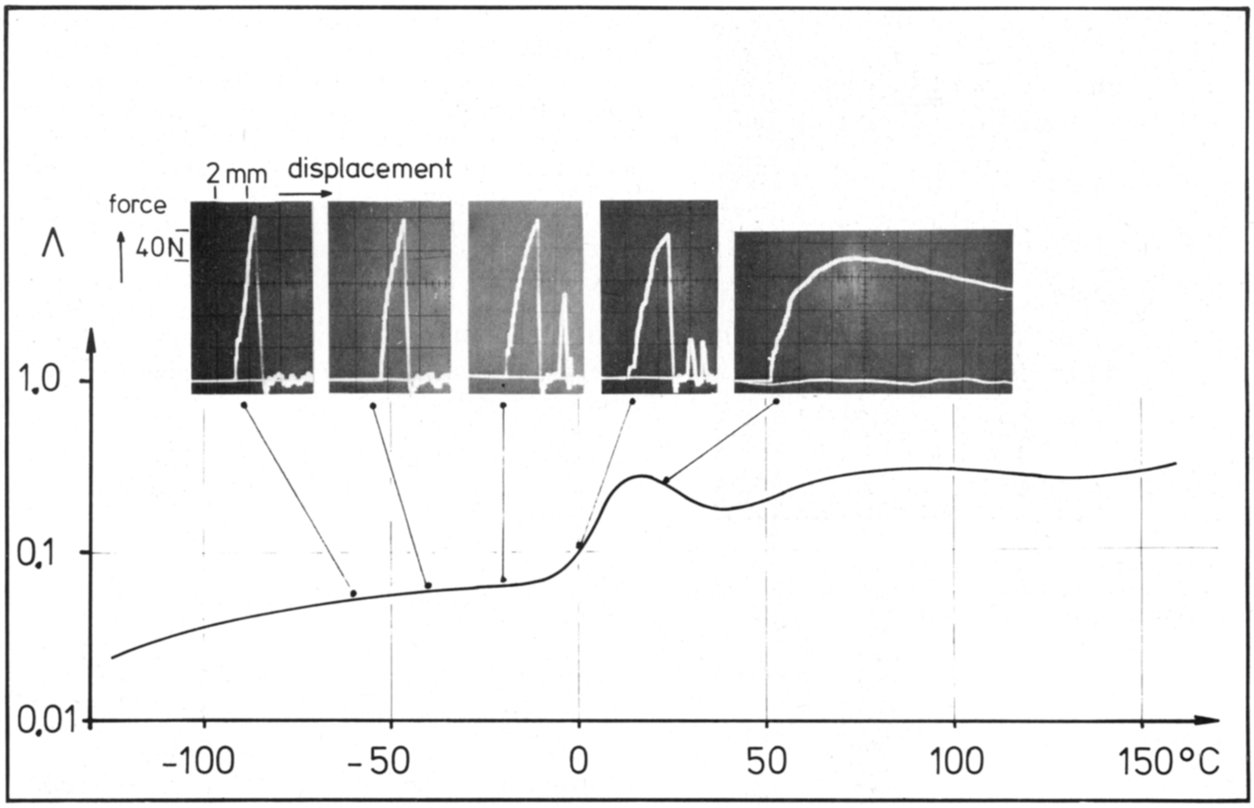

Figure 1 Log decrement Λ and force–deflection diagrams during Charpy impact test of PP (compression moulded samples)

