Post-yield fracture of plasticised cellulose acetate sheet

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The processes associated with the brittle fracture of amorphous polymer glasses have been extensively investigated and are now fairly well understood[1–5]. The materials have been shown to yield locally by cavitation to form a thin voided sheet with reduced density known as a craze. The same materials show localized necking when they are extended under tension either under conventional conditions or when external pressure is applied to suppress brittle fracture.

However, there exists a small group of amorphous polymers which do not neck and which extend uniformly under tension. So far they have not been observed to craze under conventional testing conditions and their fracture mechanism has not been demonstrated. Indeed it may be argued that, in the absence of strain softening, localization of yielding in a craze would not be expected so that the conventional craze–crack mechanism would not apply. These plastics include the cellulose esters[6,7], Kapton H[8] and 1-nylon[9]. Here we describe a short study of the fracture phenomena associated with plasticized cellulose acetate film.

MATERIALS

Secondary cellulose acetate (acetyl value 54%) plasticized with 24–27% of mixed diethyl phthalate–diphenyl phthalate esters was used as a film or sheet. Two types of commercial film were used:

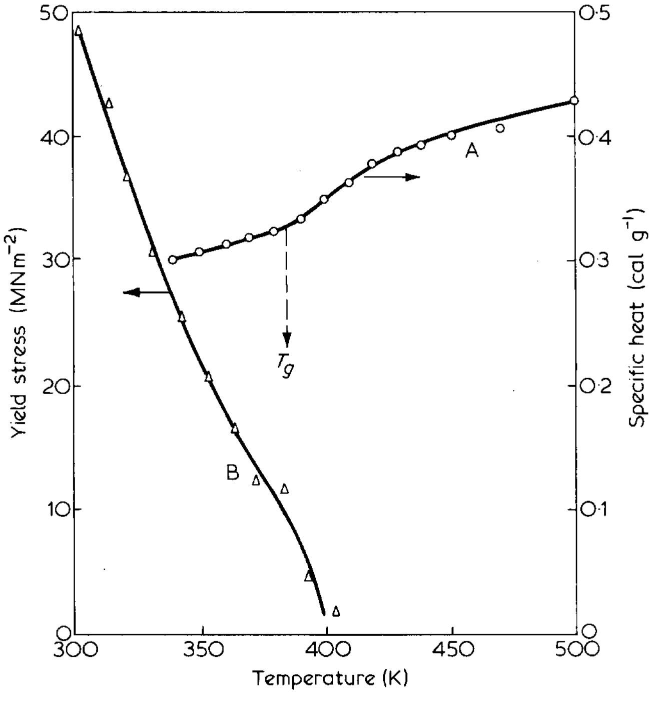

Figure 1 Effect of temperature on the properties of cellulose acetate. A, Specific heat against temperature for differential scanning calorimetry; B, effect of temperature on yield stress

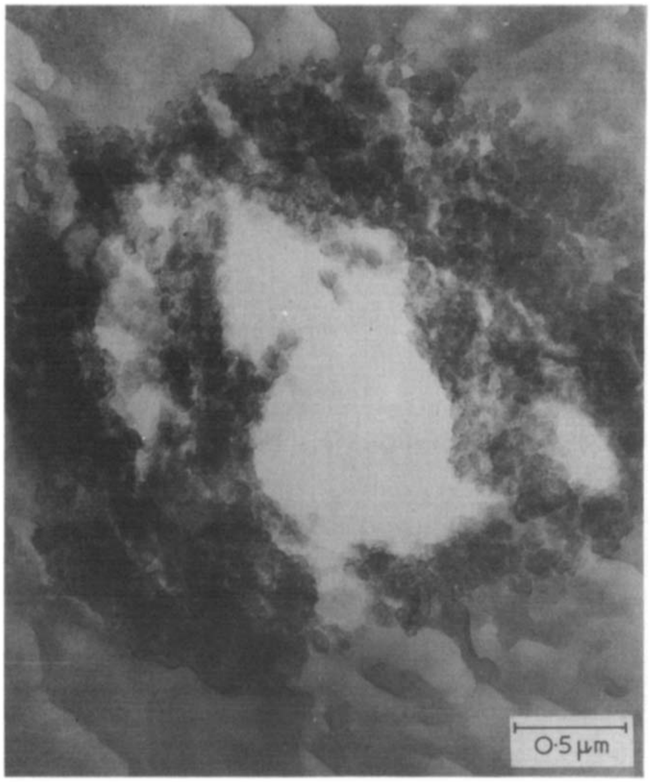

Figure 2 Transmission electron micrograph of cavity. Material (a)

(a) cast film containing a small quantity of inorganic anti-blocking agent;
(b) sheet sliced from a block

Further details of the materials and methods used are given elsewhere[10].