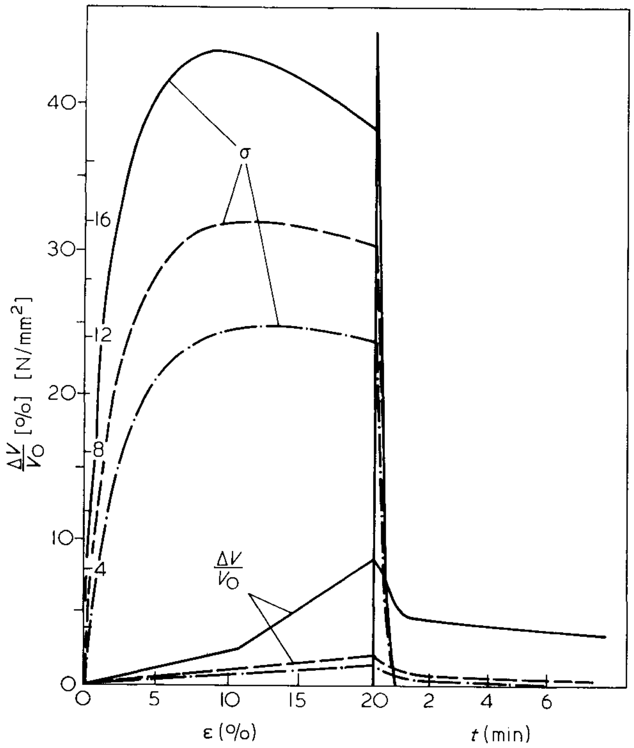

Figure 2 Deformation curves and volume change during deformation and subsequent unloading of PP. Deformation temperature: (——) 0°C; (– – –) 23°C; (— · —) 40°C. Deformation rate: 12.5 · 10^{-2} min^{-1}

PP-copolymer with PE or by copolymerization of PP with PE. In both materials the log decrement curves (*Figure 6*) reveal two further regions of enhanced mobility of molecules in relation to the PP-homopolymer: The relaxation process near -50°C is generally attributed to PP/PE-rubber[10], and the other relaxation process, less pronounced in copolymers, at -130°C is usually labelled γ-maximum in plain PE. In these PE-modified high impact PP products (HIPP) the brittle–ductile transition is shifted to lower temperatures, where relaxation processes mark a partial mobility of molecules. The decrease of brittle–ductile transition can be seen in *Figure 7* by means of the force–deflection diagrams of modified PP compared with those of plain PP in *Figure 1*. Even at -40°C a good deal of plastic deformation involving high energy dissipation is seen. This enhanced deformation of the modified PP is accompanied by voiding processes as

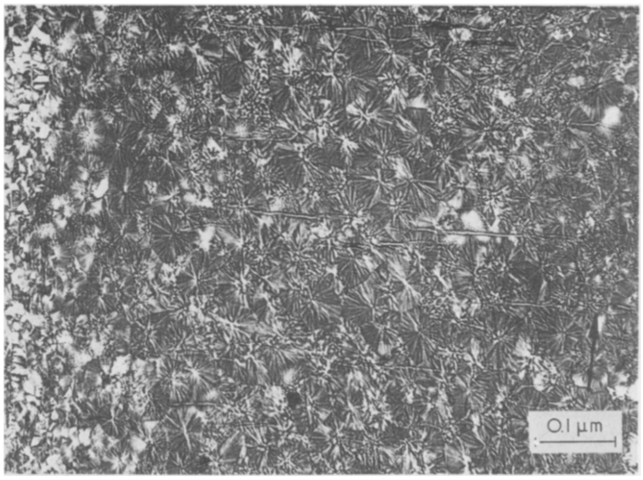

Figure 3 Spherulites and cracks in deformed PP outside the necking zone (polarized light micrograph). Arrow indicates tensile direction

can be verified by density measurements during deformation. In both products, even at 23°C, an intensive volume increase is observed. An example is given in *Figure 8* for a PP/PE copolymer, the unloading situation is also shown. This voiding behaviour is reminiscent of proceedings in the extensively investigated[11,12] rubber-modified polystyrene products (HIPS), where the brittle–ductile transition of PS is also lowered from its glass transition temperature to that of the rubber.

Due to the incompatibility of PE in PP, the longer sequences of PE preferentially segregate in a separate PE-rich phase, uninfluenced by the overall spherulite structure (*Figure 9*). This phase separation has been observed by distinct damping peaks (*Figure 6*) or other methods, e.g. d.s.c.[13], X-ray scattering[14], etc.[15,16] The most effective method for studying the individual phases in more detail is transmission electron microscopy (*Tem*),

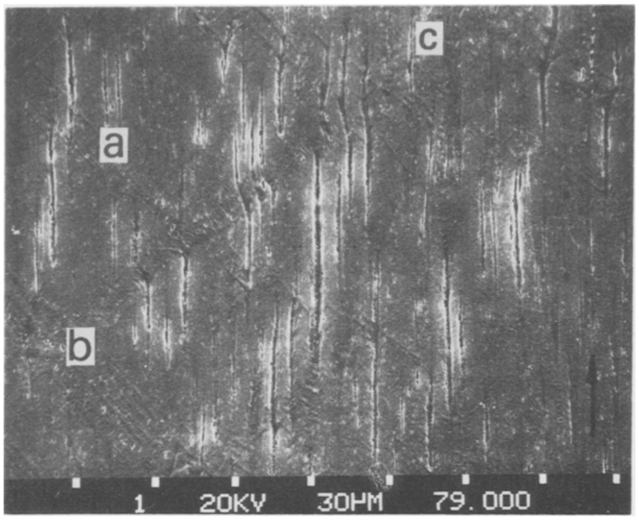

Figure 4 Scanning electron micrograph of the surface of deformed PP inside the necking zone. a: shear bands; b: voids; c: splitting off. Arrow indicates tensile direction

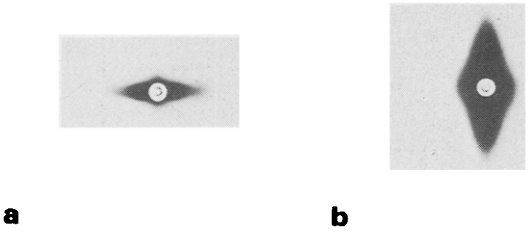

Figure 5 Pattern of SAXS of deformed PP. (a) outside the necking zone (b) inside the necking zone (tensile direction horizontal)