RESULTS

All the films showed the uniformly extending stress–strain curves characteristic of cellulose esters and a representative example of one of these has been previously published (*Figure 10c*, ref 9). The yield stress, measured at the initial maximum decreased with increasing temperature in the usual way and tended to zero at ~400K (*Figure 1*). The material showed a glass transition (measured on a Perkin–Elmer DSC-2) at 388K. However, the change in C_p (ΔC_p) at this temperature was only 0.029 cal g^{-1} which compares with 0.054 cal g^{-1} measured for polystyrene with the same equipment[9] and 0.064–0.077 cal g^{-1} reported by other workers[11–13]. Clearly even this small increase in C_p could be due to a change in plasticizer mobility, but in any case the low value of ΔC_p supports our previous argument that this quantity should be small for polymers with extended-chain configurations[9].

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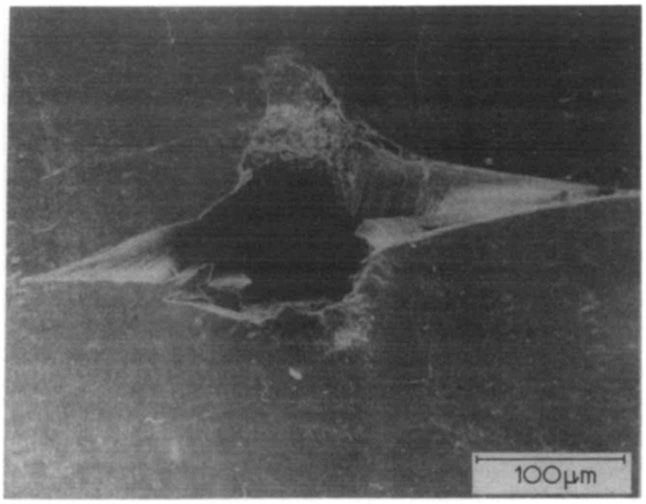

Figure 3 Flat 'diamond' cavity propagating in cellose acetate. General view at surface. Scanning electron micrograph, direction of stress ↕. Material (a)

When the cast film (a) was extended beyond yield it became cloudy, and the cloudiness increased as the fracture elongation $\sim$30% was approached. Under the optical microscope the cloudiness was seen as 'peppery inhomogeneities' just at the limit of resolution. They were distributed through the bulk of the polymer. However, because of their small size sharp optical micrographs could not be obtained although many of them were observed to have a 'split pea' structure. Qualitatively, however, it was shown that the inhomogeneities were *not* removed when the film was heated to 100°C and relaxed to within 2% of its original length. Examination of ultramicrotomed slices under a high voltage electron microscope (AE 1–7 million volt instrument) showed cavities initiated within small opaque particles, almost certainly the antiblocking agent (*Figure 2*). The sliced film (b) did not show this type of cloudiness.

When the tensile test was continued towards fracture after yield, visible voids were generated on the surface which initiated a plastic fracture of the type previously described[14,15]. However the tearing angle of the progressing crack was much smaller than that previously observed. We have now shown that this angle is largely determined by the shear of the polymer at the crack tip in the plane of the applied tension[16] and the smaller angle is presumed to reflect the low deformability of the extended cellulose ester chain in shear as in tension.

Characteristically fractures were initiated internally either from the presumed antiblocking agent or from particles of contamination. In this connection it will be appreciated that the cellulose esters, which are prepared from a natural polymer, cannot be subjected to distillation during manufacture and are therefore more difficult to obtain in a form completely free from 'dust' than the fully synthetic materials. An example of an internally initiated plastic fracture in material (b) is shown in *Figure 4*

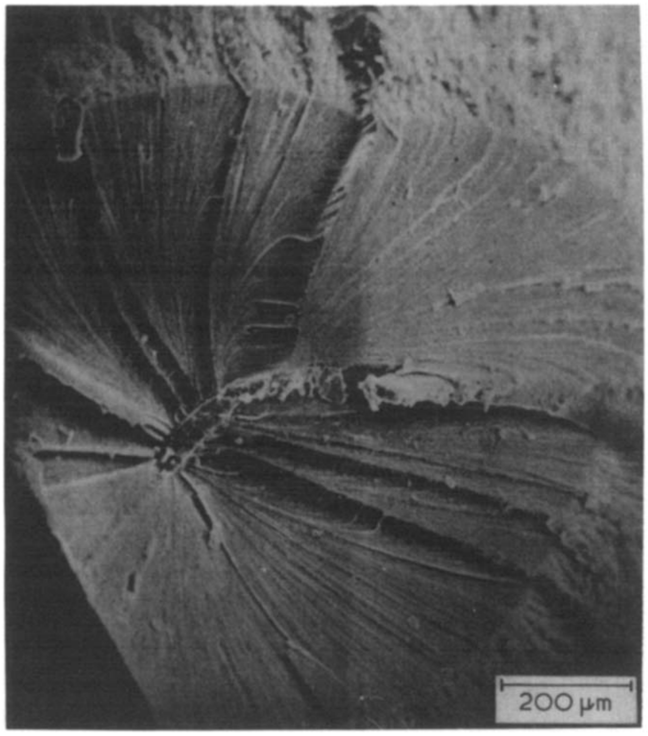

Figure 4 Fracture in type II material initiated from a particle of contamination. Scanning electron micrograph. Material (b)

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