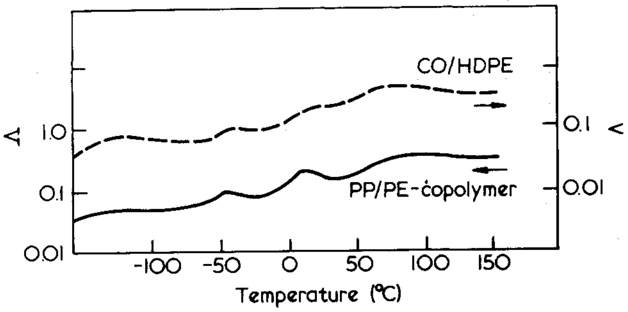

Figure 6 Log decrement of PP modified with PE

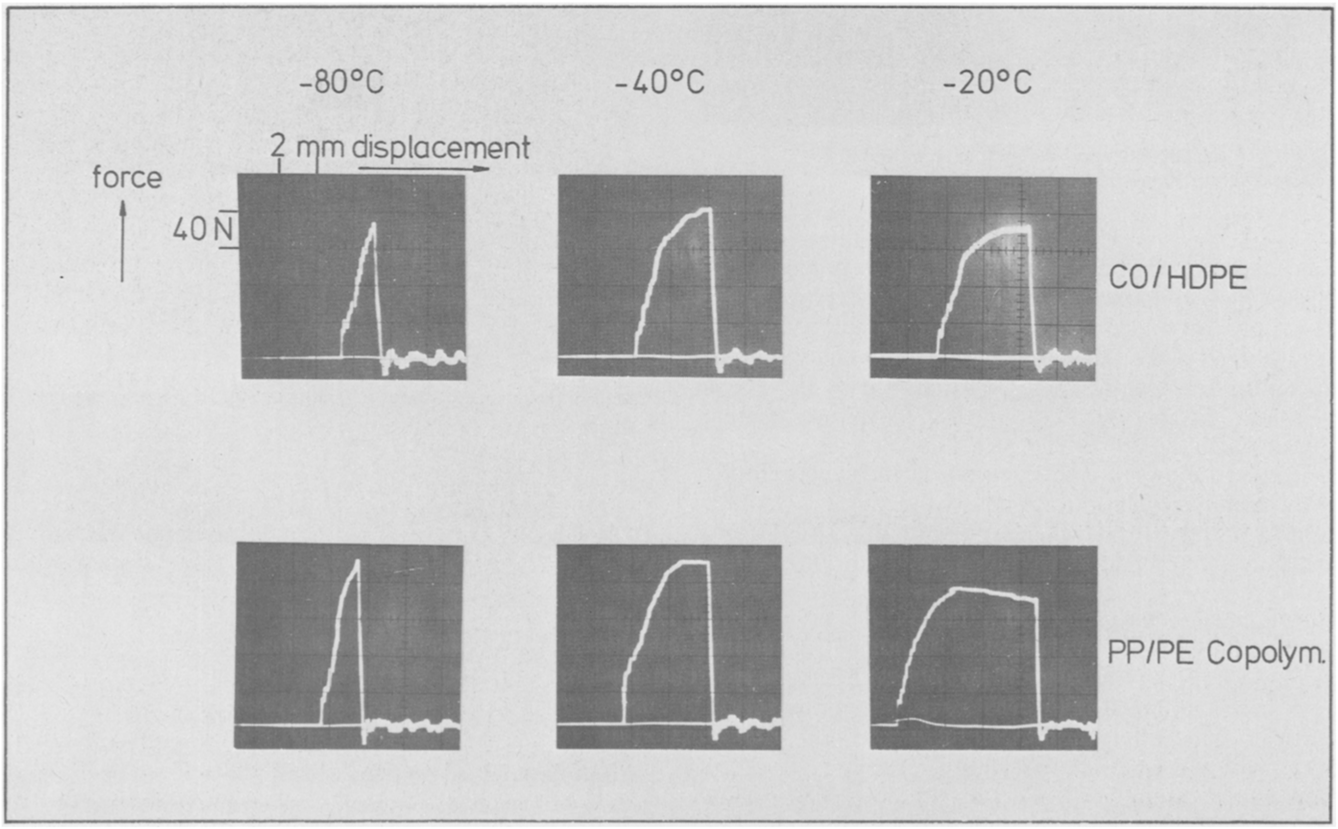

Figure 7 Force–deflection diagrams during Charpy impact test of modified PP (compression moulded)

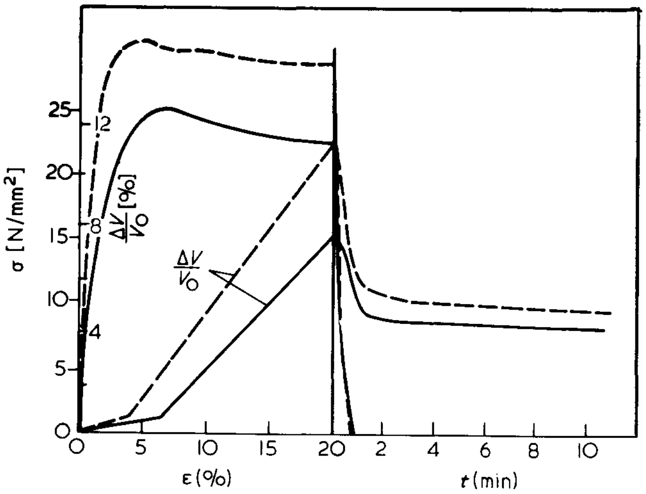

Figure 8 Stress and change of volume during deformation of PP/PE copolymer. Deformation temperature: (— —) 0°C; (——) 23°C. Deformation rate: $12.5 \cdot 10^{-2}$ min^{-1}

Figure 9 Transmission light micrographs of modified PP (a) bright field (polarized) (b) dark field

after staining the material by Kanig's procedure[17]. According to this method the material is exposed for 3 days at 60°C to chlorosulphonic acid vapour. Microtomed slices were then taken from the material, stained in uranylacetate (1%), and studied by the *TEM* technique. In the micrographs the amorphous regions appear dark, the crystalline regions white.

Figure 10 shows the transmission electron micrographs of the copolymer and the blend. In the matrix a profuse number of thin (PP) lamellae are discernable. In addition, particles are embedded in the matrix, with amorphous (dark) regions and crystalline lamellae inside. Some of these lamellae enclosed in the particles, especially those in the blend, are thicker than those in the PP matrix and are therefore believed to be PE crystals. In the copolymer both sizes of lamellae seem to be present inside the particles. The different phases are reflected in the log decrement as already discussed in *Figure 6.*

In deforming the material, voids are generated (*Figure 11*) partly in the amorphous region of the outer shell of these particles and partly at the interface. At these

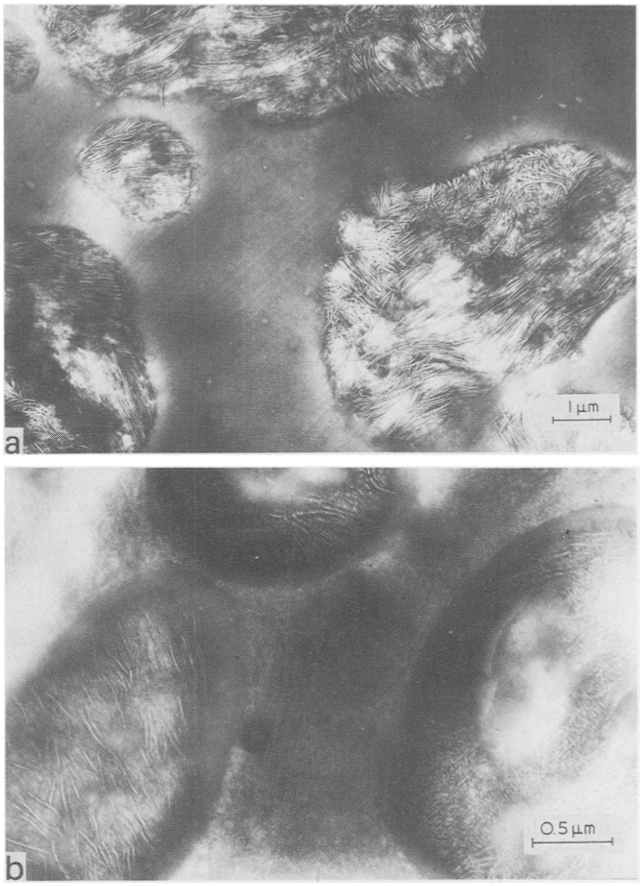

Figure 10 Transmission electron micrographs of modified PP (stained). (a) CO/HDPE (b) PP/PE–copolymer

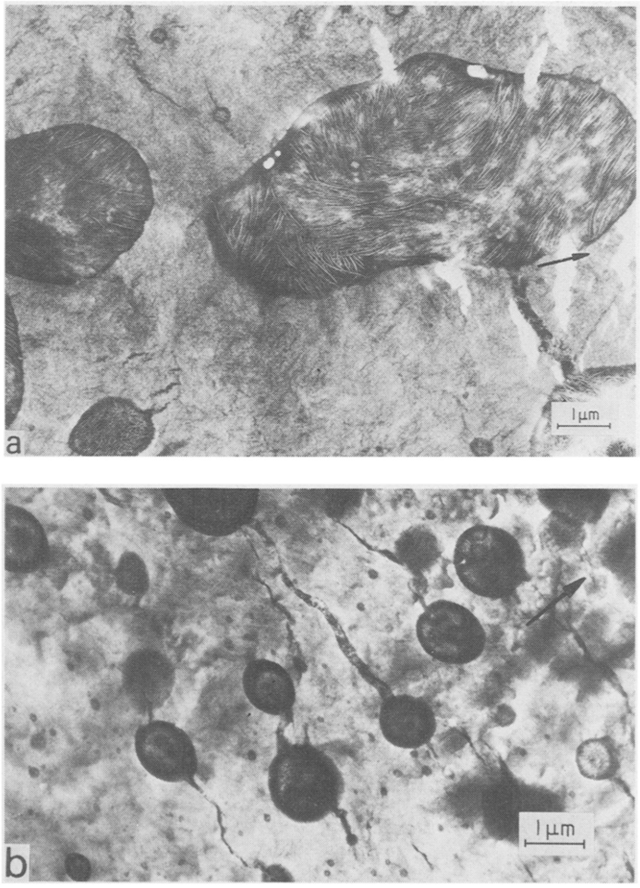

Figure 11 Transmission electron micrographs of modified PP after deformation (stained). (a) CO/HDPE (b) PP/PE–copolymer. Arrows indicate tensile direction

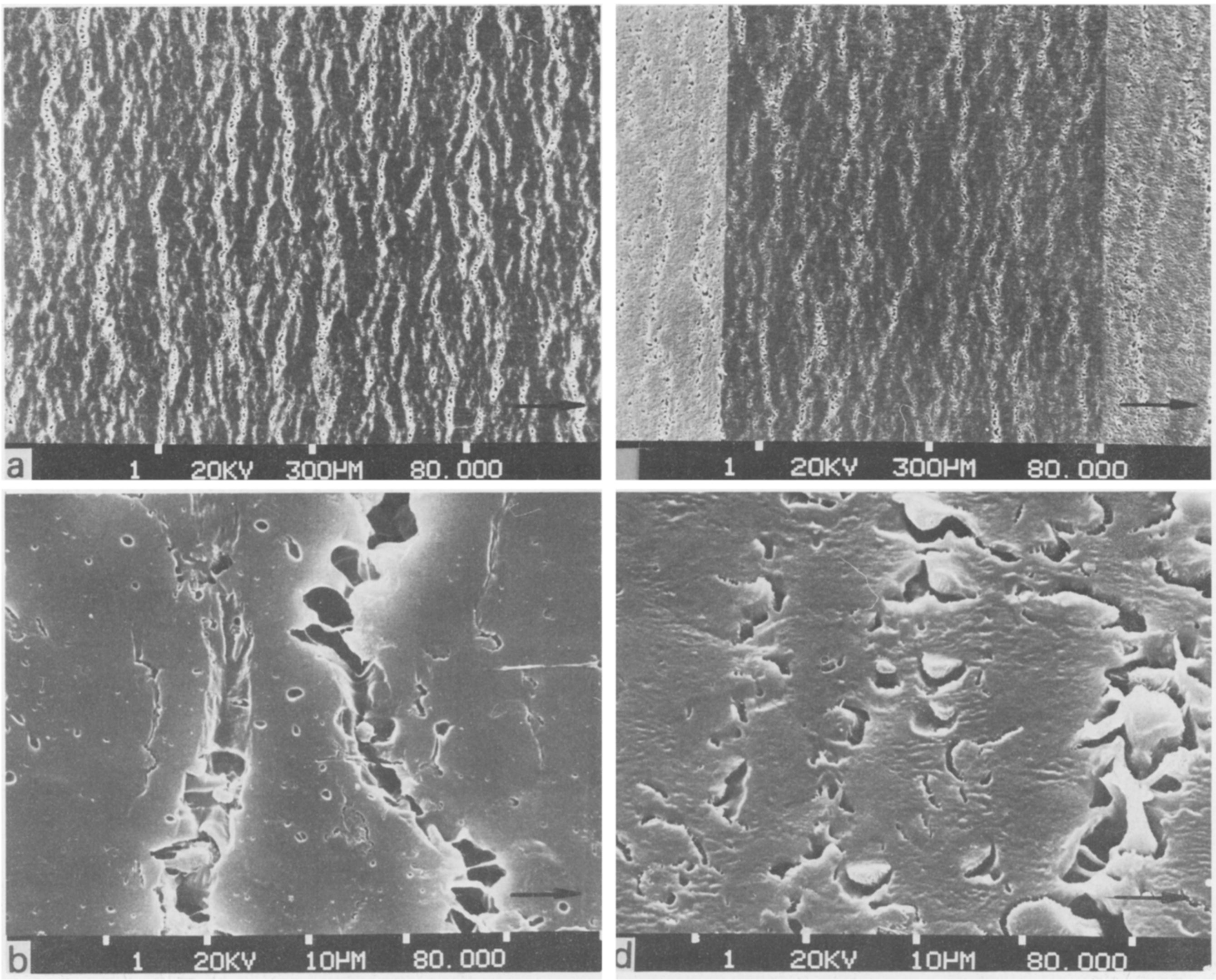

Figure 12 Scanning electron micrographs of CO/HDPE. (a) and (b) surface of the specimen; (c) and (d) microtomed slice of the interior of the specimen. Arrows indicate tensile direction

particles, in some cases, minute openings are formed and they spread out into the matrix material, more or less perpendicularly to the tensile direction. These openings are bridged by polymeric materials, especially fibrils, otherwise they would be cracks and therefore sites for the initiation of a fracture. In *Figure 11b* these originally open gaps are seen as dark lines preferentially lying perpendicular to the tensile direction. *Figure 12* shows scanning electron micrographs of a slice (*Figure 12c* and *d*) microtomed from the deformed CO/HDPE specimen. Numerous voids which are arranged in deformation zones lying perpendicular to the tensile direction are seen. Such zones in which openings are bridged with polymeric material are often called crazes. The pictures seem to indicate, that particles, presumably the segregations mentioned above, are indeed spots of enhanced voiding. It must be admitted that some of the voids in *Figure 12* (*c* and *d*) might have been produced later during the microtoming technique, especially, as these specimens had not been stained and therefore had not been reinforced before cutting, as has been done for the specimens before the *TEM* procedure. To eliminate the conceivable effect of the microtoming technique, the surface of the deformed CO/HDPE specimens has also been studied. The surface can be viewed, without any mechanical handling in preparing the specimen for *SEM*. The appearance of the deformation zones (*Fibure 12 a* and *b*) seems to be identical to that in the interior, showing that any effect of the microtoming technique does not change the void pattern fundamentally.

Also in the copolymer, voids and numerous bridged minute openings are observed (*Figure 13*) at the surface of the deformed specimen. These crazes might correspond to the deformation zones seen under *TEM* (*Figure 11b*).

In conclusion, these deformation phenomena make the high energy dissipation of PP after PE-modification understandable on a basis analogous to that of improving impact strength of PS by rubber modification. The PE-rich particles, segregated in a PP-rich matrix, initiate the formation of a profuse number of deformation zones. These deformation zones dissipate impact energy by deformation, the formation of real cracks is hindered by fibrils bridging the gap. Therefore, instead of very few voids in the matrix, which become easily overstressed in plain PP entailing the fracture, in modified PP, an abundance of energy-dissipative deformation zones is formed at the segregated particles. The initial porosity at the start of a craze in HIPS is presumed to happen in the PS matrix within the local stress field of the rubber particles. However, in PE-modified PP the deformation zones are often likely to begin in the amorphous shell of the segregates or at the interface between the particles and the matrix. Owing to the complicated structure of this type of product, it is quite natural that processing has a large influence on its mechanical properties[18–20].

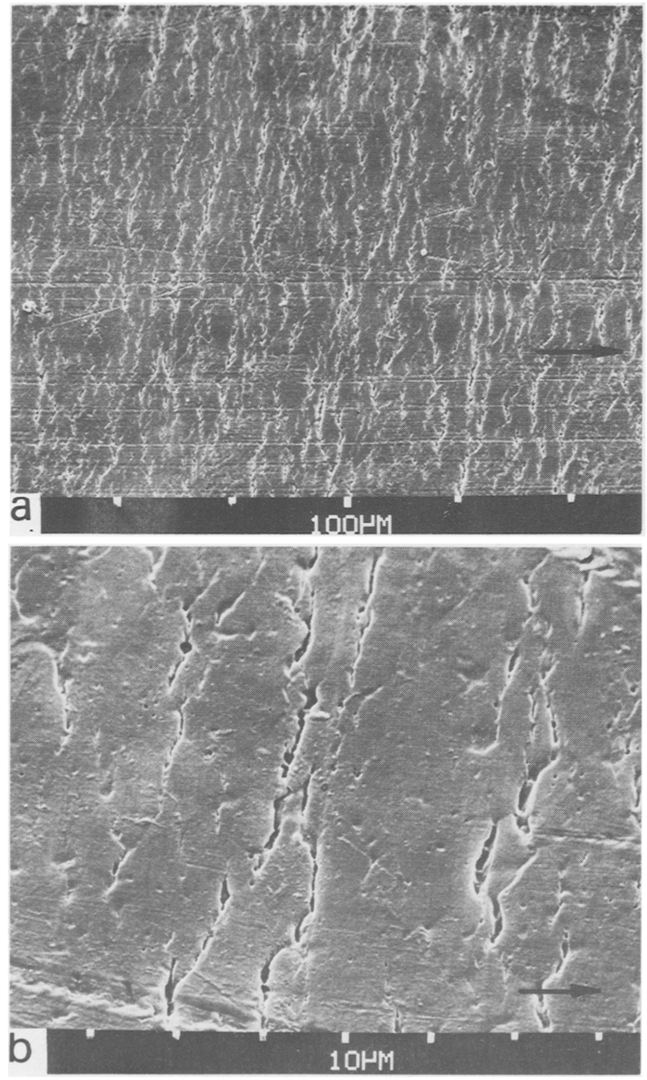

Figure 13 Scanning electron micrographs of the surface of deformed PP/PE—copolymer. Arrows indicate tensile direction

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